I. ELECTROMOTIVE FORCE MEASUREMENTS IN LIQUID AMMONIA

II. DETERMINATION OF THE STRUCTURE OF CRYSTALS AND MOLECULES BY THE DIFFRACTION OF X-RAYS AND ELECTRONS AND BY MAGNETIC MEASUREMENTS

Thesis

by

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The Potentials of Cells in Liquid Ammonia. The Thermodynamic Constants of the Ammino Zinc Chlorides and of Zinc Chloride. By Norman Elliott and Don M. Yost.

Page 1057. "Due to an arithmetical error $ZnCl_2 \cdot 10NH_3$ was stated to be the solid phase in the cell. Actually the solid phase was $ZnCl_2 \cdot 6NH_3$, and equations (1) to (5) must be modified accordingly. This change affects the thermodynamic constants only and not the e. m. f.'s."

Page 1059. Eq. (6), for $\Delta F^\circ_{298} = -2200$ cal. read $\Delta F^\circ_{298} = -6900$ Cal. The fugacity of $NH_3(g)$ was taken as 18.2 atm.

Page 1060. In line 5 of paragraph 2 read "−20,420 cal." for "−11,600 cal." Also substitute new Table II.

TABLE II

THE THERMODYNAMIC CONSTANTS OF THE AMMINO ZINC CHLORIDES AND ZINC CHLORIDE

Substance	$ZnCl_2 \cdot 10NH_3$	$ZnCl_2 \cdot 6NH_3$	$ZnCl_2 \cdot 4NH_3$
ΔF°_{298} cal.	−151,030	−142,290	−132,230
ΔH°_{298} cal.	−323,000	−250,840	−206,880
S°_{298} cal./deg.	187.3	117.6	91.8

Substance	$ZnCl_2 \cdot 2NH_3$	$ZnCl_2 \cdot NH_3$	$ZnCl_2$
ΔF°_{298} cal.	−119,860	−102,710	− 87,800
ΔH°_{298} cal.	−161,300	−130,910	− 99,550
S°_{298} cal./deg.	63.6	34.5	23.7

Page 1059, second line, second paragraph of section entitled "Free Energies, etc.," for −59,500 ± 500 cal. read −58,400 ± 500 cal.

We acknowledge the kindness of Mr. C. S. Garner in calling attention to these errors and for assistance in making the corrections."—DON M. YOST.

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 394]

The Potentials of Cells in Liquid Ammonia Solutions. The Thermodynamic Constants of the Ammino Zinc Chlorides and of Zinc Chloride

BY NORMAN ELLIOTT AND DON M. YOST

Introduction

Liquid ammonia has long been known to be an ionizing solvent, and the nature of salt solutions in it has received the careful attention of Franklin, Kraus and other investigators.[1] The few electrode potentials in this solvent which have been investigated were complicated by liquid potentials or were not reversible.[2] A cell free from these objections and one which is also convenient as a reference electrode is highly desirable, especially if the electromotive series in liquid ammonia is to have more than a qualitative basis.[3]

Inasmuch as the thermodynamic constants of thallium amalgams and thallous chloride[4] are accurately known, and since the latter substance is not very soluble in liquid ammonia at 25°, the thallium amalgam–thallous chloride couple was chosen as one half-cell. Moreover, the solid phase consists of thallous chloride alone and not an ammoniated salt.[5] As the other half-cell the zinc amalgam–decammino zinc chloride couple was selected, since the activities of the amalgams[6]

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[1] *Cf.* Kraus, "The Properties of Electrically Conducting Systems," A. C. S. Monograph, The Chemical Catalog Co., New York, 1922. An excellent review of liquid ammonia systems is given by Fernelius and Johnston, *J. Chem. Ed.*, **7**, 2600 (1930), *et ante.*

[2] *Cf. e. g.*, Johnson and Wilsmore, *Trans. Faraday Soc.*, **3**, 77 (1907); Costeanu, *Compt. rend.*, **195**, 778 (1932).

[3] Bergstrom, THIS JOURNAL, **47**, 1503 (1925); Kraus, *Trans. Am. Electrochem. Soc.*, **45**, 175 (1924).

[4] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, 1923, pp. 93, 267, 607.

[5] Stollenwerk and Biltz, *Z. anorg. Chem.*, **119**, 97 (1921).

[6] Pearce and Eversole, *J. Phys. Chem.*, **32**, 209 (1928).

are known, and the salt is only slightly soluble in liquid ammonia. Ammonium chloride was chosen as the electrolyte. The cells measured were found to have constant and reproducible electromotive forces at 25°.

Attempts were made to construct a hydrogen electrode operating at 25° in liquid ammonia solutions of ammonium chloride. A potential of about 0.42 volt against a 0.0265 N thallium amalgam was obtained, but the experimental difficulties were such that its use as a reference electrode did not prove convenient. The ammonium ion in this case corresponds, of course, to the hydrogen ion of the aqueous system.

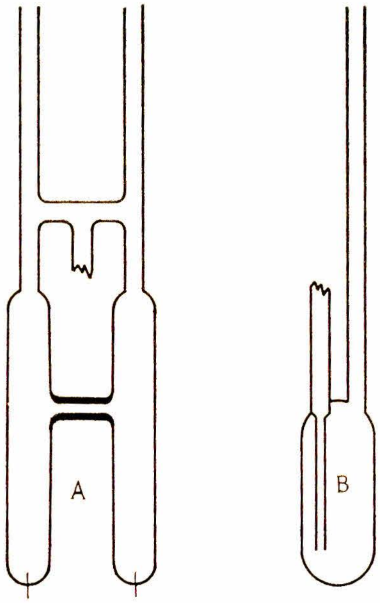

Fig. 1.

Preparation of Materials and Experimental Procedure

Ammonia.—The gas from a tank was passed over solid sodium hydroxide and metallic sodium and then condensed directly into the cell.

Thallous Chloride.—The metal of commerce was dissolved in hot dilute nitric acid, and the resulting mixture was then filtered. After treating the filtrate with hydrogen sulfide, it was again filtered and then boiled. To this solution was added an excess of hydrochloric acid to precipitate thallous chloride. After filtering, and washing repeatedly, the resulting precipitate was dried at 120° for four hours and then stored in a brown glass bottle.

Thallium.—A saturated solution of thallous chloride was electrolyzed between platinum electrodes at 100°. The resulting spongy metal was fused at 300° in a porcelain boat over which was passed a stream of dry hydrogen. The metal was then transferred to a tube containing carefully purified mercury. All operations involving the amalgams were carried out in an atmosphere of dry hydrogen.

Zinc.—The amalgams were prepared as above with purified electrolytic zinc.

Zinc Chloride.—Pure zinc chloride was fused, and, soon after solidifying, a portion was placed on the zinc amalgam in the cell. Oxygen and moisture were carefully excluded.

Ammonium Chloride.—The purest material obtainable was resublimed and stored in a vacuum desiccator.

The cell used is shown in Fig. 1. The auxiliary vessel B was used to fill the cell proper, A, with the liquid ammonia solution of ammonium chloride. After filling and sealing, the cells were placed in a thermostat at 25.00 ± 0.01°.

Results of the Experiments

Since the solubility of thallous chloride in liquid ammonia was not known, a series of measurements using the method of Hunt and Boncyk[7] were made. The results of three representative experiments gave 0.0260, 0.0261 and 0.0257 mole per 1000 g. of liquid ammonia at 25.0°.

In Table I are presented the results of the electromotive force measurements. Functions of the activities of thallium and zinc in their amalgams were plotted, and the values for the concentrations given in the table were obtained from the plot. The reference states for these activities are infinitely dilute solutions. Each cell required about four hours to attain equilibrium and after attaining it, the electromotive force remained constant for days. The thallium electrode was always positive.

The chemical reaction taking place in the cell is the following

$$\mathrm{Zn(amalg.}\ \alpha_2) + 2\mathrm{TlCl(s)} + 10\mathrm{NH_3(l)} = \mathrm{ZnCl_2{\cdot}10NH_3(s)} + 2\mathrm{Tl(amalg.}\ \alpha_1) \qquad (1)$$

and the expression for the electromotive force of the cell is

$$E = E^{\circ\prime} - 0.029575 \log\,(\alpha_1^2/\alpha_2\alpha_3^{10}) \qquad (2)$$

where α_2 and α_1 are the activities of zinc and thallium, respectively, in their amalgams at the mole fractions N_2 and N_1, and α_3 is the activity of the liquid ammonia. Since the concentrations of ammonium chloride used were small, as were also those of thallous chloride and zinc chloride, α_3 was taken equal to unity. In doing this, the standard state of liquid ammonia at 25° is assumed to be that state in which the total pressure is the vapor pressure of the liquid, and not one atmosphere. The correction to one atmosphere is probably small but cannot be made at this time since the molal volumes involved are not all known. The values of $E^{\circ\prime}$ given in the table are for the potential of the hypothetical cell

$$\mathrm{Zn(amalg.}\ \alpha_2 = 1),\ \mathrm{ZnCl_2{\cdot}10NH_3(s)},\ \mathrm{NH_4Cl(in\ NH_3(l)},f),\ \mathrm{TlCl(s)},\ \mathrm{Tl(amalg.}\ \alpha_1 = 1);\ E^{\circ\prime} = 0.9016\ \mathrm{volt} \qquad (3)$$

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[7] Hunt and Boncyk, THIS JOURNAL, **55**, 3528 (1933).

TABLE I

RESULTS OF THE ELECTROMOTIVE FORCE MEASUREMENTS

Temp., °C.	Mole fraction Tl N_1	Activity Tl α_1	Mole fraction Zn N_2	Activity Zn α_2	Formality NH_4Cl, f	E. m. f. observed, E, volt	Standard potential $E°'$, volt	Standard potential $E°$, volt
25	0.0265	0.0369	0.0289	0.0255	0.0380	0.9392	0.9016	0.8293
	.0265	.0369	.0289	.0255	.0725	.9396	.9020	.8297
	.0265	.0369	.0289	.0255	.0573	.9395	.9019	.8296
	.0265	.0369	.0289	.0255	.0379	.9392	.9016	.8293
	.0265	.0369	.0301	.0263	.0648	.9393	.9013	.8290
	.428 satd.	3.316	.0289	.0255	.0306	.8231	.9011	.8288
	.0913	0.250	.0289	.0255	.084	.8900	.9015	.8292
						Mean	.9016	.8293
1.75	.0265		.0301		.0648	.9680		
18.50	.0265		.0301		.0648	.9470		

$\alpha_2 = 0.04819$ for a saturated Zn amalgam.

Equation 2 shows that the observed electromotive forces E should be practically independent of the concentration of ammonium chloride when the solutions are dilute and, as the table shows, this was found to be the case. The effect of varying the concentrations of thallium and zinc in the amalgams is also that predicted by equation 2. This is evident from the constancy of the $E°'$ values. The cell is, therefore, reversible.

In the last column of the table are given the standard potentials $E°$ for the cell

$$Zn(s), ZnCl_2 \cdot 10NH_3(s), NH_4Cl(\text{in } NH_3(l), f), TlCl(s), Tl(s); \quad E° = 0.8293 \text{ volt} \qquad (4)$$

for which the chemical reaction is

$$Zn(s) + 2TlCl(s) + 10NH_3(l) = 2Tl(s) + ZnCl_2 \cdot 10NH_3(s) \qquad (5)$$

and the total pressure is the vapor pressure of the liquid ammonia at 25°. In arriving at the values of $E°$, account was taken of the fact that the potential of pure thallium is higher than that of the saturated amalgams by 0.0025 volt.[4] The solid phase of the saturated amalgam consists of some mercury dissolved in the thallium.

Discussion

It appears from the results of the measurements of the cell here described that either half-cell could be used as a standard reference electrode. In case very refined measurements were undertaken, account would have to be taken of the appreciable solubility of thallous chloride, if that half-cell were used. If the solubility of the decammino zinc chloride proves to be of the same order of magnitude as calomel or silver chloride in water, then the zinc half-cell would be superior as a reference electrode.

If the hydrogen electrode were measured against the thallium or zinc electrode, then all other half-cells could be compared with either of the two latter, and thus the further use of the troublesome gas cell could be avoided. Direct use of the gas cell could be avoided entirely if the activities and free energies of ammonium chloride solutions in liquid ammonia were known. It is planned to determine these quantities later.

Free Energies and Heat Contents of the Ammino Zinc Chlorides and Zinc Chloride.—The standard free energy change accompanying reaction (5) is given by $\Delta F°_{298} = -NE°F$ and is found to be −38,238 cal. The free energies of formation of thallous chloride and of liquid ammonia are −44,164 cal. and −2570 cal., respectively, at 25°. On combining these values the free energy of formation of $ZnCl_2 \cdot 10NH_3(s)$ at 25° becomes −152,270 cal.

The change in heat content accompanying reaction (5) is −59,500 ± 500 cal. and it was calculated from the temperature coefficient of one of the cells, −0.00121 volt/deg., and the heats of solution of thallium[4] and zinc[6] in their amalgams. The heats of formation[8] of thallous chloride and liquid ammonia are 48,700 cal. and 15,840 cal., respectively. The heat of formation of $ZnCl_2 \cdot 10NH_3$ from the elements becomes, therefore, 315,360 cal., and this is in satisfactory agreement with the less reliable value 327,400 cal. given in the "International Critical Tables."

Sufficient data are available for calculating the free energies of the other four ammoniated zinc chlorides. From the data given in "International Critical Tables"[8,9] the following equations have been derived.

$$ZnCl_2 \cdot 10NH_3(s) = ZnCl_2 \cdot 6NH_3(s) + 4NH_3(g) \qquad (6)$$
$$\Delta F°_{298} = -2200 \text{ cal.} \quad \Delta H = 28,390 \text{ cal.}$$

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(8) "International Critical Tables," Vol. V, pp. 184, 178, 185.

(9) "International Critical Tables," Vol. VII, p. 252.

$$\mathrm{ZnCl_2{\cdot}6NH_3(s) = ZnCl_2{\cdot}4NH_3(s) + 2NH_3(g)} \qquad (7)$$
$$\Delta F^\circ_{298} = 2240 \text{ cal.} \quad \Delta H = 22{,}080 \text{ cal.}$$

$$\mathrm{ZnCl_2{\cdot}4NH_3(s) = ZnCl_2{\cdot}2NH_3(s) + 2NH_3(g)} \qquad (8)$$
$$\Delta F^\circ_{298} = 4550 \text{ cal.} \quad \Delta H = 23{,}700 \text{ cal.}$$

$$\mathrm{ZnCl_2{\cdot}2NH_3(s) = ZnCl_2{\cdot}NH_3(s) + NH_3(g)} \qquad (9)$$
$$\Delta F^\circ_{298} = 13{,}240 \text{ cal.} \quad \Delta H = 19{,}450 \text{ cal.}$$

The heat of the reaction $\mathrm{ZnCl_2{\cdot}NH_3(s) = ZnCl_2(s) + NH_3(g)}$ has not been determined accurately, and the value given for it appears to be a rough estimate.[10] The more reliable value of −11,600 cal. was obtained by combining equations (6) to (9) with the heat of formation of zinc chloride[8] and that of $\mathrm{ZnCl_2{\cdot}10NH_3(s)}$ derived above. In making the calculation the heat of formation of ammonia gas was taken to be 10,940 cal.[8] The "International Critical Tables" gives an experimentally determined dissociation pressure for the monoammino zinc chloride at only one temperature. This was used in connection with the heat of dissociation just given to calculate the free energy change at 25°. The following equation expresses the results of the calculations.

$$\mathrm{ZnCl_2NH_3(s) = ZnCl_2(s) + NH_3(g)} \qquad (10)$$
$$P_{498.1} = 0.0088 \text{ atm.} \quad \Delta H = 11{,}590 \text{ cal.} \quad \Delta F^\circ_{298} = 7350 \text{ cal.}$$

It is now possible to construct a table of the thermodynamic constants for all of the ammino zinc chlorides and zinc chloride. In making the calculations the free energy of formation of ammonia gas at 25° was taken to be −3910 cal.[4] and the standard virtual entropies at 25° of zinc[4] chloride,[11] nitrogen[12] and hydrogen[13] to be 9.83, 53.31, 45.79 and 31.23 cal./deg., respectively. The results are presented in Table II. The free energy and heat content values are referred to the elements in their standard states of 25° and one atmosphere.

