

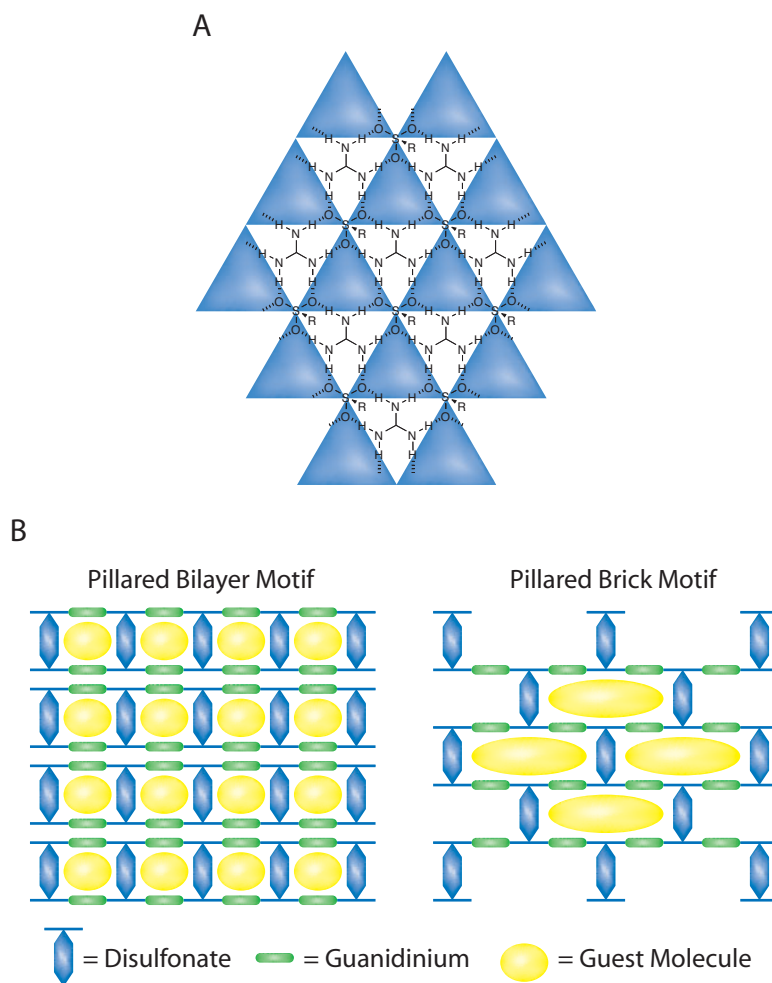
**Chapter 7: Use of Crystal Engineering to Design a Novel  
Family of Frustrated Magnetic Materials based on  
Guanidinium 5,5'-Salen Disulfonate**

## 7.1 Introduction

Molecular magnetic materials are a potential source of novel interesting magnetic materials, but the design of these materials has proven to be extremely difficult (Kahn, 1993; Miller and Epstein, 1994; Turnbull et al., 1996). One potential solution to the difficulties associated with designing magnetic materials is the use of organic crystal engineering. Organic crystal engineering provides a method with well-defined structural rules that can be used to template magnetic materials. Despite the identification of many organic crystal engineering motifs (Aakeroy, 1997; Desiraju, 1988), these motifs have not been applied successfully to the development of molecular magnetic materials.

### 7.1.1 The “Ward Lattice”

The guanidinium sulfonate motif developed by Ward and co-workers is one of the most resilient organic crystal engineering motifs (Evans et al., 1999; Russell et al., 1994a; Russell et al., 1994b; Russell et al., 1997; Russell and Ward, 1996; Russell and Ward, 1997; Russell and Ward, 1998; Swift et al., 1998a; Swift et al., 1998b; Swift et al., 1997; Swift and Ward, 2000). Generally, this motif consists of a triangular array of hydrogen bonded guanidinium cations and sulfonate anions (Figure 7.1A). It has also been shown that incorporation of disulfonates into this motif gives one of two three-dimensional structures: a pillared bilayer motif or a pillared brick motif. Each motif contains large cavities, and the motif obtained depends on the guest molecules around which the structure is templated (Russell et al., 1997; Swift et al., 1998a). The different motifs are illustrated in Figure 7.1B.