TABLE II

THE THERMODYNAMIC CONSTANTS OF THE AMMINO ZINC CHLORIDES AND ZINC CHLORIDE AT 25°

Substance	$\mathrm{ZnCl_2{\cdot}10NH_3}$	$\mathrm{ZnCl_2{\cdot}6NH_3}$	$\mathrm{ZnCl_2{\cdot}4NH_3}$	$\mathrm{ZnCl_2{\cdot}2NH_3}$	$\mathrm{ZnCl_2{\cdot}NH_3}$	$\mathrm{ZnCl_2}$
ΔF°_{298} cal.	−152,270	−138,830	−128,770	−116,400	− 99,250	−87,990
ΔH°_{298} cal.	−314,200	−242,040	−198,070	−152,480	−112,080	−99,550[8]
S°_{298} cal./deg.	217.4	134.8	109.6	81.5	53.0	24.3

S°_{298} is the standard virtual entropy.

Summary

With liquid ammonia as the solvent, the cells Zn (amalgam N_2), $\mathrm{ZnCl_2{\cdot}10NH_3(s)}$, $\mathrm{NH_4Cl}$ (in $\mathrm{NH_3}$-$(l), f$), TlCl(s), Tl (amalgam N_1) were measured at 25°. The cells are reversible and give constant and reproducible electromotive forces. When the zinc and thallium are present in the amalgams at unit activity the standard potential is $E^{\circ\prime}_{298} = 0.9016$ volt. When zinc and thallium are present as the pure metals the standard potential is $E^\circ_{298} = 0.8293$ volt.

From the cell potential and its temperature coefficient, together with the results of other investigators, the free energies, heat contents and virtual entropies for five ammoniated zinc chlorides and zinc chloride itself were calculated and are presented in Table II.

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[10] Biltz and Messerknecht, *Z. physik. Chem.*, **129**, 161 (1923).

[11] Giauque and Overstreet, THIS JOURNAL, **54**, 1731 (1932).

[12] Giauque and Clayton, *ibid.*, **55**, 4875 (1933).

[13] Giauque, *ibid.*, **52**, 4816 (1930).

Part 2

Introduction

In the last few years the electron-pair bond theory first suggested by Lewis has received much attention. With the aid of quantum mechanics Pauling[1] and other investigators have extended this theory to a quantitative state whereby a large variety of data concerning the nature of molecules in gas, solid, or solution phases can be correlated.

An early application[2] of the covalent bond theory in its present form was made to the study of magnetic moments of complex ions. Two independent results coming from this work are the relation between valence and magnetic moment, and the relation between spatial configuration of a molecule or complex ion and its magnetic moment.

For some time an interesting subject to chemists has been the investigation of complex compounds in which an element appears in two different valence states. The prussian blues are perhaps the best known examples of this phenomenon. Such compounds usually possess intense colors, and the suggestion has been made that in these substances the central atoms do not have their normal valences but exist in an intermediate state. In some cases such as that of ammonium hexabromo-hypo-antimonate, $(NH_4)_4Sb_2Br_{12}$, and cesium aurous auric chloride, $Cs_2Au_2Cl_6$, this theory may be simply tested. If the antimony or the gold is in a valence state intermediate between the normal ones the compounds will contain impaired electrons and be paramagnetic. If the atoms are in normal valence states, however, diamagnetism is to be expected. A measurement of magnetic susceptibility, then, would lead to an unequivocal decision regarding the theory. The results of such experiments are stated in the first and second sections which follow.

When the central atom of a complex ion is diamagnetic in both the covalent and ionic states a measurement of magnetic susceptibility leads to no information about the spatial configuration of the complex. The best means for obtaining this knowledge would be by an x-ray investigation of single crystals of the substance. Unfortunately there are very many synthetic inorganic compounds which can only be prepared in a micro-crystalline state. An x-ray study of these must necessarily be by the powder method. In case the crystal system is sufficiently simple, however, and the number of atomic parameters small this technique may give reliable results. Cesium aurous auric chloride and cesium argentous auric chloride have twice been studied in this manner, and the final structure determination is entirely satisfactory. The results of the experiments are given in the second and third sections.

The theory of the additivity of covalent radii advanced by Pauling and Huggins[3] correlated the data derived from x-ray and electron diffraction investigations of covalently bonded molecules and complex ions. The theory is by no means fully developed. Such things as the effect on bond distance of ionic character, formal charge, and the perturbation due to neighboring atoms need thorough investigation.

A criticism[4] of the theory has been made indirectly that similar results may be achieved with ionic radii even in covalent compounds. The report of an investigation of the "manganese anomaly" given in the fourth section of this series definitely refutes the criticism. An interesting relation between magnetic moment and interatomic distance is also observed.

The technical and theoretical advancement in the theory of the interaction of x-rays and crystals has made it possible to obtain now more information concerning the structure of molecules than could be found only a few years ago. Interatomic distances dependent upon a parameter determination may be fixed with an error of less than 0.004 Å in favorable circumstances. It is becoming increasingly important therefore in connection with the study of molecular structure to reinvestigate many simple crystals. To mention just two examples, it would be very interesting to redetermine accurately the O-O distance in the peroxides and the $C\equiv C$ distance in calcium acetylide.

Further research on the crystal structures of calcite and sodium nitrate has been carried out in these laboratories. Investigation of crystal structure by means of Laue photographs is perhaps the most informative of all x-ray methods for three reasons: the Laue photograph shows reflections from planes with large indices; different planes with the same interplanar distance and scattering x-rays of the same wave length may be compared, resulting in the elimination of all variables in the intensity formula except the form and scattering factors; the development of integrating photometers by Astbury[5] and Robinson[6] allows very accurate determinations of the intensities of reflections on Laue photographs to be made. The first results of a study in which advantage has been taken of all these things is reported in the fifth section.

Research by means of x-rays on crystals containing complex ions or covalently bonded molecules has shown that these substances do indeed have the same groups of atoms which appear so often as units in chemical reactions. Until the present time it has been more or less assumed that to a very good approximation the principal binding forces are the covalent bonds between the atoms of the complex. Only recently through the development of the electron diffraction method of determining the structure of gas molecules has it become possible to test this assumption. The investigation of gaseous SeO_2 given in the sixth section may be compared with the research on solid SeO_2 by McCullough[7]. It is shown that a large change in the type of bonding may sometimes be expected as a substance changes from the crystalline to the gaseous state.

When it may safely be assumed that a molecule has essentially the same configuration in the gaseous and solid phases, a combined attack on the structural problem by electron diffraction and x-ray methods is very useful. Crystals of aluminum chloride are monoclinic and contain two molecules of Al_2Cl_6 in the unit cell. Seven parameters must be known to determine the complete structure. In gaseous aluminum chloride, however, only three parameters need be found. The electron-diffraction study of the gas molecules has been carried out for all the volatile halides of aluminum. The results are reported in the seventh section of this dissertation. They may be readily applied to the problem of investigating the solid halides. This is now reduced to a single parameter determination, the parameter being the angle of rotation of the Al_2Cl_6 molecule around the two-fold axis, if the assumption be made that the molecules retain their configuration in the crystals.

The theory of the additivity of radii will perhaps prove most useful in the analysis of complex organic compounds by means of x-rays. Crystals of these substances often possess low symmetry and have a great many molecules in the unit cell. With present technique it is not usually possible to obtain the correct structure from purely space group and intensity theory. Instead a model of reasonable dimensions, and one compatible with the known chemistry of the compound in question, must be assumed. The problem then becomes one of finding the orientation of the model in the unit cell. In this connection physical properties and space group theory are very important. Their consideration alone often limits the molecule's orientation to quite a narrow range of angles. The investigation of chloral hydrate is interesting in this connection. Pronounced cleavage parallel to the (100) face and the presence of a glide plane in the (001) direction almost certainly fix the chlorine atoms in close-packed layers perpendicular to the b-axis. The dimensions obtained for the unit cell are in agreement with those calculated by assuming interatomic distances taken from Pauling and Huggins' table of radii. The data for the space group and unit cell determination are to be found in the final section of this dissertation.

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4. W. H. Zachariasen, Zeit. für Krist., (A) <u>80</u>, 137 (1931)

5. Astbury, Proc. Roy. Soc., <u>123</u>, 575 (1929)

6. Robinson, Jour. Sci. Instr. Vol. X, No. 8 (1933)

7. J. D. McCoullough, J. A. C. S., <u>59</u>, 789 (1937)

Section 1

The magnetic susceptibility of ammonium hexabromo-hypoantimonate, $(NH_4)_2SbBr_6$, was determined in order to obtain some information about the valence of antimony in this compound.

The substance was prepared by the method of Ephraim and Weinberg[1]. It was dried by centrifuging. The product was a deep black powder, apparently similar in properties to Well's compound.

The determination of the specific magnetic susceptibility by the Gouy method led to a value, $x = - 0.36 \times 10^{-6}$ cgsm., the substance thus being shown to be diamagnetic. Ammonium hexabromohypoantimonate, therefore, does not contain unpolymerized complexes involving a quadrivalent antimony atom, for such complexes would contain an odd number of electrons and hence give rise to strong paramagnetism. It is probable that the substance is a double salt containing one trivalent and one quinquivalent antimony atom corresponding to the formula, $(NH_4)_4Sb^{III}Sb^{V}Br_{12}$. The observed diamagnetism could be made compatible with the presence of quadrivalent antimony by assuming that the quadrivalent antimony atoms occur in groups of two joined by shared electron-pair bonds, Sb:Sb, similar to the group $Hg:Hg^{++}$ in mercurous salts. This, however, seems improbable because the stoichiometric formula, $(NH_4)_2SbBr_6$, suggests that each antimony atom is surrounded by six bromine atoms which would prevent close approach of the antimony atoms.

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(1) Berichte 42, 4450 (1909).

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The Crystal Structure and Magnetic Susceptibility of Caesium Argentous Auric Chloride, $Cs_2AgAuCl_6$, and Caesium Aurous Auric Chloride, $Cs_2AuAuCl_6$

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The triple salts $Cs_2AgAuCl_6$ and $Cs_2AuAuCl_6$ have been investigated by means of magnetic susceptibility measurements and x-ray powder photographs in order to obtain information regarding the general nature of these compounds. Both compounds were found to be diamagnetic. X-ray powder-photographic data lead to a cubic structural unit with $a_0=5.33$A for both crystals. The observed intensity values are in general agreement with the perovskite structure. Small discrepancies, however, suggest that the atomic arrangement varies slightly from the ideal perovskite structure. The detailed nature of the distortion was not determined. The bearing of these results on the valence type of the substances is discussed.

IN 1922 Wells[1] discovered an interesting series of triple salts when he attempted to prepare a caesium silver auric chloride, $Cs_6Ag_2Au_3Cl_{17}$, analogous to Pollard's[2] ammonium silver auric chloride, $(NH_4)_6Ag_2Au_3Cl_{17}$. The substance he obtained was a jet black, finely-divided powder with the stoichiometric formula $Cs_2AgAuCl_6$ and properties quite unlike those of Pollard's salt. Further investigation led to the discovery of several other triple salts having the formulae $Cs_2AuAuCl_6$, $Cs_4CuAu_2Cl_{12}$ and $Cs_4HgAu_2Cl_{12}$. All of these compounds crystallize isomorphously, as shown by solid solution formation, and have colors varying from black to light yellow.

In order to obtain information regarding the valence of the metals and the general nature of these compounds, I have investigated two of them, $Cs_2AgAuCl_6$ and $Cs_2AuAuCl_6$, at the suggestion of Professor Linus Pauling, by means of x-ray powder photographs and magnetic susceptibility measurements. The results of the study are contained in this paper.

We can formulate four reasonable structure types for these salts; (1) Each heavy metal atom may be bivalent and not attached by covalent bonds to other heavy metal atoms. (2) Both heavy metal atoms may be bivalent, the two being joined by a covalent bond forming the group Ag : Au in the case of $Cs_2AgAuCl_6$ and Au : Au in the case of $Cs_2AuAuCl_6$. (3) One heavy metal atom may be univalent and the other trivalent. (4) Each heavy metal atom may resonate between a univalent and a trivalent state.

If the first suggested structure were correct, the compounds would contain groups with an odd number of electrons and hence be paramagnetic. A measurement of their specific magnetic susceptibilities was therefore made by the Gouy method. Both compounds proved to be diamagnetic. The value $\chi=-0.33\times10^{-6}$ c.g.s.m. was found for $Cs_2AgAuCl_6$ and $\chi=-0.25\times10^{-6}$ c.g.s.m. for $Cs_2AuAuCl_6$. The results eliminate a structure with each heavy metal atom bivalent and separate, and we must consider the three remaining structure types.

X-ray powder photographs of $Cs_2AgAuCl_6$ and $Cs_2AuAuCl_6$ were prepared by using molybdenum radiation filtered through zirconia. These were not entirely satisfactory, the lines being rather faint and difficult to measure. However, it was possible to measure about fifteen lines on each photograph. The regular spacing of the lines suggested at once that the crystals are cubic, and, on assigning indices, all the lines could be accounted for on the basis of cubic units with $a_0=5.33\pm0.02$A for both $Cs_2AgAuCl_6$ and $Cs_2AuAuCl_6$. The lines which occur, together with their estimated intensities, are shown in Figs. 1 and 2. No lines occurred requiring a larger unit.

These cubic units contain only one-half of a stoichiometric molecule, $Cs_2AgAuCl_6$ or $Cs_2AuAuCl_6$, as estimated from the atomic volumes of the constituent atoms. The calculated values of the density are 4.266 g/cm^3 and 4.753 g/cm^3, respectively, for $Cs_2AgAuCl_6$ and $Cs_2AuAuCl_6$.

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[1] Wells, Am. J. Sci. 3, 315 (1922).

[2] Pollard, Am. J. Sci. 3, 257 (1922).

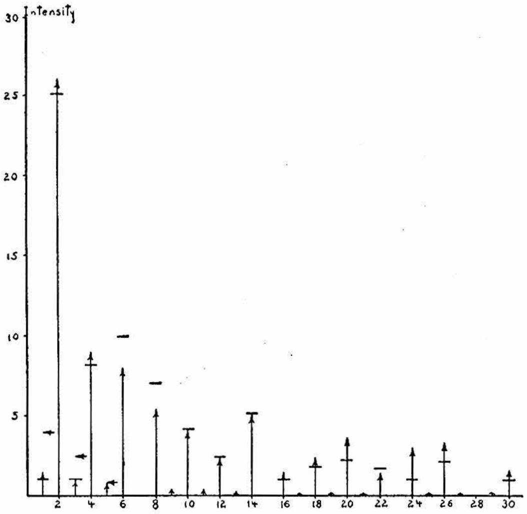

FIG. 1. Powder-photographic x-ray data for $Cs_2AgAuCl_6$. Relative intensities calculated for arrangement *A* are shown by vertical arrows. Horizontal arrows indicate the relative intensities calculated for arrangement *B*. Arrangements *A* and *B* give the same intensities for those lines for which $h^2+k^2+l^2$ is even. Horizontal bars show the observed intensity values.

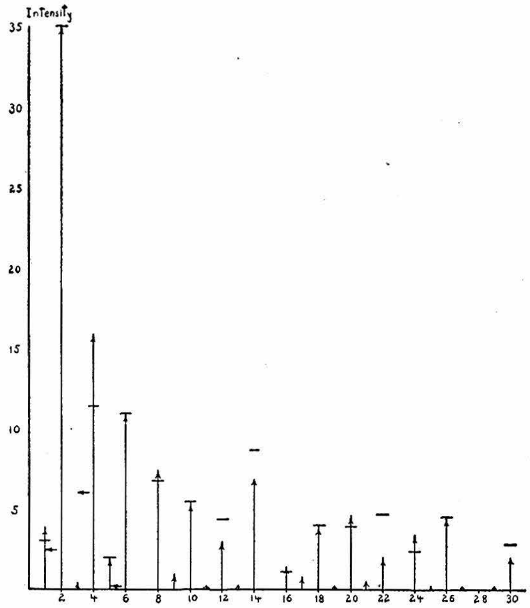

FIG. 2. Powder-photographic x-ray data for $Cs_2AuAuCl_6$. The symbols are the same as for Fig. 1.

No directly measured density values are available for comparison. If these are the true units of structure, the silver compound must contain Ag and Au atoms distributed at random in equivalent positions. We shall first proceed on the assumption that units with $a_0=5.33$A are the true units of structure.

The theory of space groups provides only two ways of arranging 1 M (M = Ag, Au), 1 Cs, and 3 Cl in a cubic unit of structure. These are the following arrangements *A* and *B*.

Arrangement *A*:	Arrangement *B*:
Cs at 000	M at 000
M at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$	Cs at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$
Cl at $0\frac{1}{2}\frac{1}{2}$, $\frac{1}{2}0\frac{1}{2}$, $\frac{1}{2}\frac{1}{2}0$	Cl at $0\frac{1}{2}\frac{1}{2}$, $\frac{1}{2}0\frac{1}{2}$, $\frac{1}{2}\frac{1}{2}0$.

The only difference in these forms is the exchange in position of Cs and M.

With the *f*-values of Pauling and Sherman,[3] values of the intensity of reflection from various planes for these two arrangements were calculated according to the usual intensity formula, including the Lorentz, polarization, and frequency factors. Visual estimates of the intensities were made and compared with the theoretical intensities. The results are shown in Figs. 1 and 2. The positions of the vertical arrowheads give the relative calculated intensities for arrangement *A*, and those of the horizontal arrowheads show the values for arrangement *B*. For $h^2+k^2+l^2$ even, both arrangements have the same values. Horizontal bars indicate observed intensities. It is seen that arrangement *B* is in pronounced disagreement with experiment even for simple planes. Thus (111), $h^2+k^2+l^2=3$, for $Cs_2AuAuCl_6$ is not observed, though calculated for arrangement *B* to be over ten times as strong as (210), $h^2+k^2+l^2=5$. Hence the atomic arrangement is *A*. This is known as the perovskite structure. It may be described as a cubic close-packed arrangement of the large atoms Cs and 3 Cl with the smaller metal atoms, *M*, introduced at the centers of octahedra with six chlorine atoms for corners, each chlorine atom forming a corner of two such octahedra.

The agreement in the observed and calculated intensities is sufficiently good to show that this arrangement must be the actual structure of these crystals or very close to it. Therefore, structure type 2 containing Ag : Au and Au : Au complexes is not correct.

If the perovskite structure were the actual structure of these compounds, equivalence of all the gold atoms would be required in $Cs_2AuAuCl_6$;

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[3] Pauling and Sherman, Zeits. f. Krist. **81**, 1 (1932).

that is, structure type 4, involving resonance of each metal atom between the univalent and trivalent state, would be correct. However, there are some small discrepancies. The calculated and observed intensities of the lines $h^2+k^2+l^2=24$ in Fig. 1 and $h^2+k^2+l^2=22$ in Fig. 2 show definite disagreement when compared with the values of neighboring lines. These discrepancies are sufficient to eliminate the perovskite structure and the valence type 4. It is probable that the structures are based on a larger unit and that the atomic arrangement is a distortion of the perovskite structure so that the six chlorine atoms are brought closer to the trivalent gold atom (valence type 3) than to the univalent gold or silver atom. The data are not sufficiently extensive to permit the detailed discussion of this point. We hope to continue the investigation and to determine completely the structure of these crystals.

Section 3

The Crystal Structure of Cesium Aurous Auric Chloride, $Cs_2AuAuCl_6$, and Cesium Argentous Auric Chloride, $Cs_2AgAuCl_6$

By Norman Elliott and Linus Pauling

The substances cesium aurous auric chloride, $Cs_2AuAuCl_6$, and cesium argentous auric chloride, $Cs_2AgAuCl_6$, discovered by Wells[1], are of interest because of their jet black color, which has been ascribed[2] to the presence of the same element or two closely similar elements in two valence states.[3] In a preliminary investigation carried out some time ago[4] the substances were found to be diamagnetic, showing that they contain gold and silver in the univalent and trivalent exidation states rather than the bivalent state. Powder photographs were also prepared with molybdenum x-radiation. These photographs, each with about fifteen lines, were interpreted as showing the crystals to have a structure closely related to the cubic perovskite type, the unit cube, with $a_0 = 5.33$ Å for each substance, containing 1 Cs at 000, 1 (Au,Ag) at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, and 3 Cl at $\frac{1}{2}\frac{1}{2}0$, $\frac{1}{2}0\frac{1}{2}$, $0\frac{1}{2}\frac{1}{2}$. Although the agreement between the intensities of x-ray reflection calculated for this structure and the observed values was good in general, there were one or two points of pronounced discrepancy

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[1] H. L. Wells, Am. J. Sci. 3, 395 (1922).

[2] H. L. Wells, ibid. 3, 497 (1922).

[3] Norman Elliott, Jour. Chem. Phys. 2, 298 (1934).

[4] Norman Elliott, J. Chem. Phys. 2, 419 (1934).

for each substance, and the conclusion was reached that the structures are actually distorted somewhat from the ideal perovskite arrangement.

In the course of the investigation described below x-ray powder photographs were prepared with copper and iron radiation, giving greater dispersion, and it was found that cesium aurous auric chloride is tetragonal, and contains the complex ions $[AuCl_2]^-$, which is linear, and $[AuCl_4]^-$, which is square. A similar structure occurs for heat-treated samples of cesium argentous auric chloride, which also exists in a cubic modification involving some randomness in atomic arrangement.

The Determination of the Structure of Cesium Aurous Auric Chloride. - Powder photographs of cesium aurous auric chloride were prepared with copper K radiation filtered through nickel and with iron K radiation, the camera radius being 5.005 cm. The photographs show about fifty well defined lines, occurring as multiplets near the angles expected for reflections from a cubic crystal. This suggests that the unit of structure of the crystal is closely related to a cube. The observation that the cubic line (200) occurs as a doublet, with the outer component twice as strong as the inner one, suggests that the crystal is tetragonal. This is supported by the multiplet structure of the other lines, the octahedral reflections being single, reflections with two indices equal double, and those with all three indices different triple.

The tetragonal unit of structure with $a_0 = 7.49 \pm 0.02$ Å and $c_0 = 10.87 \pm 0.02$ Å accounts for the presence of all observed lines(5). The lattice can be taken as body centered, no reflections with $h + k + l$ odd being observed. No classes of planes other than those indicated by the lattice are absent on the photographs. The space group is accordingly D_{4h}^{17} - $I\,4/m\,m\,m$ or one of

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(5) This unit is obtained from the small pseudo-cubic unit by rotating about c through 45° and doubling c_0. It corresponds to the dimensions $a_0 = 5.28$ Å, $c_0 = 5.44$ Å for the small pseudo-unit, with axial ratio 1.03.

its subgroups with the same unit. It was found possible with the assumption of holohedry to determine an atomic arrangement which accounts completely for the x-ray data; it is accordingly probable that the space group of the crystal is $D_{\underline{4h}}^{17}$.

The density of the substance was determined by displacement of benzene to have the value 4.57 g/cc. This corresponds to 1.94 $Cs_2AuAuCl_6$ per unit, the calculated value of the density for two molecules per unit being 4.72 g/cc. There are 4 Cs, 2 Au^{I}, 2 Au^{III}, and 12 Cl atoms to be located. The sets of equivalent positions for $D_{\underline{4h}}^{17}$ are[6]

2a: $000, \frac{1}{2}\frac{1}{2}\frac{1}{2}$;

2b: $00\frac{1}{2}, \frac{1}{2}\frac{1}{2}0$;

4c: $0\frac{1}{2}0, \frac{1}{2}00, \frac{1}{2}0\frac{1}{2}, 0\frac{1}{2}\frac{1}{2}$;

4d: $0\frac{1}{2}\frac{1}{4}, \frac{1}{2}0\frac{1}{4}, \frac{1}{2}0\frac{3}{4}, 0\frac{1}{2}\frac{3}{4}$;

4e: $00z, 00\bar{z}, \frac{1}{2}\frac{1}{2}\frac{1}{2}+z, \frac{1}{2}\frac{1}{2}\frac{1}{2}-z$;

8h: $xx0, \bar{x}\bar{x}0, x\bar{x}0, \bar{x}x0, \frac{1}{2}+x\ \frac{1}{2}+x\ \frac{1}{2}, \frac{1}{2}-x\ \frac{1}{2}-x\ \frac{1}{2}, \frac{1}{2}+x\ \frac{1}{2}-x\ \frac{1}{2}, \frac{1}{2}-x\ \frac{1}{2}+x\ \frac{1}{2}$;

together with 8f, 8g, 8i, 8j, and positions for sets of 16 and 32 equivalent atoms. The photographs show that the atoms are in positions close to those of the perovskite arrangement. This can be achieved only in the following way:

2 Au^{III} in 2a;

2 Au^{I} in 2b;

4 Cs in 4d;

4 Cl in 4e, with $\underline{z} = 1/4$;

8 Cl in 8h, with $\underline{x} = 1/4$;

(The assignemet of Au^{III} to 2b and Au^{I} to 2a leads to the same structures.)

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(6) International Crystal Structure Tables.

The parameters x and z were evaluated from the intensity data given in Table I. The observed intensity values I_{obs} were obtained from microphotometer records of the photographs and from visual estimates made on a series of photographs taken under identical conditions except for varied time of exposure. Intensity values were calculated with the equation

$$I_{calc} \sim \frac{1 + \cos^2\theta}{\cos\theta \sin^2\theta} hF^2$$

in which h is the frequency factor and F the structure factor. F is given by the equation

$$F = f_{Au} + f_{Au \text{ or } Ag} \cos 2\pi\frac{h+k}{2} + (-1)^{l/2} f_{Cs}\left(\cos 2\pi\frac{h}{2} + \cos 2\pi\frac{k}{2}\right)$$
$$+ 2f_{Cl}\left\{\cos 2\pi u(h+k) + \cos 2\pi u(h-k) + \cos 2\pi lv\right\}$$

Screening-constant f values were used[7], without temperature correction. The parameter values obtained in this way, with especial emphasis on comparisons between adjacent lines on the photographs, are x = 0.228 ± 0.003 and z = 0.288 ± 0.003. The excellence of the agreement between observed and calculated intensities with these parameter values is shown in Table I and Figure 1.

The Determination of the Structure of Cesium Argentous Auric Chloride.- Copper-radiation photographs of samples of cesium argentous auric chloride which had been standing at room temperature since their preparation two to three years before were found to show only reflections (about thirty in number) which could be explained by a cubic unit of structure with $a_0 = 5.28 \pm 0.01$ Å, containing $\frac{1}{2}$ $Cs_2AgAuCl_6$. The lines on the photographs are sharp, and the absence of fine structure comparable in magnitude with the clearly resolved Cu $K\alpha_1 - \alpha_2$ doublet for the wide-angle reflections shows that the approximation to a cubic structure is within 0.1 percent.

After the sample had been heated in a sealed evacuated tube at 350°C for 72 hours and cooled slowly to room temperature over a period

Table I

Powder Photographic Data for Cesium Aurous Auric Chloride

Copper radiation.   = 1.539 Å

hkl	d obsd.	d calcd.	I obsd.	I calcd.
002	5.46 Å	5.43 Å	100	128
110	5.28	5.22	200	250
112,200	3.76	3.75	2400	2230
103	3.28	3.26	13	16
121	3.21	3.20	9	7
202	3.11	3.08	16	14
004	2.71	2.72	300	340
220	2.645	2.647	600	660
114,301	2.414	2.420, 2.425	50	52
310,222	2.369	2.370, 2.390	100	106
204	2.200	2.200	300	315
312	2.169	2.177	600	660
105	2.097	2.112	4	2
224	1.892	1.910	450	420
400	1.868	1.872	200	209
006	1.804	1.809	10	10
411,314	1.790	1.793,1.787	26	27
402,330	1.774	1.772,1.767	26	30
116	1.712	1.735	200	191
332,420	1.678	1.698,1.674	300	333
404	1.537	1.546	200	214
226,235	1.498	1.508,1.510	18	18
334,501	1.483	1.485,1.483	13	13
510	1.466	1.467	13	13
136	1.439	1.450	200	213

Table I (cont.)

hkl	d obsd.	d calcd.	I obsd.	I calcd.
244	1.423	1.430	175	172
152	1.415	1.417	175	185
008	1.360	1.358	30	32
118,440	1.320	1.335,1.323	110	131
208,530	1.276	1.292,1.283	50	50
336	1.262	1.272	75	76
600,352	1.248	1.230,1.250	200	214
228	1.207	1.220	100	87
444,620	1.190	1.192,1.184	200	188
156	1.140	1.147	100	114
604	1.133	1.136	40	45
408	1.100	1.100	75	67
264,0·0·10 338	1.085	1.086,1.086 1.085	100	112
446	1.069	1.074	40	36
1·1·10, 550, 710	1.059	1.063, 1.060, 1.060	50	46
248	1.050	1.053	55	57
356	1.043	1.045	140	147
370,554,266, 3·1·10,714	0.986	0.983,0.988, 0.955,0.998, 0.988	150	140
372,644,528	0.966	0.968,0.971, 0.976	150	136
448,40,10	0.951	0.948,0.950	50	55
800,538	0.937	0.937,0.939	35	32
3·3·10,802	0.927	0.924,0.925	50	50
556,608	0.917	0.917,0.917	75	87

Figure 1

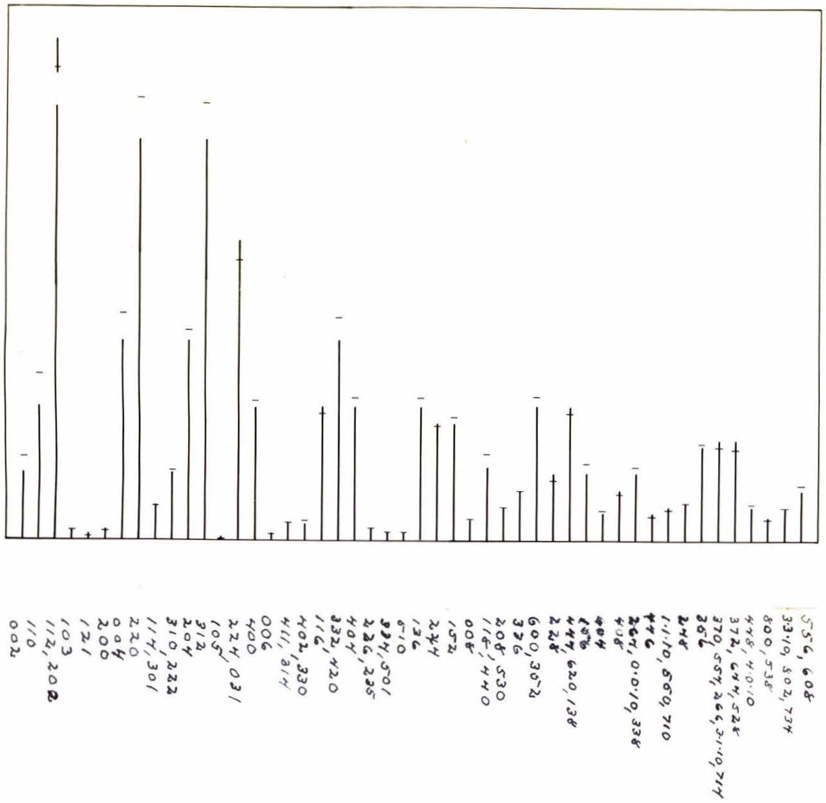
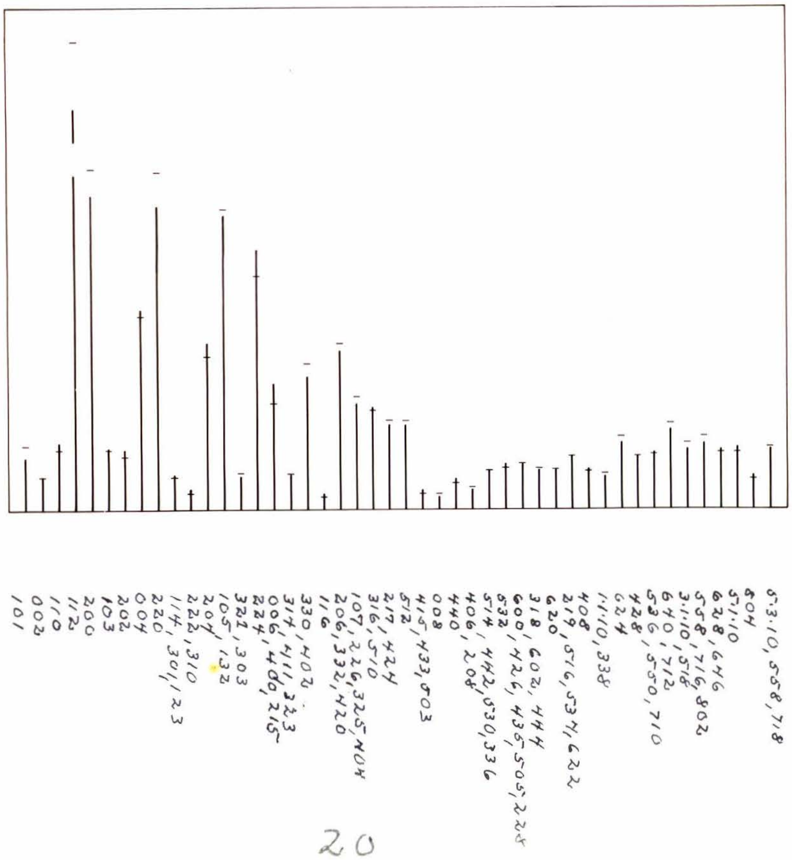


Figure 2



Legends for Figures

Fig. 1. Calculated and observed intensities of reflections on powder photographs of cesium aurous auric chloride. The vertical lines show the observed values of the relative intensities, and the horizontal crossbars the calculated values.