**Figure 7.1:** A) Schematic representation of the sheet-like hydrogen bonded networks formed from guanidinium cations and sulfonate anions. B) Schematic representation of layered materials synthesized from guanidinium cations and disulfonates, as viewed along the long axis of the hydrogen bonded ribbons contained in the nominal planar guanidinium sulfonate networks.

### 7.1.2 Design Strategy

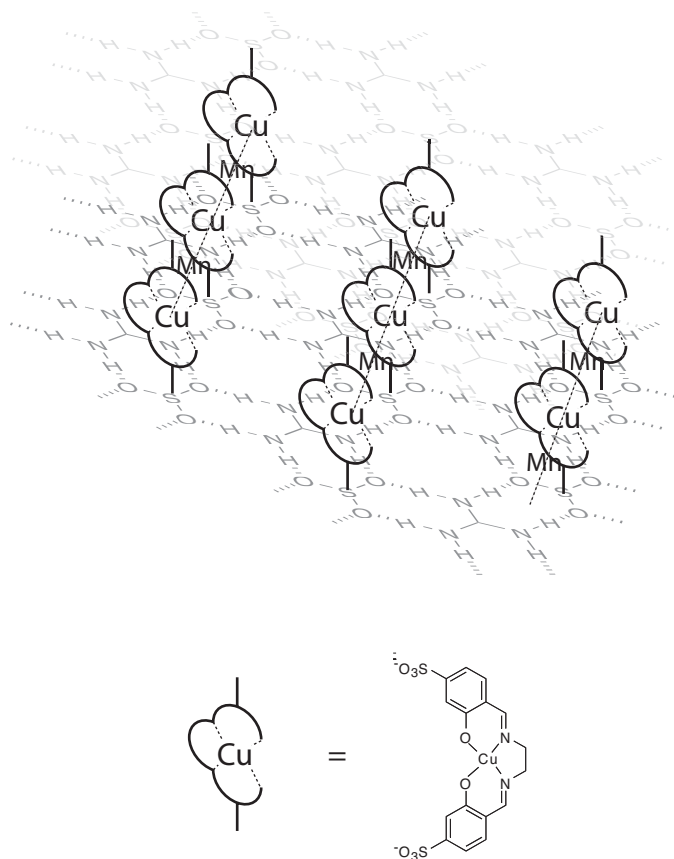
Our strategy for preparing novel molecular magnetic materials was based on the pioneering work of Kahn. Mixed systems of alternating Cu(II) and Mn(II) have produced ferromagnetic and ferrimagnetic materials with relatively high critical temperatures, around 20 K (Kahn et al., 1988; Pei et al., 1987; Stumpf et al., 1993a; Stumpf et al., 1993b). When using first row transition metals to prepare mixed metal systems Cu(II)

and Mn(II) typically produce the best results, since antiferromagnetic coupling between adjacent metal ions is common and upon antiferromagnetic coupling a copper-manganese pair has the largest residual spin value ( $S=2$ ). We reasoned that the “Ward lattice” might provide a means to specifically position rigidly alternating Cu(II) and Mn(II) ions, by binding one of the metal ions to the disulfonate pillar and incorporating the second metal ion into the structure as guest molecule.

The chemistry and magnetic properties of metal Schiff base complexes have been extensively studied (Holm et al., 1966). Additionally, copper salen complexes are well known and their magnetic behaviors are fully documented (O'Brian, 1984). One would expect a copper salen complex with appropriate sulfonic acid substituents could fit into a “Ward lattice,” and leave open coordination sites. Using these open coordination sites bridging ligands could then be used to interact a second high spin metal with the first metal. This metal coordination strategy should give rise to ferromagnetic or ferrimagnetic linear chains (Figure 7.2).