Fig. 2. Calculated and observed intensities of reflections on powder photographs of the tetragonal modification of cesium argentous auric chloride. The vertical lines show the observed values of the relative intensities, and the horizontal crossbars the calculated values.

Fig. 3. The atomic arrangement in tetragonal crystals of $Cs_2AgAuCl_6$ and $Cs_2AuAuCl_6$. Large full circles represent cesium atoms, large open circles chlorine atoms, and small circles gold and silver atoms.

of about five hours, it gave quite different x-ray photographs, the cubic lines being split into components similar to those for the aurous-auric compound, but with still greater separation. The photographs could be completely indexed on the basis of a tetragonal unit with $a_0 = 7.38 \pm 0.02$ Å and $c_0 = 11.01 \pm 0.02$ Å. The unit is body centered, and the observed reflections correspond to the space group $D_{4h}^{17} - I\,4/m\,m\,m$ or one of its subgroups. The atomic arrangement described above for $Cs_2AuAuCl_6$, with Ag^I replacing Au^I and with the parameter values $x = 0.220 \pm 0.03$ and $z = 0.285 \pm 0.003$, accounts completely for the observed intensities, as shown in Table II and Figure 2.

Discussion of the Structures.- The structure found for the tetragonal form of cesium argentous auric chloride (after heating at 350°C) is shown in Figure 3. The structure is closely related to the perovskite structure, the arrangement of the large cesium and chlorine atoms corresponding approximately to cubic closest packing, with the silver and gold atoms alternating in positions at the centers of chlorine octahedra. The distortion from the ideal perovskite structure is such as to show the presence of $(AgCl_2)^-$ and $(AuCl_4)^-$ complexes. Each silver atom has two closest chlorine atoms at the distance 2.36 Å, which is just the sum of the covalent radii for silver (with coordination number two) and chlorine[8]; the other four chlorine atoms of the distorted octahedron are 2.92 Å from the silver atom. The $(Cl-Ag-Cl)^-$ complexes are linear, and are oriented parallel to the c axis of the crystal. Each gold atom has four nearest chlorine neighbors, arranged about it at the corners of a square, at the distance 2.30 Å, which is the sum of the covalent radii of trivalent gold and chlorine. The distance from the gold atom to the two other chlorine atoms in its neighborhood is 3.13 Å.

Table II

Powder Photographic Data for Cesium Argentous Auric Chloride

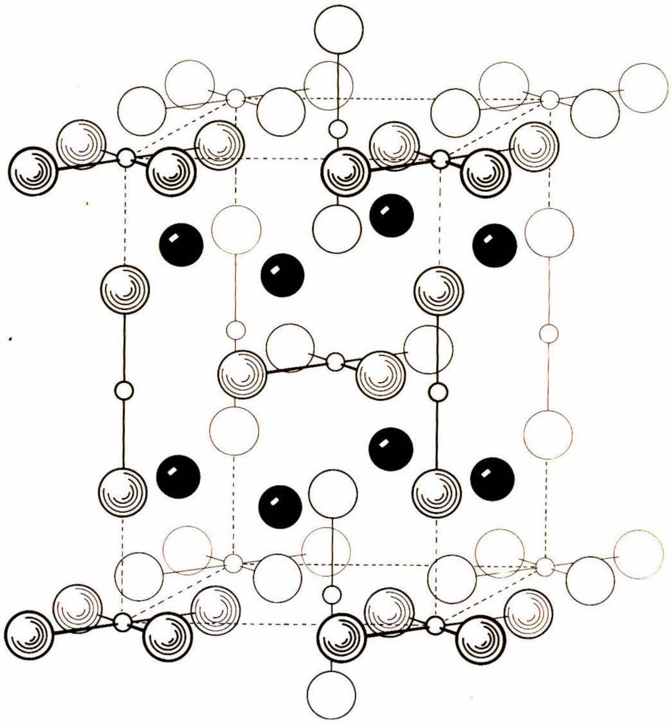
Copper radiation, = 1.539 Å.

hkl	d obsd.	d calcd.	I obsd.	I calcd.
101	6.12 Å	6.10 Å	40	50
002	5.50	5.50	25	26
110	5.24	5.22	50	46
112	3.77	3.77	600	637
200	3.685	3.690	250	270
103	3.275	3.280	50	49
202	3.055	3.054	50	44
004	2.750	2.750	170	163
220	2.601	2.598	260	290
114,301,123	2.436	2.430,2.393, 2.440	30	29
222,310	2.329	2.350,2.325	18	15
204	2.206	2.203	150	136
105,132	2.145	2.107,2.140	265	270
321,303	2.050	2.05,2.06	30	36
224	1.896	1.890	250	220
006,400,215	1.842	1.830,1.835, 1.825	125	105
314,411,323	1.783	1.775,1.760, 1.780	35	36
330,402	1.735	1.732,1.740	135	145
116	1.678	1.690	25	21
332,420,206	1.655	1.652,1.644 1.640	160	170
107,226,325 404	1.530	1.536,1.500, 1.494,1.525	120	126
316,510	1.444	1.440,1.442	120	117

Table II (cont.)

217,424	1.415	1.418,1.412	100	105
512	1.400	1.395	100	107
415,433,503	1.382	1.384,1.380, 1.381	25	20
008	1.373	1.375	16	20
440	1.305	1.300	40	36
406,208	1.293	1.295,1.288	25	29
514,442,530, 336	1.267	1.277,1.265, 1.261,1.259	50	52
532	1.232	1.229	60	55
600,426,435 505,228	1.220	1.225,1.223, 1.222,1.222, 1.215	60	62
318,602,417, 444	1.181	1.183,1.195, 1.178,1.175	55	57
620	1.170	1.167	55	56
622,516,534	1.138	1.140,1.135, 1.145	75	74
408	1.107	1.100	60	58
1.1.10	1.083	1.082	50	54
624	1.076	1.078	100	110
428	1.062	1.055	80	80
710,550,536	1.045	1.044,1.044, 1.039	85	83
640,712	1.026	1.024,1.025	120	130
3.1.10,518	1.003	0.994,0.997	90	100
556,716	0.910	0.905,0.905	100	110
628	0.890	0.888	90	85
5.1.10	0.880	0.875	90	85
804	0.876	0.873	50	45
5.3.10,558 718	0.830	0.836,0.836, 0.836	90	93

Figure 3



The atomic arrangement in tetragonal crystals of $Cs_2AgAuCl_6$ and $Cs_2AuAuCl_6$. Large full circles represent cesium atoms, large open circles chlorine atoms, and small circles gold and silver atoms.

that the structures of the substances would be identical. The low value of the axial ratio of the aurous auric compound suggests that in the sample of this substance used for preparing the photographs the ideal structure with completely oriented complex ions had not been achieved, and that some of the complexes were oriented in a random manner. Some further support for this idea is given by the value of the parameter x, which makes the Au^{III}-Cl distance 0.12 Å larger than in the argentous auric compound; it seems likely that the change in intensities of the lines caused by the partial randomness of the structure has caused a small error in the parameter determination. An effort to test this hypothesis was made by heating the sample of $Cs_2AuAuCl_6$ to 350°C for 24 hours; the photograph obtained of the sample after this treatment was identical with the earlier ones, however, showing that the partial randomness of structure, if it exists, represents the stable state at ordinary temperatures and not a metastable state.

An investigation of cesium aurous auric chloride and cesium argentous auric chloride has been reported recently by Ferrari[12], leading to results different from ours. Ferrari reported the substances to give powder photographs (taken with iron radiation) corresponding to cubic units with a_0 = 5.23 Å in each case, except that a few very faint lines were observed indicating the true units to have values of a_0 twice as large. He suggested a structure involving distortion from the ideal perovskite arrangement such as to give $(AuCl_6)^=$ complexes with the configuration of a regular octahedron. It seems improbable to us that this complex exists; and we believe that the samples studied by Ferrari represent random structures, as described above, with admixture of the tetragonal ordered modifications in sufficient amounts to give the faint extra lines which he observed.

Summary

Crystals of tetragonal cesium aurous auric chloride have a body-centered unit of structure, with a_0 = 7.49 ± 0.02 Å and c_0 = 10.87 ± 0.02 Å, containing 2 $Cs_2AuAuCl_6$. The space group is D_{2h}^{17} - $I\,4/m\,m\,m$, and the atoms are in the following positions of this space group: 2 Au^{III} in 2a; 2 Au^{I} in 2b; 4 Cs in 4d; 4 Cl in 4e, with z = 0.288 ± 0.003; 8 Cl in 8h, with x = 0.228 ± 0.003. Tetragonal cesium argentous auric chloride, $Cs_2AgAuCl_6$, has a similar unit, with a_0 = 7.38 ± 0.02 Å and c_0 = 11.01 ± 0.02 Å, and a similar atomic arrangement (with Ag^{I} replacing Au^{I}), the parameter values being z = 0.285 ± 0.003 and x = 0.220 ± 0.003. These crystals contain linear $(AgCl_2)^-$ and $(AuCl_2)^-$and $(AuCl_2)^-$ ions, similar to $Ag(CN)_2{}^-$, and square coplanar $(AuCl_4)^-$ ions, similar to the $(PdCl_4)^=$ and $(PtCl_4)^=$ ions.

In addition a metastable cubic modification of $Cs_2AgAuCl_6$, capable of conversion into the stable tetragonal modification by heating, was studied. The apparent unit of structure of this is cubic, with a_0 = 5.28 ± 0.01 Å. It contains $\frac{1}{2}$ $Cs_2AgAuCl_6$, and appears to have the perovskite structure, with $\frac{1}{2}(Ag + Au)$ at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, Cs at 000, 3 Cl at $\frac{1}{2}\frac{1}{2}0$, $\frac{1}{2}0\frac{1}{2}$, $\frac{1}{2}\frac{1}{2}0$. It is probable that the crystal contains $AgCl_2''\,^-$ and $AuCl_4{}^-$ complexes with random distribution among the positions and orientations provided by the perovskite structure. Evidence for the existence of a similar modification of $Cs_2AuAuCl_6$ is given by the work of Ferrari.

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3. Norman Elliott, Jour. Chem. Phys. 2, 298 (1934)
4. Norman Elliott, ibid. 2, 419 (1934)
5. This unit is obtained from the small pseudo-cubic unit by rotating about c through 45° and doubling c_o. It corresponds to the dimensions $a_o = 5.28$ Å, $c_o = 5.44$ Å for the small pseudo-unit, with axial ratio 1.03.
6. International Crystal Structure Tables.
7. L. Pauling and J. Sherman, Z. Krist. 81, 1 (1932)
8. L. Pauling and M. L. Huggins, Z. Krist. 87, 205 (1934)
9. J. L. Hoard, ibid. 84, 231 (1933)
10. R. G. Dickinson, J. A. C. S., 44, 2404 (1922).
11. L. Pauling, J. A. C. S., 53, 1367 (1931)
12. A. Ferrari, Gazz. Chim. Ital. 67, 94 (1937)

Section 4

[Reprint from the Journal of the American Chemical Society, **59**, 1958 (1937).]

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 612]

The Crystal Structure of Manganese Diselenide and Manganese Ditelluride

BY NORMAN ELLIOTT

The properties of substances having the pyrite or similar type of structure have usually been interpreted as showing that in these compounds all the bonds are covalent. From x-ray data on pyrite, FeS_2, hauerite, MnS_2, skutterudite, $CoAs_3$, etc., Pauling and Huggins[1] have obtained octahedral radii for metal atoms in the transition groups of the third and fourth rows of the periodic table. They observed that the radius of manganese in hauerite and manganese ditelluride, 1.55–1.59 Å., did not agree with the radius, 1.15 Å., obtained by extrapolating the sequence Ni^{II} Co^{II} Fe^{II} Mn^{II}. A safer extrapolation of the isoelectronic sequence Ni^{IV} Co^{III} Fe^{II} Mn^{I} gave a value 1.24 Å. for Mn^{I} which should be an upper limit for $Mn.^{II}$

The parameter in hauerite was redetermined by Offner[2] as a check on the discrepancy. The value found gave a sulfur radius in excellent agreement with the one assumed by Pauling and Huggins[1] but did not remove the anomaly of the large manganese radius.

In order to extend the investigation to other compounds, the substances manganese diselenide and manganese ditelluride[3] have been prepared and studied by means of x-rays. The results are described in this paper. The discussion of the experimental data includes an interpretation of the magnetic susceptibility measurements made on these and related compounds by Haraldsen and Klemm.[4]

The compounds were prepared by sealing stoichiometric proportions of the elements in evacuated Pyrex glass tubes and heating these in a furnace at 550° for forty-eight hours.

Powder photographs were taken of manganese diselenide and manganese ditelluride using copper radiation filtered through nickel. The photographs are reproduced in Figs. 1 and 2. As both manganese disulfide and manganese ditelluride are known to have the pyrite structure, it was assumed that manganese diselenide also has this structure. The photographs were indexed on the basis of cubic units. Weak extraneous lines were accounted for by the presence of small amounts of manganese selenide and selenium or manganese telluride and tellurium.[4a] Data which were used in determining the selenium and tellurium positions are given in Tables I and II.

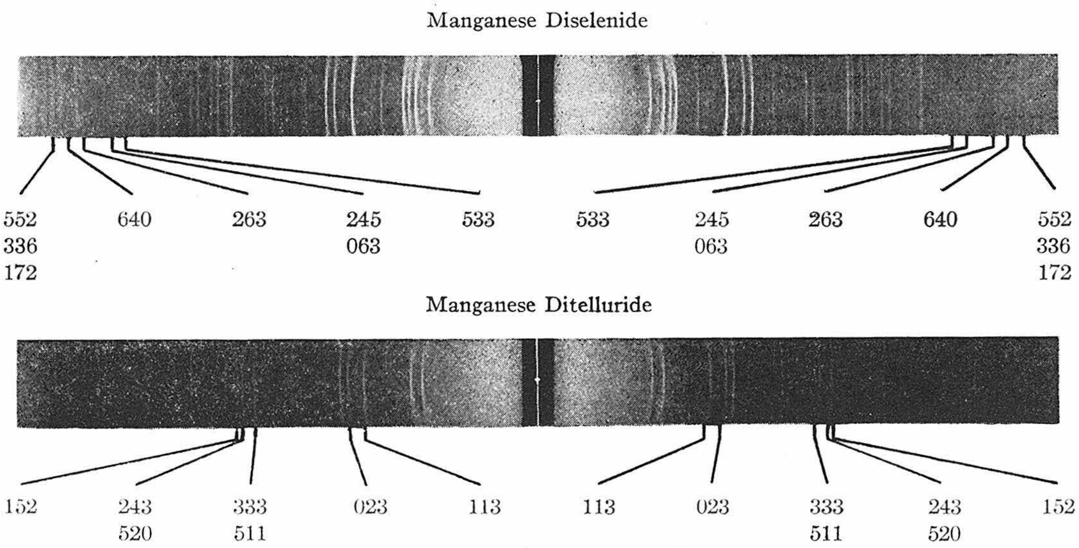

Fig. 1.

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[1] Linus Pauling and M. L. Huggins, *Z. Krist.*, **87**, 205 (1934).

[2] Franklin Offner, *ibid.*, **89**, 182 (1934).

[3] The structure of manganese ditelluride has been determined by Oftedal, *Z. physik. Chem.*, **135**, 291 (1928). In the present investigation a more accurate parameter determination has been made.

[4] Haraldsen and Klemm, *Z. anorg. Chem.*, **223**, 409 (1935).

[4a] Since the writing of this paper pure manganese diselenide has been prepared. X-ray powder photographs of this preparation do not show the extraneous lines observed in earlier work.

TABLE I

MANGANESE DISELENIDE

Copper radiation. λ_α = 1.539 Å. Camera radius 5.005 cm.

2D, cm.	Θ	Sin Θ	hkl	I, obsd.	I, calcd.
4.19	0.2095	0.2080	111	10	8
4.84	.2420	.2397	200	144	144
5.42	.2710	.2677	210	214	226
5.95	.2975	.2932	211	214	214
6.92	.3460	.3391	220	55	52
8.57	.4285	.4155	222	16	14
8.94	.4470	.4322	320	120	120
9.30	.4650	.4484	321	145	145
10.01	.5005	.4797	400	18	19
10.33	.5165	.4939	322 410	16	15
11.00	.5500	.5227	331	6	6
11.32	.5660	.5363	420	2	3
11.63	.5815	.5492	421	50	44
12.55	.6275	.5871	422	8	8
13.15	.6575	.6112	510	9	11
13.44	.6720	.6225	333 511	76	80
14.02	.7010	.6450	432 520	52	55
14.32	.7160	.6565	521	28	30
14.90	.7450	.6780	440	40	44
16.05	.8025	.7190	442 600	18	15
16.35	.8175	.7294	610	7	7
17.48	.8740	.7669	443 540 621	14	15
18.09	.9045	.7860	533	10	10
18.68	.9340	.8040	542 630	14	14
19.91	.9955	.8391	632	16	16
20.55	1.0275	.8560	551 711	16	15
20.88	1.0440	.8645	640	38	38
21.55	1.0775	.8807	633 721 552	40	40
23.41	1.1705	.9209	731 553	42	43

TABLE II

MANGANESE DITELLURIDE

Copper radiation. λ_α = 1.539 Å. Camera radius 5.005 cm.

2D, cm.	Θ	Sin Θ	hkl	I, obsd.	I, calcd.
5.01	0.2505	0.2480	210	198	207
5.50	.2750	.2722	112	208	183
7.54	.3770	.3681	113	99	99
8.24	.4120	.4003	023	87	87
8.57	.4285	.4140	132	117	117
9.20	.4600	.4440	400	18	24
10.67	.5335	.5085	241	45	48
10.95	.5475	.5206	332	24	24
11.48	.5740	.5430	422	3	4
12.29	.6145	.5766	333 511	45	43
12.81	.6405	.5975	432 520	45	48
13.07	.6535	.6080	521	27	30
13.57	.6785	.6275	440	33	36
15.07	.7535	.6841	532 611	33	36

The unit cells of pyrite type structures contain four molecules and have atomic positions defined by the following coördinates of T_h^6:

R: $0\ 0\ 0;\ \frac{1}{2}\ \frac{1}{2}\ 0;\ \frac{1}{2}\ 0\ \frac{1}{2};\ 0\ \frac{1}{2}\ \frac{1}{2}$

X: $u\ u\ u;\ \frac{1}{2}+u, \frac{1}{2}-u, \bar{u};\ \bar{u}, \frac{1}{2}+u, \mathrm{a}-u;\ \frac{1}{2}-u, \bar{u}, \frac{1}{2}+u$

$\bar{u}\ \bar{u}\ \bar{u};\ \frac{1}{2}-u, \frac{1}{2}+u, u;\ u, \frac{1}{2}-u, \frac{1}{2}+u;\ \frac{1}{2}+u, u, \frac{1}{2}-u$

The structure factor for the reflection (*hkl*) with *h*, *k*, and *l* all odd or all even is $F = 4f_R + 8f_X \cos 2\pi\, hu \cos 2\pi\, ku \cos 2\pi\, lu$ and for *h*, *k* even and *l* odd or *h*, *k* odd, *l* even $F = 8f_X \cos 2\pi\, hu \sin 2\pi\, ku \sin 2\pi lu$.

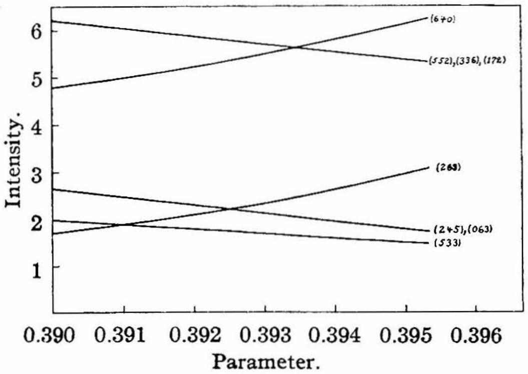

Fig. 2.

The calculated intensities in the sixth columns of Tables I and II are given by the equation

$$I \sim \frac{1 + \cos^2 \Theta}{\cos \Theta \sin^2 \Theta} hF^2$$

where *h* is the frequency factor. The atomic scattering factors used are those of Pauling and Sherman.[5]

The relative observed intensities in the fifth columns were obtained from microphotometer records of the photographs. The estimated accuracy of these results is about ± 20%.

For convenience in making comparisons the lattice constants, parameters, and interatomic distances found for hauerite, manganese diselenide, and manganese ditelluride are shown in Table III. The value of the manganese diselenide parameter is limited to a narrow region, 0.3912–0.3935, by the comparisons (263) > (533), (127)+(336)+(552) > (640), and (263) = (245) +(063). Similarly the comparisons (113) > (023), (520)+(243) = (511)+(333), and (152) = 3/5 {(520)+(243)} require the manganese ditelluride parameter to lie between 0.384 and 0.388. The intensities of these reflections as functions of the parameters are shown in Figs. 2 and 3 for the diselenide and ditelluride, respectively.

The agreement found between observed and calculated intensities of manganese diselenide and ditelluride for the parameter values given in Table III may be seen in Figs. 4 and 5. The lengths of the vertical lines represent relative

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[5] Linus Pauling and J. Sherman, *Z. Krist.*, **81**, 1 (1932).

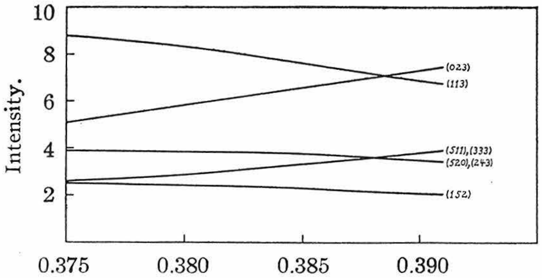

Fig. 3.

observed intensities, the cross bars show the calculated intensities.

TABLE III

Compound	Unit cell dimension, Å.	Parameter	Mn–X distance, Å.	X–X distance, Å.
MnS_2	6.097 ± 0.005[1]	0.4012 ± 0.0004[2]	2.59	2.086 ± 0.008
$MnSe_2$	6.417 ± 0.005	.393 ± 0.001	2.70	2.38 ± 0.02
$MnTe_2$	6.943 ± 0.002[3]	.386 ± 0.002	2.90	2.74 ± 0.05

The sulfur–sulfur, selenium–selenium, and tellurium–tellurium distances found in hauerite, manganese diselenide, and manganese ditelluride are 2.086 ± 0.008, 2.38 ± 0.02, and 2.74 ± 0.05 Å., respectively. The corresponding covalent radii of sulfur, selenium, and tellurium are half these distances. In Table IV the observed radii are compared with the tetrahedral and the normal valence covalent radii of Pauling and Huggins.[1]

If the compounds under investigation were covalent, the observed radii would be expected to agree well with the tetrahedral radii of Table IV. However, the agreement is distinctly better with the normal valence radii, suggesting that each non-metal atom is forming only one covalent bond and that the manganese–non-metal bond is, therefore, an ionic bond.

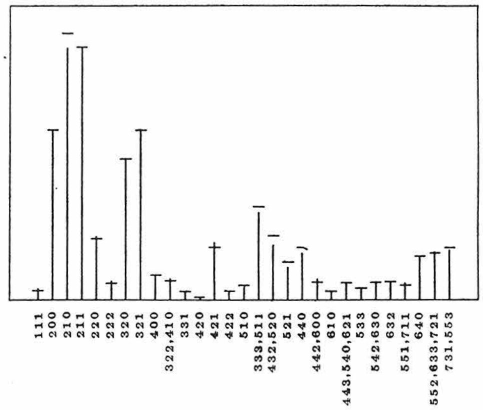

Fig. 4.

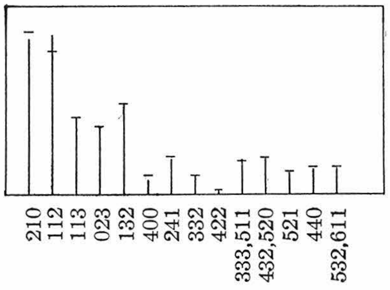

Fig. 5.

TABLE IV

Element	Tetrahedral radius, Å.	Normal valence radius, Å.	Observed radius, Å.
Sulfur	1.04	1.04	1.043 ± 0.004
Selenium	1.14	1.17	1.19 ± 0.01
Tellurium	1.32	1.37	1.37 ± 0.02

It should be possible by means of magnetic susceptibility measurements, as discussed by Pauling,[6] to distinguish between covalent d^2sp^3 bonds and ionic bonds. Divalent manganese ion has five odd electrons filling the five $3d$ orbitals, with a resultant spin moment $\mu = 5.92$ Bohr magnetons. If the bonds are covalent, however, two of the $3d$ orbitals are used in bond formation; two of the odd electrons must therefore pair, leaving only three unpaired with a spin moment $\mu = 3.88$ Bohr magnetons.

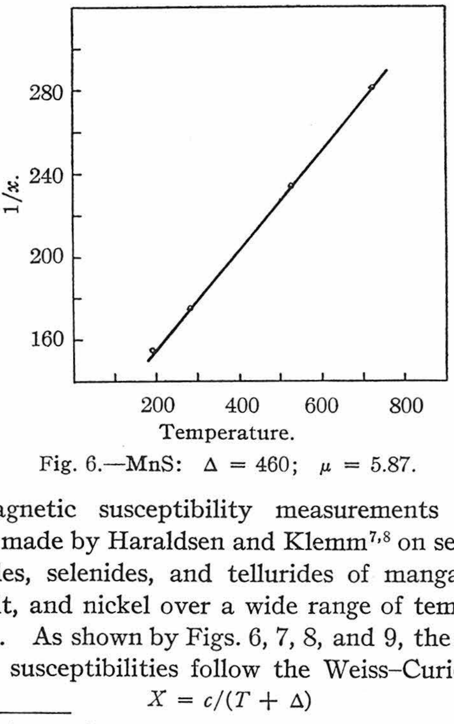

Fig. 6.—MnS: Δ = 460; $\mu = 5.87$.

Magnetic susceptibility measurements have been made by Haraldsen and Klemm[7,8] on several sulfides, selenides, and tellurides of manganese, cobalt, and nickel over a wide range of temperatures. As shown by Figs. 6, 7, 8, and 9, the magnetic susceptibilities follow the Weiss–Curie law

$$X = c/(T + \Delta)$$

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(6) Linus Pauling, THIS JOURNAL, **53**, 1391 (1931).

(7) Haakon Haraldsen and Wilhelm Klemm, *Z. anorg. Chem.*, **220**, 183 (1934).

(8) Haakon Haraldsen and Wilhelm Klemm, *ibid.*, **223**, 409 (1935).

The values of Δ may be obtained from the graphs. The magnetic moments are then calculated from the equation

$$\mu = 2.84\sqrt{X_{\text{mol.}}\,(T + \Delta)}$$

The moments found for manganous sulfide and manganese disulfide are 5.87 and 6.13. The values are very close to the value 5.92 predicted for divalent manganese ion and are in definite disagreement with the presence of d^2sp^3 bonds in either compound. Since alabandite, manganous sulfide, has been shown by Wyckoff[9] to have the rock-salt structure or one very similar, a moment of about 5.92 was to be expected. The experimental value, 5.87, not only substantiates Wyckoff's[9] structure determination, but, in addition, it confirms the present interpretation of Haraldsen and Klemm's[7,8] magnetic susceptibility measurements.

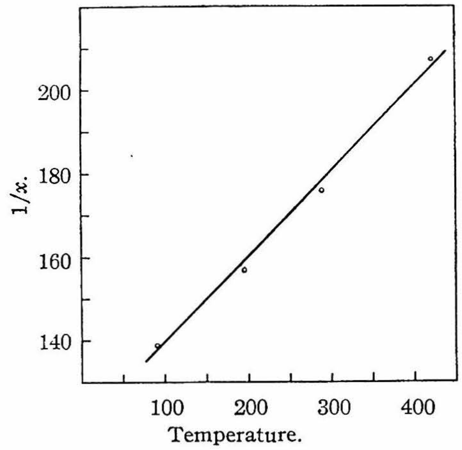

Fig. 7.—MnS_2: $\Delta = 528$; $\mu = 6.13$.

The observed moment of cobalt disulfide, 1.99, is in agreement with the assumption that here the cobalt is forming octahedral d^2sp^3 bonds, the predicted spin moment in this case being 1.73. The moment observed for nickel disulfide does not permit a decision to be made regarding the type of bond between the nickel and sulfur. Either ionic or covalent octahedral bonds leave the nickel atom with two odd electrons and a predicted moment of 2.83 Bohr magnetons which is close to the observed value, 2.71. The comparison of the covalent radii of the transition elements made earlier in this paper leads, however, to the natural supposition that in nickel disulfide the nickel–sulfur bonds are covalent also.

The anomalous manganese radius may thus be accounted for readily by saying the bonds of manganese in pyrite type structures are essentially ionic while those of iron, cobalt, and nickel are essentially covalent.

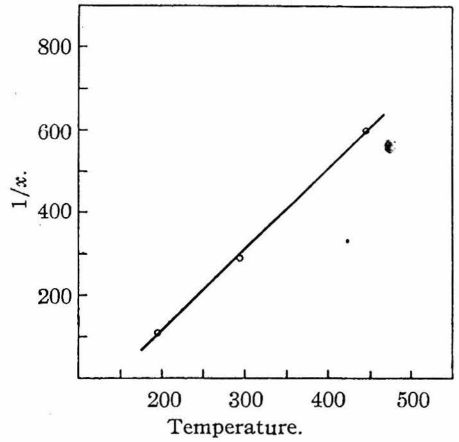

Fig. 8.—CoS_2: $\Delta = -150$; $\mu = 1.99$.

Another explanation suggested by Professor Pauling is that the manganese bonds resonate between ionic and sp^3d^2 bonds, the sp^3d^2 bonds involving $4d$ rather than $3d$ orbitals. In this case a non-metal–non-metal distance intermediate between the sum of the tetrahedral and the sum of the normal valence covalent radii would be expected. It may be concluded from the observed selenium–selenium and tellurium–tellurium distances in manganese diselenide and ditelluride that the amount of resonance is rather small.

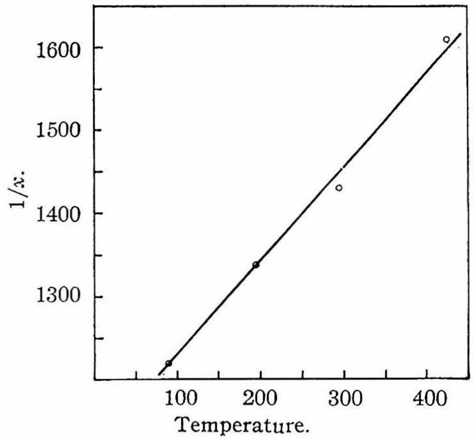

Fig. 9.—NiS_2: $\Delta = 1025$; $\mu = 2.71$.

It is interesting to note that further tests may be made on cobalt and nickel diselenide and ditelluride. If these compounds are covalent the selenium–selenium and tellurium–tellurium distances should agree closely with the sum of the

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[9] Wyckoff, *Am. J. Sci.*, **2**, 239 (1921).

tetrahedral radii for these elements. These values, 2.28 and 2.64 Å., would be shorter than the distances observed in the corresponding manganese compounds. It is planned to prepare several of these substances and to investigate their magnetic susceptibilities and crystal structures in these Laboratories.

Acknowledgment.—The author wishes to thank Professor Linus Pauling for his interest and help in this investigation; his suggested interpretation of the magnetic measurements of Haraldsen and Klemm proved especially valuable. The author also wishes to thank Dr. James H. Sturdivant for his kind advice concerning the preparation of the powder photographs.

Summary

The crystal structures of manganese diselenide and manganese ditelluride have been investigated with x-rays and found to belong to the pyrite type of structure. The cubic unit of manganese diselenide has the dimension $a_0 = 6.417 \pm 0.005$ Å. and the parameter $u = 0.393 \pm 0.001$. For manganese ditelluride the corresponding values are $a_0 = 6.943 \pm 0.002$ Å. and $u = 0.386 \pm 0.002$.

The results obtained suggest that in the pyrite type structures the manganese–non-metal bonds are either ionic or resonate between ionic and covalent, the covalent part involving 4*d* orbitals from the manganese rather than 3*d* orbitals.

The magnetic susceptibility measurements of Haraldsen and Klemm,[7,8] on the sulfides of manganese, cobalt, and nickel, are interpreted as supporting the results of the X-ray investigation, and, further, as showing that cobalt and nickel probably form covalent d^2sp^3 bonds in these compounds.

PASADENA, CALIF. RECEIVED JULY 19, 1937

Section 5

[Reprint from the Journal of the American Chemical Society, **59**, 1380 (1937).]

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 601]

A Redetermination of the Carbon–Oxygen Distance in Calcite and the Nitrogen–Oxygen Distance in Sodium Nitrate

BY NORMAN ELLIOTT

For the case of carbon–carbon interaction in molecules an empirical function has been found[1] which relates the observed interatomic distances to the type of bond formed. The same function, with a suitable translation and change of scale, has been used to predict distances between other atoms, notably carbon–oxygen and nitrogen–oxygen distances. A large discrepancy occurs for the carbonate ion between the predicted distance, 1.32 Å., and the distance reported for calcite.[2] This disagreement and the desirability of testing the assumptions involved in the use of the function have led to a reinvestigation of the parameters in calcite and sodium nitrate.

Crystals of calcite and sodium nitrate were ground on (111) and (211) faces[3] and Laue photographs obtained of each substance in two orientations, one with the primary beam perpendicular to the cleavage plane, the other with the X-rays parallel with the three-fold axis. On each set of photographs pairs of reflections were found having nearly the same values of sin Θ and of $n\lambda$. The relative intensities of each pair were estimated visually by comparing photographs having different known exposures. The more important reflections were photometered on an alpha-ray integrating microphotometer.[4]

Theoretical structure factors, F_{hkl}, were based on the Pauling and Sherman[5] tables of atomic scattering factors. Since the comparisons involve the ratio of intensities of reflections having approximately the same wave length and scattering angle, no other terms need be included in the calculations. The ratio of the intensities reflected from two planes, (hkl) and $(h'k'l')$, was then assumed to be equal to the ratio of the squares of the corresponding structure factors

$$I_{hkl}/I_{h'k'l'} = F^2_{hkl}/F^2_{h'k'l'}$$

The possibility that the intensities might be proportional to the first power of the structure factors was also considered.[6] When calculations are made on this basis, the individual intensity ratios of Tables I and II lead to a very wide range of parameter values, whereas the spread is small when the squares of the structure factors are used. This indicates strongly that for the separate crystal sections used in this investigation the intensities are closely proportional to F^2.

In Tables I and II there are given the results of the microphotometric measurements for calcite and sodium nitrate, respectively. In all cases but one, two carbon prints were measured for

TABLE I

PARAMETER DETERMINATION FOR CALCITE USING MICROPHOTOMETER VALUES OF INTENSITIES

Reflecting planes	Interplanar distance	Wave length	I/I'		Parameter	
$1\bar{7}2$	1.032	0.37	2.46	2.30	0.2624	0.2633
905	1.040	.36				
5.12.7	1.031	.37	1.95		.2614	
$4\bar{5}3$	1.031	.36				
921	0.530	.32	1.63	1.79	.2630	.2656
$37\bar{2}$	.535	.32				
$7\bar{1}6$	.530	.32	1.75	1.71	.2650	.2642
$37\bar{2}$	.535	.31				
$37\bar{2}$	.535	.32	1.16	1.02	.2631	.2670
$17\bar{2}$	.534	.31				
720	.628	.35	12.11	13.18	.2628	.2637
$45\bar{2}$	.635	.36				
$\bar{1}27$	.591	.36	4.25	4.13	.2640	.2646
$74\bar{1}$	.580	.36				

Weighted average value of the parameter, 0.2635 ± 0.0011.

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(1) Pauling, Brockway and Beach, THIS JOURNAL, **57**, 2705 (1935).

(2) Wyckoff, *Am. J. Sci.*, **50**, 317 (1920).

(3) The indices employed in this paper refer to the smallest rhombohedral units of structure. The lattice constants for calcite are a_0 = 6.36Å., α = 46°6′; those for sodium nitrate are a_0 = 6.32 Å., α = 47°15′. The space group of both substances is $D^6_{3d} - R\bar{3}c$, with atoms in the positions

Ca or Na: $^1/_4\ ^1/_4\ ^1/_4;\ ^3/_4\ ^3/_4\ ^3/_4$
C or N: $0\ 0\ 0;\ ^1/_2\ ^1/_2\ ^1/_2$
O: $u\ \bar{u}\ 0;\ \bar{u}\ 0\ u;\ 0\ u\ \bar{u};\ ^1/_2 - u,\ ^1/_2 + u,\ ^1/_2;$
$^1/_2 + u,\ ^1/_2,\ ^1/_2 - u;\ \ ^1/_2,\ ^1/_2 - u,\ ^1/_2 + u.$

(4) The application of the alpha-ray integrating microphotometer to the determination of X-ray intensities was first reported by Astbury, *Proc. Roy. Soc.*, **123**, 575 (1929). The microphotometer measures the intensity of alpha-rays passing through a carbon print of an X-ray negative. The necessary conditions for obtaining integrating properties are that a linear relation exist between the X-ray intensity of a given reflection and the corresponding alpha-ray intensity, taken as the rate of discharge of an electroscope; and that zero X-ray intensity correspond to zero alpha-ray intensity. These conditions are easily met by adjusting the constants of the apparatus.

(5) Pauling and Sherman, *Z. Krist.*, **81**, 1 (1932).

(6) This phenomenon has been observed in the case of calcite by P. E. Tahvonen, *Societas Scientiarum Fennica, Commentationes Physico-Mathematicae*, VIII, 6 (1935), and other investigators.

TABLE II

PARAMETER DETERMINATION FOR SODIUM NITRATE USING MICROPHOTOMETER VALUES OF INTENSITIES

Reflecting planes	Interplanar distance	Wave length	I/I'		Parameter	
207	0.670	0.45	2.10	2.11	0.2400	0.2400
$\bar{1}36$	.695	.46				
$\bar{2}34$	.800	.44	2.17	2.14	.2385	.2390
$\bar{1}25$	.825	.44				
$\bar{1}50$	.790	.39	1.84	2.00	.2398	.2392
$\bar{2}34$	.800	.38				

Weighted average value of the parameter, 0.2394 ± 0.0005.

TABLE III

PARAMETER DETERMINATION FOR CALCITE USING VISUAL ESTIMATES OF INTENSITIES

Reflecting planes	Interplanar distance	Wave length	I/I'	Parameter
$1\bar{1}4$	0.970	36	2.5	0.260
$42\bar{1}$	.960	37		
723	.807	34	6.5	.261
241	.798	33		
12.7.7	.534	36	2.5	.262
$\bar{3}64$	.529	36		
$5\bar{2}3$	.690	43	2.0	.265
945	.635	44		
$\bar{3}43$	.650	32	7.0	.261
$6\bar{1}4$	.640	33		
$\bar{3}56$	.492	30	2.0	.262
10.1.3	.484	30		
$\bar{2}37$	.535	30	1.5	.257
$\bar{2}71$	.534	29		

Weighted average value of the parameter, 0.261 ± 0.002.

TABLE IV

PARAMETER DETERMINATION FOR SODIUM NITRATE USING VISUAL ESTIMATES OF INTENSITIES

Reflecting planes	Interplanar distance	Wave length	I/I'	Parameter
$\bar{1}14$	0.995	0.41	1.33	0.235
$2\bar{1}4$	.985	.41		
$\bar{1}50$	.790	.40	1.90	.240
106	.760	.40		
$5\bar{1}4$	.750	.40	1.75	.239
106	.760	.40		
$\bar{5}01$	.790	.47	1.60	.240
163	.810	.47		

Weighted average value of the parameter, 0.239 ± 0.002.

each pair of reflections, giving the intensity ratios I/I' in the fourth columns.

In Figs. 1 and 2, corresponding to Tables I and II, the intensity ratios of pairs of reflections are plotted as ordinates with the parameters as abscissas. The final parameter values in the fifth columns of the tables were read directly from these graphs.

Each parameter value was multiplied by the slope of the corresponding intensity curve as a weight factor in obtaining the average values, for it is clear that, other effects being equal, the reliability of a single result is proportional to this slope. The limits of error are taken as the average deviations.

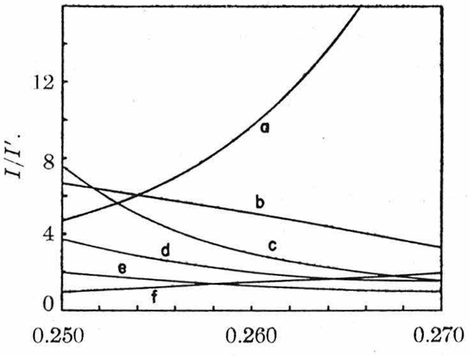

Fig. 1.—$a = I_{720}/I_{45\bar{2}}$; $b = I_{\bar{1}27}/I_{74\bar{1}}$; $c = I_{1\bar{7}2}/I_{905}$; $d = I_{5\cdot12\cdot7}/I_{4\bar{5}3}$; $e = I_{37\bar{2}}/I_{17\bar{2}}$; $f = I_{7\bar{1}6}/I_{37\bar{2}}$; and $I_{921}/I_{37\bar{2}}$.

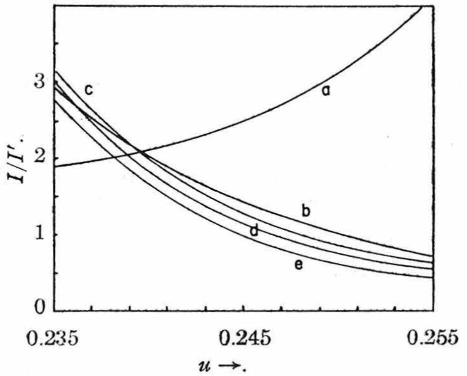

Fig. 2.—$a = I_{207}/I_{\bar{1}36}$; $b = I_{\bar{2}34}/I_{\bar{1}25}$; $c = I_{\bar{1}50}/I_{106}$; $d = I_{\bar{1}50}/I_{\bar{2}34}$; $e = I_{5\bar{1}4}/I_{106}$.

The parameter values found for calcite and sodium nitrate, 0.2635 and 0.2394, respectively, are not in disagreement with the results of Wyckoff's[2,7] experiments which allow a range of 0.24 to 0.26 with the probable value 0.25 in each case.

The observation of a weak reflection ($31\bar{1}$) on several photographs of both substances in the present investigation suggests that the parameters cannot be exactly 0.25. This reflection has zero amplitude for $u = 0.25$ inasmuch as the structure factor has the form $f_0 \sin 2u(h-k) + \sin 2u(k-l) + \sin 2u(l-h)$ for planes the sum of whose indices is odd. Other planes of this type are too weak to reflect and do not appear on the

(7) Wyckoff, *Phys. Rev.*, **16**, 149 (1920).

photographs. Failure to observe ($31\bar{1}$) on Wyckoff's photographs is due to the excessive fogging of the negatives by the incident radiation in the region around the central image.

The values found for the C–O and N–O distances are 1.313 and 1.210 Å. On comparing these with the values 1.32 and 1.26 Å., respectively, predicted by Pauling, Brockway and Beach,[1] we see that the disagreement which had existed in the case of the carbonate ion has been removed, but that a difference of 0.05 Å. is found for the nitrate ion.[8] It seems probable that this difference shown by the nitrate ion is to be attributed to a previously unrecognized phenomenon, namely, the effect of resultant charge of an atom on its covalent radius. From the electronic-structural point of view we interpret the decrease in the sequence of values 0.77, 0.70, 0.66, 0.64 Å. for the single-bond covalent radius of carbon, nitrogen, oxygen, fluorine, respectively, as due to an increase in effective nuclear charge of the atoms, which can be estimated with the use of screening constants to amount to about 0.6 unit from one atom to the next.[9] In the case of a bond between two atoms with formal charges of opposite sign, the interatomic distances would be given approximately by the sum of the radii for neutral atoms, since the increase in radius of the negatively charged atom would be approximately compensated for by the decrease in radius of the positively charged atom. In the nitrate ion a nitrogen atom with formal charge $+1$ is connected by single bonds to oxygen atoms with formal charge -1 and by a double bond to a neutral oxygen atom. For the single bond we accordingly expect approximately the normal single-bond distance, but for the double bond we expect a distance shorter than the normal value, corresponding to an increase for nitrogen of about one unit in effective nuclear charge. This would lead to a value for the double-bond radius between those of oxygen and fluorine, that is, about 0.05 Å. less than the normal double-bond radius of nitrogen. Resonance between this double bond and the single bonds would lead to an expected nitrogen to oxygen distance in the nitrate ion 0.05 Å. less than that predicted by Pauling, Brockway and Beach, and in exact agreement with the new experimental value. This agreement between the experimental value and the value predicted by the above straightforward argument provides strong evidence for the correctness of the postulated dependence of the covalent radius on effective nuclear charge. The phenomenon should be observed in many other substances, such as, for example, the tetramethylammonium ion; experiments to test these predictions are planned.

The author wishes here to express his thanks to Professor Linus Pauling for suggesting this research, for his continued help and interest throughout the course of the investigation, and for a major contribution to the discussion at the end of this paper, and to Dr. J. H. Sturdivant for kind advice and direction in the preparation of the Laue photographs and in the use of the alpha-ray microphotometer.

Summary

A reinvestigation of the parameters of calcite and sodium nitrate has been carried out using data obtained from Laue photographs. The parameters found are 0.2635 for calcite and 0.2394 for sodium nitrate. These values lead to the interatomic distances 1.313 Å. for the carbon–oxygen bond and 1.210 Å. for the nitrogen–oxygen bond. A comparison with the distances predicted by Pauling, Brockway, and Beach[1] is made, and agreement found for the carbonate ion. The short nitrogen–oxygen distance is discussed in relation to the effect of resultant charge of an atom on its covalent radius.

PASADENA, CALIF. RECEIVED MAY 25, 1937

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(8) The revision of the table of covalent radii and of the resonance curve reported by Pauling and Brockway, THIS JOURNAL, **59**, 1223 (1937), leads to no change in the predicted distances.

(9) See Pauling and Sherman, *Z. Krist.*, **81**, 1 (1932).

Section 6

The Molecular Structure of Selenium Dioxide Vapor

By K. J. Palmer and Norman Elliott.

Electron diffraction photographs of selenium dioxide vapor were taken and interpreted in the way already described in the literature.[1] The photographs showed five well-defined but rather broad maxima, whose relative positions and intensities were approximately those to be expected for a diatomic molecule. This is due to the relative unimportance of the oxygen-oxygen scattering as compared to the selenium-oxygen scattering. The values of s_o $(= \frac{4\pi \sin\Theta/2}{\lambda})$, the visually measured intensities (I), and C $(= Is_o^2 e^{-as_o})$ are given in Table I. The values of C and s_o were used in calculating a radial distribution curve as recently suggested[2], and the resulting curve is reproduced in Fig. 1. The well-defined peak at 1.61 Å corresponds to the selenium-oxygen distance; the other peaks lying farther out are too unreliable to be of any importance in determining the oxygen-oxygen distance.

Two simplified intensity curves were calculated, one for a linear model and the other for a model having an O-Se-O angle of 120°. The latter is reproduced in Fig 2. The two curves are so nearly identical, both with regard to shape and position of the maxima, that it is impossible from a qualitative comparison with the photograph to make a choice between them. The quantitative comparison of s_c/s_o given in Table I leads to the selenium-oxygen distance 1.61 ± 0.03 Å, in exact agreement with the radial distribution curve. In analogy with sulfur dioxide, the O-Se-O angle is probably close to 125°. Using this value for the angle the oxygen-oxygen distance is 2.86 Å

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(1) L. O. Brockway, Rev. Modern Phys. 8, 231 (1936).

(2) V. Schomaker and C. Degard, To be published soon.

Discussion:

The value 1.61 Å is considerably lower than the sum of the double bond radii of selenium and oxygen. The double bond factor for third row elements is 0.93. This gives 1.66 Å for the selenium-oxygen double bond distance. On correction for the formal charge effect as suggested by Elliott[3], this is reduced to the value 1.64 Å. If one considers only the electronic structures representing resonance between a selenium-oxygen double bond and a single bond, then each bond would possess 50 % double bond character. The interatomic distance, found by application of the usual resonance curve, is 1.69 Å. The discrepancy between this value and that observed is probably due to the importance of electronic structures in which the oxygen is bonded to the selenium atom by a triple bond. A bond of this type is possible because selenium is not restricted rigorously by the octet rule.

The observed sulfur-oxygen distance in sulfur dioxide bears about the same relation to the radii as that found for selenium dioxide, and the two molecules are probably closely similar in electronic structure.

The selenium dioxide crystal[4] does not contain discrete SeO_2 molecules, but instead consists of infinite chains. The observed Se-O distances in the crystal, 1.78 Å and 1.73 Å, have been discussed by McCullough.

We are indebted to Dr. James D. McCullough for furnishing us with the sample of selenium dioxide, and to Professor Linus Pauling for his aid and criticism during the course of this investigation.

Summary

Electron diffraction photographs of selenium dioxide vapor have been

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(3) Norman Elliott, J. A. C. S. 59, 1380 (1937).

(4) James D. McCullough, J. A. C. S. 59, 789 (1937).

interpreted to lead to the value 1.61 ± 0.03 Å for the Se-O distance. The value of the angle O-Se-O could not be determined.

Table I

Max.	Min.	I	C	s_o	s_c*	s_c/s_o
1		10	33	5.185	4.32	(0.833)
	2			6.800	6.00	.882
2		7	50	8.771	7.88	.898
	3			10.700	9.55	.893
3		4	38	12.404	11.28	.909
	4			14.690	13.15	.895
4		2	17	16.652	14.75	.886
	5			18.458	16.50	.894
5		1	6	20.391	18.37	.901
			Average			0.894
			Average deviation			0.006

Se-O = (1.80)(0.894) = 1.61 ± 0.03 Å

* Calculated for the model with Se-O = 1.80 Å and the angle O-Se-O = 120°.

Figure 1

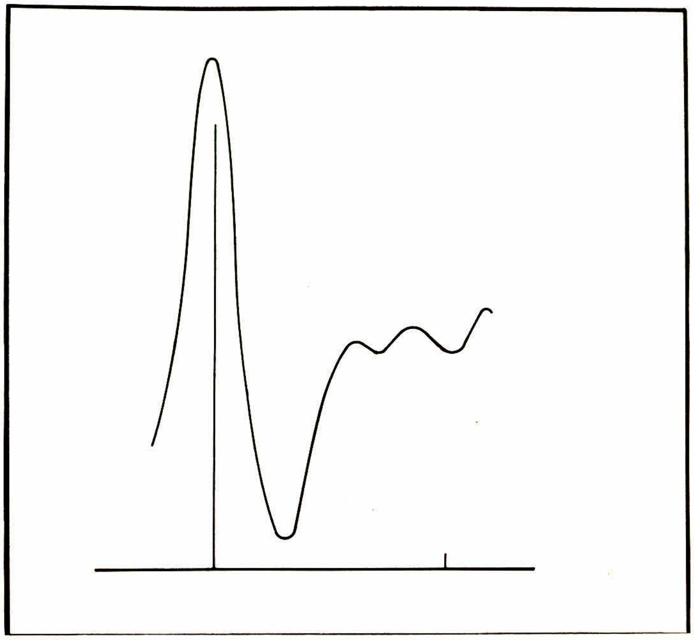
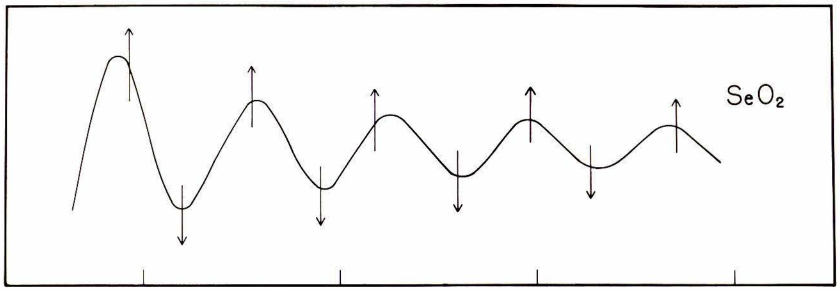


Figure 2



Legends to figures:

Fig. 1. Radial distribution curve for selenium dioxide.

Fig. 2. Intensity curve for selenium dioxide, calculated for Se-O = 1.80 Å and O-Se-O angle = 120°. The positions of the arrows, indicating measured maxima and minima, have been decreased by 8.9 percent to indicate the quantitative agreement with the final model with Se-O = 1.61 Å

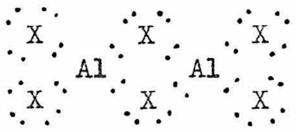
Section 7

The Electron Diffraction Investigation of Aluminum Chloride, Bromide, and Iodide.

By K. J. Palmer and Norman Elliott

The unusual physical and chemical properties of aluminum chloride, bromide, and iodide lend considerable interest to the electron diffraction investigation of these compounds in the gas phase. Vapor density measurements have shown that in the gaseous state below approximately 400°C the substances exist as the dimeric molecules Al_2Cl_6, Al_2Br_6, and Al_2I_6.

The same configuration is suggested for these molecules by considerations based on the extreme ionic and the extreme covalent point of view. The radius ratio of the ions Al^{3+} and Cl^- is 0.40 (ratio of univalent radii[1]), which corresponds to tetrahedral coordination. This can be achieved for a molecule Al_2X_6 by the sharing of an edge between two tetrahedra, as shown in Fig. 1. From the covalent point of view this configuration would be expected as the result of the tendency of the aluminum atoms to complete their octet valence shells, the electronic structure of the molecule being



The suggestion of this as a possible structure for the aluminum halides was made by Fajans[2].

We have carried out the study of these substances by the electron dif-

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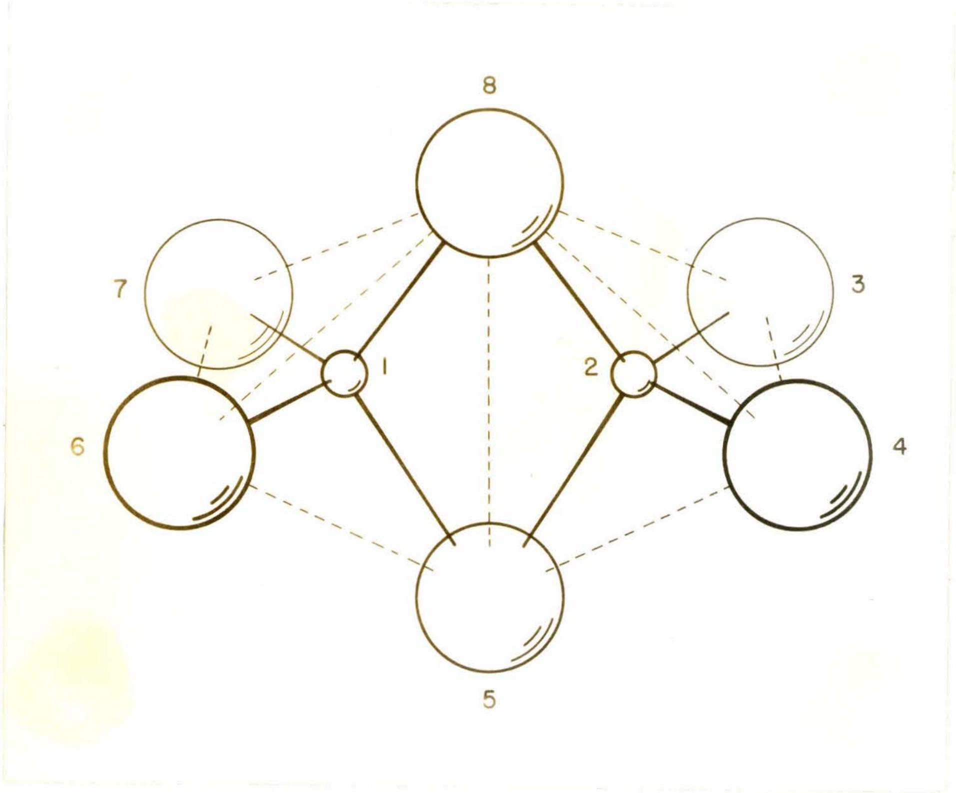
(1) Linus Pauling, J.A.C.S.

(2) K. Fajans, Zeit. f. Electrochemie 34, 502 (1928).

Figure 1



fraction method, and have verified the double-tetrahedral configuration of Fig. 1, with some deformation of the tetrahedra, as described below.

Experimental

The electron diffraction photographs were obtained and interpreted in the usual way.[3] The wave length of the electrons was 0.0613 Å and the camera distance 10.85 cm for the chloride and bromide and 20.16 cm for the iodide.

The strong tendency of the aluminum halides to hydrolyze made it necessary to transfer the samples to the high temperature nozzle inside a moisture proof box. The nozzle[4] could then be sealed and inserted into the electron diffraction apparatus, the sample not being allowed to come into contact with moist air. This procedure proved to be satisfactory, as was verified by inspection of the nozzle after the exposures were made. In no case was there any sign of decomposition.

Merck's C.P. aluminum chloride was used without further purification. The aluminum bromide was made by the method of Richards and Krepelka[5]. The aluminum iodide was prepared by heating iodine with excess aluminum in an evacuated glass tube held in a vertical position. The temperature was maintained at 300°C for six hours, in which time the color due to the iodine vapor had completely disappeared. The aluminum iodide which collected in the lower part of the tube along with the excess aluminum was separated from the latter by distilling it to the upper part of the tube and then sealing the tube off

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(3) L. O. Brockway, Rev. Modern Phys. 8, 231 (1936).

(4) L. O. Brockway and K. J. Palmer, J. A. C. S., 59, 2181 (1937).

(5) W. Richards and H. Krepelka, J. A. C. S., 42, 2221 (1920).

at the center. The product appeared in the form of colorless highly refractive crystals. There was no evidence of any iodine vapor being present either during or after the distillation. These crystals were used without further purification.

Aluminum Chloride.-- The photographs of aluminum chloride show nine maxima. The averaged values of s_o, I (the visually estimated intensities), and C (equal to $Is_o^2e^{-as_o^2}$) are given in Table I. The qualitative appearance of the photographs is well represented by curve F of Fig. 3 which was calculated for the finally accepted model. The radial distribution curve[6], curve A of Fig. 2, calculated using the values of C (Table I) in place of I, shows principal peaks at 3.56 and 2.11 Å. These values are interpreted as the Cl-Cl and the short Al-Cl distances respectively. The ratio of these, 1.69, is close to that (1.633) for a regular tetrahedral arrangement of chlorine atoms about the aluminum atoms. Strong support for this structure is provided by the simplified theoretical intensity curve calculated for the regular tetrahedral model (Curve A of Fig. 3), which shows good, although not complete, agreement with the characteristics of the photographs.

In order to find a model in which the ratio of Cl-Cl to Al-Cl is 1.69, all of the edges of the two tetrahedra except the shared edge were assumed to have the value 3.56 Å, and the eight smallest Al-Cl distances the value 2.11 Å. The shared edge would then have the value 2.58 Å. Although this distance is much less than the distance of closest approach (2.86 Å) observed for two non-bonded chlorine atoms, a theoretical intensity curve was calculated for this model(curve B, Fig 3), which again is in good but not complete agreement with the photographs. Curves C and D, Fig. 3, were calculated for models in which

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(6) L. Pauling and L. O. Brockway, J. A. C. S., 57, 2684 (1935). The use of the values of C in place of I has been suggested by V. Schomaker and C. Degard. They will publish an account of their investigation soon in This Journal.

Figure 3

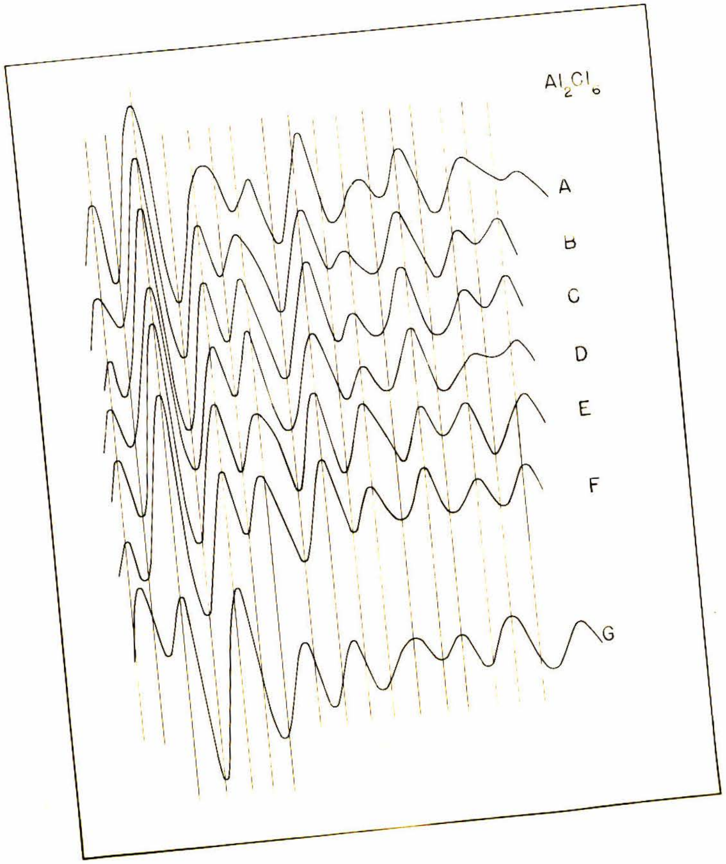
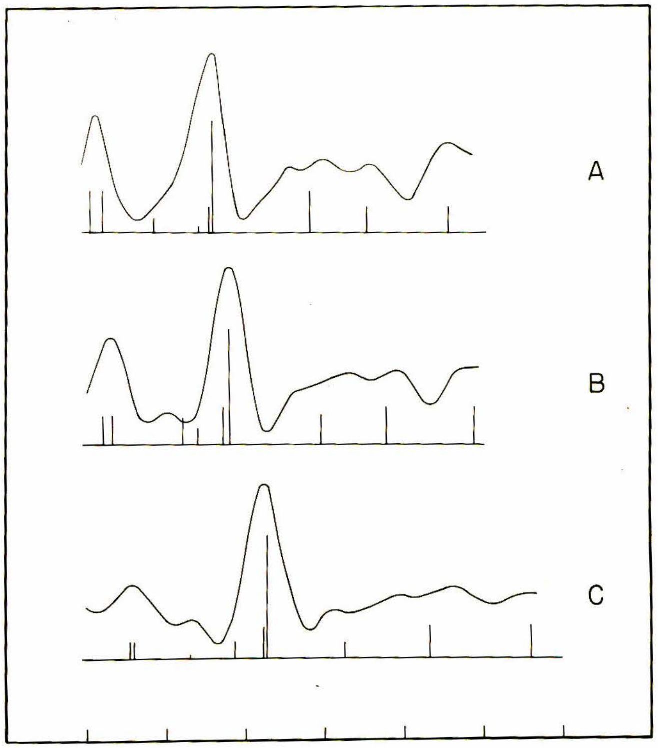


Figure 2



the shared edge has the value 2.75 Å and 2.85 Å respectively. The other ten edges have the values 3.56 Å in model C and 3.54 Å in model D and the smallest Al-Cl distances the values 2.12 and 2.11 Å respectively. These curves do not agree with the photographs quite so well as does curve B.

A very large decrease in the value of the shared edge is necessary in order to obtain the ratio 1.69 when at the same time one keeps the other edges of the tetrahedron about equal to 3.56 Å and the short Al-Cl distances all equal to 2.11 Å. Thus it is evident that the models so far assumed have been over-simplified, and that the stable configuration, although approximating two regular tetrahedra sharing an edge, is in reality considerably distorted. In order to obtain an insight into the type of distortion to be expected the following calculation was made.

The molecule is assumed to be completely ionic, and to be represented by the potential function

$$V = - \sum_{ij} \frac{e_i e_j}{r_{ij}} + \sum_{ij} \frac{B_{ij} e_i e_j}{r_{ij}^n}$$

in which r_{ij} is the distance between the i^{th} and j^{th} atoms, B_{ij} is the Born coefficient, <u>n</u> is a constant, taken to have the value 9 for this calculation, and e_i, e_j are the charges on the i^{th} and j^{th} atoms, taken equal to -1 and +3 for chlorine and aluminum respectively. It was further assumed that the ratio of the B's is given by the expression

$$\frac{B_{Al-Cl}}{B_{Cl-Cl}} = \frac{(R_{Al} + R_{Cl})^8}{(2R_{Cl})^8}$$

where R_{Al} and R_{Cl} are the ionic radii of aluminum and chlorine respectively. The absolute magnitudes of the B's were obtained by setting $\frac{V}{r} = 0$ and using r_{ij}'s corresponding to two regular tetrahedra with all short Al-Cl distances equal to 2.11 Å. The values so obtained are $B_{Al-Cl} = 48.15$ and $B_{Cl-Cl} = 1.755$. These values were retained throughout the calculation.

A method of successive approximations was used to carry out the calculation. Each of the four independent parameters necessary to specify the structure was successively varied, the process being repeated once. The final values of the parameters so obtained indicate the type of distortion to be expected in such a structure. With a charge of +3 assumed to reside on each of the two aluminum atoms the repulsion between them is very strong, and the most notable changes in going from two regular tetrahedra to the final equilibrium configuration are the decrease in the length of the shared edge and the increase in the Al-Al distance. This latter effect changes the values of the short Al-Cl distances by a large amount. The final values of the interatomic distances calculated in this way are Al_1-Al_2 = 3.60, Al_2Cl_6 = 1.99, Al_2-Cl_8 = 2.31, Al_2-Cl_6 = 4.89, Cl_3-Cl_4 = 3.49, Cl_3-Cl_8 = 3.57, Cl_5-Cl_8 = 2.90, Cl_3-Cl_7 = 5.52, Cl_3-Cl_6 = 6.52 Å. The subscripts on the atomic symbols refer to the position of the atoms as given in Fig. 1. The average of the four Al_2-Cl_3 distances equal to 1.99 Å and the four Al_2-Cl_8 distances equal to 2.31 Å (refer to Fig. 1) is 2.15 Å, in fair agreement with the radial distribution peak at 2.11 Å. However, if this were the correct model, the two shortest Al_2-Cl distances would probably appear as separate peaks in the radial distribution curve. Moreover, the intensity curve calculated for this model, (curve E, Fig. 3) does not agree qualitatively with the photographs; the sixth maximum is too high and the eighth and ninth minima are not of equal depth.

Seven additional intensity curves were calculated for models in which the four parameters were varied. The model finally selected gives an intensity curve (curve F, Fig. 3) which reproduces the qualitative features of the photographs in every respect. The values of the interatomic distances for this model are listed in Table II. Table I gives the values of s and s_0 and their ratio, s/s_0, for model F.

Table I

Electron Diffraction Data for Aluminum Chloride

Max.	Min.	I	C	s_o	s*	s/s_o
1		5	2	2.24	2.35	(1.049)
	2			3.08	2.91	(0.946)
2		10	14	4.08	3.93	(.963)
	3			4.96	4.91	(.989)
3		5	12	5.86	5.86	1.000
	4			6.61	6.51	0.985
4		3	10	7.43	7.18	.967
	5			8.33	8.40	1.008
5		4	16	9.23	9.32	1.009
	6			10.11	10.20	1.009
6		1	4	10.98	10.90	0.993
	7			11.90	11.91	1.000
7		3	12	12.71	12.77	1.005
	8			13.42	13.71	1.022
8		1	3	14.47	14.60	1.009
	9			15.22	15.41	1.013
9		2	5	16.07	16.30	1.014
			Average			1.003
			Average deviation			0.010

*Calculated for model F

Table II

Interatomic Distances in Aluminum Chloride

	Distance	Number of times distance occurs in molecule.
Al_2-Cl_3	2.06 ± 0.04 Å	4
Al_2-Cl_8	2.21 ± 0.04	4
Cl_5-Cl_8	2.83 ± 0.1	1
Cl_3-Cl_4	3.53 ± 0.04	2
Cl_3-Cl_8	3.56 ± 0.02	8
Al_1-Al_2	3.41 ± 0.20	1
Cl_3-Cl_7	5.49 ± 0.05	2
Cl_3-Cl_6	6.52 ± 0.05	2
Al_2-Cl_6	4.77 ± 0.15	4

Aluminum Bromide.-- The photographs of aluminum bromide show seven well defined rings and have the same qualitative features as those for aluminum chloride. The radial distribution curve has two well defined peaks at 2.28 and 3.77 Å. The ratio of 3.77 to 2.28 is 1.65, indicating that the tetrahedra in this molecule are probably not distorted to so great an extent as for the chloride. Curve A of Fig. 4 was calculated for two regular tetrahedra sharing an edge. The curve is in good but not complete qualitative agreement with the photographs. Curves B and C of Fig. 4 were calculated for models having the same type of distortion as that found for the chloride, but smaller in magnitude. The two models are essentially the same except for the length of the shared edge. In model B this edge was assumed to be 3.36 Å and in model C 3.20 Å. The Al_2-Br_3 and Al_2-Br_8 distances were taken equal to 2.21 and 2.33 Å respectively in model C, and 2.21 and 2.35 Å in model B.

The qualitative agreement of curve C with the photographs is better than that of curve B in that the fifth maximum in the former is slightly more intense than the fourth, in agreement with the appearance of the photographs. The differences in these two curves are, however, very slight in spite of the fact that the Br_5-Br_8 distance has been changed by 0.16 Å. The insensitiveness of the intensity curves to variations in this parameter makes it necessary to assign to it a large probable error. In Table III there are listed the values of I, C, s_0, s (for model C), and the ratio of s/s_0, and in Table IV there are given the values of the interatomic distances for the molecule and their estimated probable errors.

Table III

Electron Diffraction Data for Aluminum Bromide

Max.	Min.	I	C	s_o	s*	s/s_o
1		5	2	2.11	2.11	1.000
	2			2.85	2.87	1.007
2		10	11	3.78	3.72	0.998
	3			4.68	4.61	0.999
3		6	11	5.48	5.60	1.022
	4			6.28	6.22	0.990
4		4	9	7.02	6.88	0.980
	5			7.85	7.88	1.004
5		5	13	8.73	8.78	1.006
	6			9.59	9.68	1.009
6		1	2	10.38	10.35	0.997
	7			11.19	11.17	0.998
7		2	3	11.84	12.08	1.023
			Average			1.003
			Average deviation			0.009

* Calculated for model C

Table IV

Interatomic Distances in Aluminum Bromide

	Distance	Number
Al_2-Br_3	2.21 ± 0.04 Å	4
Al_1-Br_8	2.33 ± 0.04	4
Br_5-Br_8	3.20 ± 0.10	1
Br_3-Br_4	3.72 ± 0.03	2
Br_3-Br_8	3.78 ± 0.03	8
Al_1-Al_2	3.39 ± 0.10	1
Br_3-Br_7	5.76 ± 0.10	2
Br_3-Br_6	6.86 ± 0.10	2
Al_2-Br_6	4.93 ± 0.10	4

Figure 4

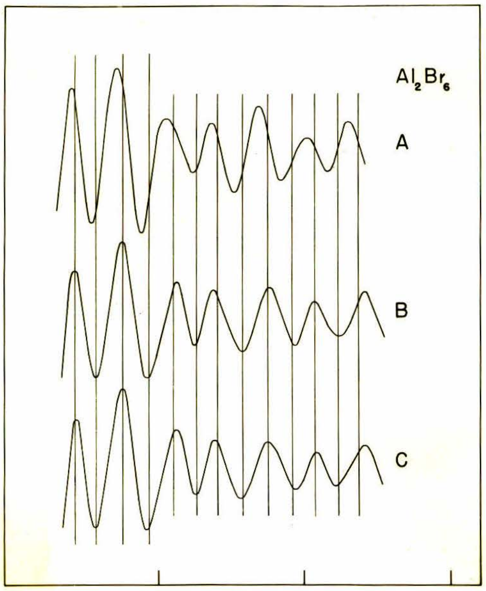
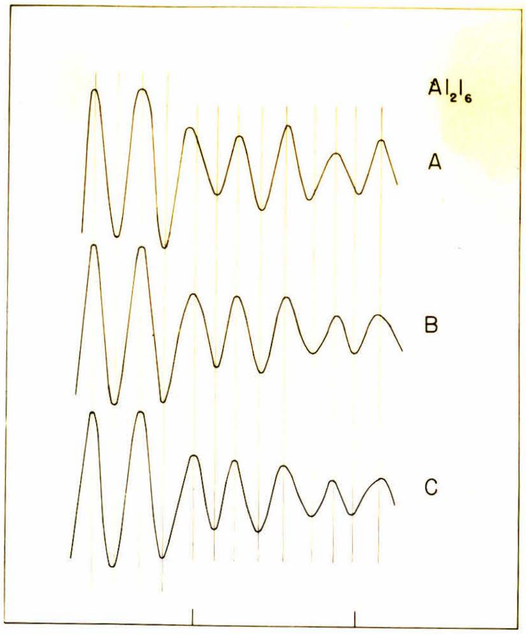


Figure 5



Aluminum Iodide.-- The photographs of aluminum iodide, taken with a camera distance of 20.16 cm, show seven well defined maxima, the general appearance of the photographs being closely similar to that for the chloride and bromide. This similarity is strong evidence for the assumption that the structures of the three molecules are similar in configuration.

The radial distribution curve (curve C, Fig. 2), shows principal peaks at 2.58 and 4.23 Å. The ratio of the latter to the former distance is 1.64, indicating that the structure is very nearly that of two regular iodine tetrahedra sharing an edge.

The ratio of the scattering due to the iodine atoms to that due to the aluminum atoms is very large in aluminum iodide; this makes the determination of the positions of the aluminum atoms with any degree of accuracy impossible. The intensity curves shown in Fig. 5 were calculated for models approximating those described for aluminum bromide. Curve A is for undistorted tetrahedra, and curves B and C for tetrahedra whose shared edge has the value 4.00 and 3.85 Å respectively, and for which the Al_2-I_3 and Al_2-I_8 distances have the values 2.58 and 2.54 Å respectively. Curve A does not agree with the photographs in that the relative intensities of the maxima are unsatisfactory. Curve C gives a somewhat better representation of the appearance of the photographs than curve B, but the differences in these two curves, namely the variation of the intensities of the third, fourth, and fifth maxima, are so small that, as in the case of the bromide, it is impossible to determine the length of the shared edge with much accuracy. The values of the interatomic distances with their extimated probable errors are given in Table VI. The quantitative comparison of the s values obtained from curve C with the observed s_0 values is given in Table V.

Table V

Electron Diffraction Data for Aluminum Iodide

Max.	Min.	I	C	s_o	s*	s/s_o
1		9	3	1.88	1.87	0.995
	2			2.51	2.52	1.004
2		10	9	3.32	3.33	1.003
	3			4.14	4.08	0.986
3		7	10	4.85	4.99	1.029
	4			5.56	5.65	1.016
4		6	9	6.29	6.26	0.995
	5			7.03	7.00	.996
5		5	10	7.80	7.75	.994
	6			8.62	8.67	1.006
6		2	3	9.27	9.29	1.002
	7			9.95	9.89	0.994
7		1	1	10.67	10.70	1.003
			Average			1.002
			Average deviation			0.008

* Calculated for model C.

Table VI

Interatomic Distances in Aluminum Iodide

	Distance	Number
Al_2-I_3	2.53 ± 0.04 Å	4
Al_2-I_8	2.58 ± 0.04	4
I_5-I_8	2.90 ± 0.15	1
I_3-I_4	4.20 ± 0.03	2
I_3-I_8	4.24 ± 0.02	8
Al_1-Al_2	3.24 ± 0.15	1
I_3-I_7	6.24 ± 0.15	2
I_3-I_6	7.54 ± 0.10	2
Al_2-I_6	5.22 ± 0.15	4

Discussion: The only report on the structures of aluminum chloride, bromide, or iodide previous to the present one is that of Ketelaar[7] on the structure of aluminum chloride crystals. He found that the chlorine atoms are in hexagonal closest packing, this arrangement being compatible with that found for the gas molecule in this investigation. However, he chose to place two aluminum atoms inside an octahedron of chlorine atoms, and only 0.56 Å apart, rather than one each inside of two tetrahedra sharing an edge, both of these possibilities being provided by the hexagonal closest packed arrangement. The extent to which the x-ray data can be accounted for by this latter configuration is being investigated by one of us.

Curve G, Fig. 2, is the simplified theoretical intensity curve calculated for the "octahedral" model of Ketelaar; it is apparent from a comparison with curve F that this model cannot represent the structure of the gas molecule.

The large difference in electronegativity between aluminum and the halogen atoms leads one to expect that the Al-X bond will be largely ionic, and this is confirmed by the observed contraction of the shared edge. The percentage decrease in length of the shared edge is found to be largest in the chloride and least in the iodide which is in accordance with expectation.

The sums of the tetrahedral radius of aluminum and the normal radii for the halogen atoms are 2.24, 2.40, and 2.59 Å for the chloride, bromide, and iodide respectively. These values are to be compared with the observed values, 2.06, 2.21, and 2.53 Å, which are the Al_2-X_5 distances, and 2.21, 2.33, and 2.58 Å, which are the Al_2-X_8 distances , for the chloride, bromide, and

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[7] J. A. A. Ketelaar, Z. Krist. 90, 237 (1935).

iodide respectively. The observed shortening in the case of the Al_2-X_3 distances is probably due to the excited structures in which an X_3 halogen atom swings in a pair of electrons and forms a double bond with the aluminum atom. This type of resonance is not expected to occur to the same degree for halogen atoms forming two bonds, which accounts for the fact that the observed Al_2-X_8 distances are nearly equal to the sum of the appropriate radii.

It is interesting to note that the observed values of the Al_2-X_3 distances show a greater tendency for the chlorine and bromine atoms to form double bonds than of iodine atoms; this is compatible with the results of other investigations.

We wish to express our thanks to Professor Linus Pauling for his aid and helpful criticism during the course of this investigation.

Summary: It is shown that in the gaseous state the dimeric molecules of aluminum chloride, bromide, and iodide consist of two tetrahedra sharing an edge with six halogen atoms at the corners, each tetrahedron containing one aluminum atom. The final values of the interatomic distances are as follows:

	Al_2Cl_6	Al_2Br_6	Al_2I_6
Al_1-Al_2	3.41 ± 0.20 Å	3.39 ± 0.10 Å	3.24 ± 0.15 Å
Al_2-X_3	2.06 ± 0.04	2.21 ± 0.04	2.53 ± 0.04
Al_2-X_8	2.21 ± 0.04	2.33 ± 0.04	2.58 ± 0.04
Al_2-X_6	4.77 ± 0.15	4.93 ± 0.10	5.22 ± 0.15
X_3-X_4	3.53 ± 0.04	3.72 ± 0.03	5.30 ± 0.03
X_3-X_8	3.56 ± 0.02	3.78 ± 0.03	4.24 ± 0.02
X_5-X_8	2.83 ± 0.10	3.20 ± 0.10	2.90 ± 0.15
X_3-X_7	5.49 ± 0.05	5.76 ± 0.10	6.24 ± 0.15
X_3-X_6	6.52 ± 0.05	6.86 ± 0.10	7.54 ± 0.10

The subscripts on the atoms refer to their positions in the molecule as given in Fig. 1.

Section 8

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The Unit of Structure and Space Group of Chloral Hydrate.

By **Norman Elliott.**

(Contribution from the Gates and Crellin Laboratories of Chemistry,
California Institute of Technology, No. 613.)

A crystal structure investigation of chloral hydrate was begun in order to determine whether or not one of the carbon atoms in a molecule of this substance is attached to two hydroxyl groups, as is supposed by organic chemists. The difficulties encountered in the problem have proved greater than was expected; and in view of the existence of excellent evidence concerning the structure of the chloral hydrate molecule obtained recently by other investigators, the study has been carried no farther than the space group determination.

The Raman study of chloral and chloral hydrate by Petrikaln and Hochberg[1]) has shown that the $C = O$ frequency is present in chloral but not in chloral hydrate. The infra-red absorption spectra of solutions of chloral hydrate in carbon tetrachloride obtained by Professor Badger and Dr. Bauer[2]) of these Laboratories reveal an OH doublet similar to the doublet found for o-chlorophenol[3]). These data may best be interpreted as confirming the organic chemists' structure in which two hydroxyl groups are directly attached to a single carbon atom.

The crystals used in this investigations were thick tabular rhombs. The large, well-developed face referred to by Groth as the *c*-face was taken as the (100) face. For convenience the *b*- and *c*-axes were chosen lying in the (100) plane. The other developed faces were then (011) and $(01\bar{1})$.

The lattice constants were obtained from layer line measurements of x-ray photographs prepared by oscillating a crystal of chloral hydrate around its *a*-, *b*-, and *c*-axes. The constants are $a_0 = 11.57 \pm 0.15$ Å, $b_0 = 6.04 \pm 0.03$ Å, $c_0 = 9.60 \pm 0.03$ Å, and $\beta = 120° 7'$. From the density, $\sigma = 1.90$, the number of molecules in the unit cell is 4.03.

Laue and oscillation photographs were indexed and the following types of reflections were observed:

hkl present for all orders,
$h0l$ present for $l = 2n$ only,
$0k0$ present for all orders.

These observations lead to the space groups C_{2h}^4 or C_s^2; the crystallographic data reported by Groth provide strong evidence for holohedry, so that the space group C_{2h}^4 is to be assigned to the crystal.

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[1]) Petrikaln and Hochberg, Z. physik. Chem. (B) 4 (1929) 299.

[2]) Private communication from Prof. R. M. Badger and Dr. Simon Bauer.

[3]) O. R. Wulf and U. Liddel, J. Amer. chem. Soc. 57 (1935) 1464.

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Summary of Thesis

The subject of Part 1 is the measurement of electromotive forces in liquid ammonia solutions at room temperature.

Part 2 is concerned with the experimental determination of the structures of molecules and complex ions. Special emphasis has been placed on the accurate determination of interatomic distances. The results are discussed from the viewpoint of the covalent bond theory.