In addition to the ability to orient bimetallic materials, the triangular nature of the “Ward lattice” suggested that it might be possible to engineer frustrated magnetic systems using this motif. Magnetic frustration has received a great deal of attention since its introduction in the late 1970's (Toulouse, 1977; Villain, 1977). Spin frustration arises in systems where competing interactions lead to a degenerate ground state (Kahn, 1993). Extensive work has led to the development of many theoretical and computational models to describe long-range spin frustration on extended lattices (Becca and Mila,

2002; Garcia-Adeva and Huber, 2002; Kruger and Richter, 2001; Siurakshina et al., 2001; Tsunetsugu, 2001; Zukovic et al., 2002), such as would be observed for a Kagomé lattice or a pyrochlore lattice. Despite theoretical interest in magnetic frustration, very few experimental examples of frustrated magnetic systems exists. However it is known that orientation of magnetic moments on a triangular lattice leads to spin frustration (Coey, 1987; Manson et al., 2000).



**Figure 7.2:** Schematic representation of copper-manganese ferromagnetic or ferrimagnetic linear chains in a guanidinium sulfonated crystal lattice.

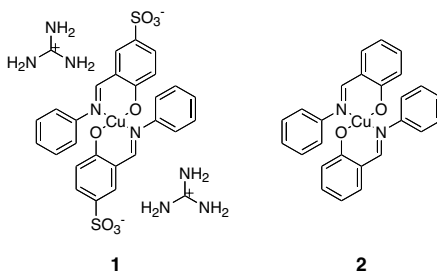
Here we report a series of magnetically interesting complexes designed using the “Ward lattice.” The majority of compounds are a novel family of magnetically frustrated

bimetallic solids designed using the guanidinium sulfonate crystal engineering motif with a 5,5'-salen disulfonic acid pillar. This pillar is capable of binding and positioning a metal ion within the triangular lattice of the guanidinium sulfonate motif. Although a number of different bimetal compounds were prepared, we focus here on dc magnetic analysis of the copper-manganese complex.

## 7.2 Results and Discussion

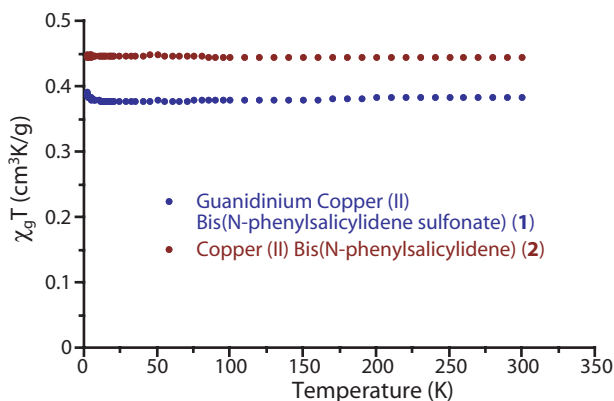
### 7.2.1 Guanidium *N*-phenylsalicylidene sulfonate Complexes

The guanidinium complex of copper (II) bis(*N*-phenylsalicylidene sulfonate) (**1**) was prepared by mixing guanidinium acetate, copper acetate, and *N*-phenylsalicylidene sulfonic acid. The resulting complex was confirmed by elemental analysis and magnetically characterized. Figure 7.3 shows the susceptibility temperature product as a function of temperature for the complex.



The magnetic data for compound **1** show a weak ferromagnetic interaction at very low temperature, as indicated by the slight up turn in the data. The strength of the interaction suggests that it is most likely a result of intramolecular ferromagnetic coupling.

Although long-range ferromagnetic interactions are not unprecedented, typically long range interactions in molecular solids are antiferromagnetic.



**Figure 7.3:** Variable temperature magnetic data for compounds **1** and **2**.

To verify if the intermolecular interaction was a result of crystal packing imposed on the structure by the “Ward lattice,” copper (II) Bis(N-phenylsalicylidene) (**2**) was synthesized from copper acetate and N-phenylsalicylidene. The variable temperature magnetic data for **2** are also shown in Figure 7.3. Compound **2** does not exhibit the ferromagnetic upturn at low temperature seen for compound **1**, suggesting that the ferromagnetic behavior observed for compound **1** is imposed as a result of the “Ward lattice.”

Compound **1** was recrystallized from water to give small yellow crystals. A crystal structure of these crystals was obtained and stereoviews of the structure along the three principle crystallographic axes are shown in Figure 7.4. Unfortunately the crystals obtained upon recrystallization lacked copper and the structure is therefore of

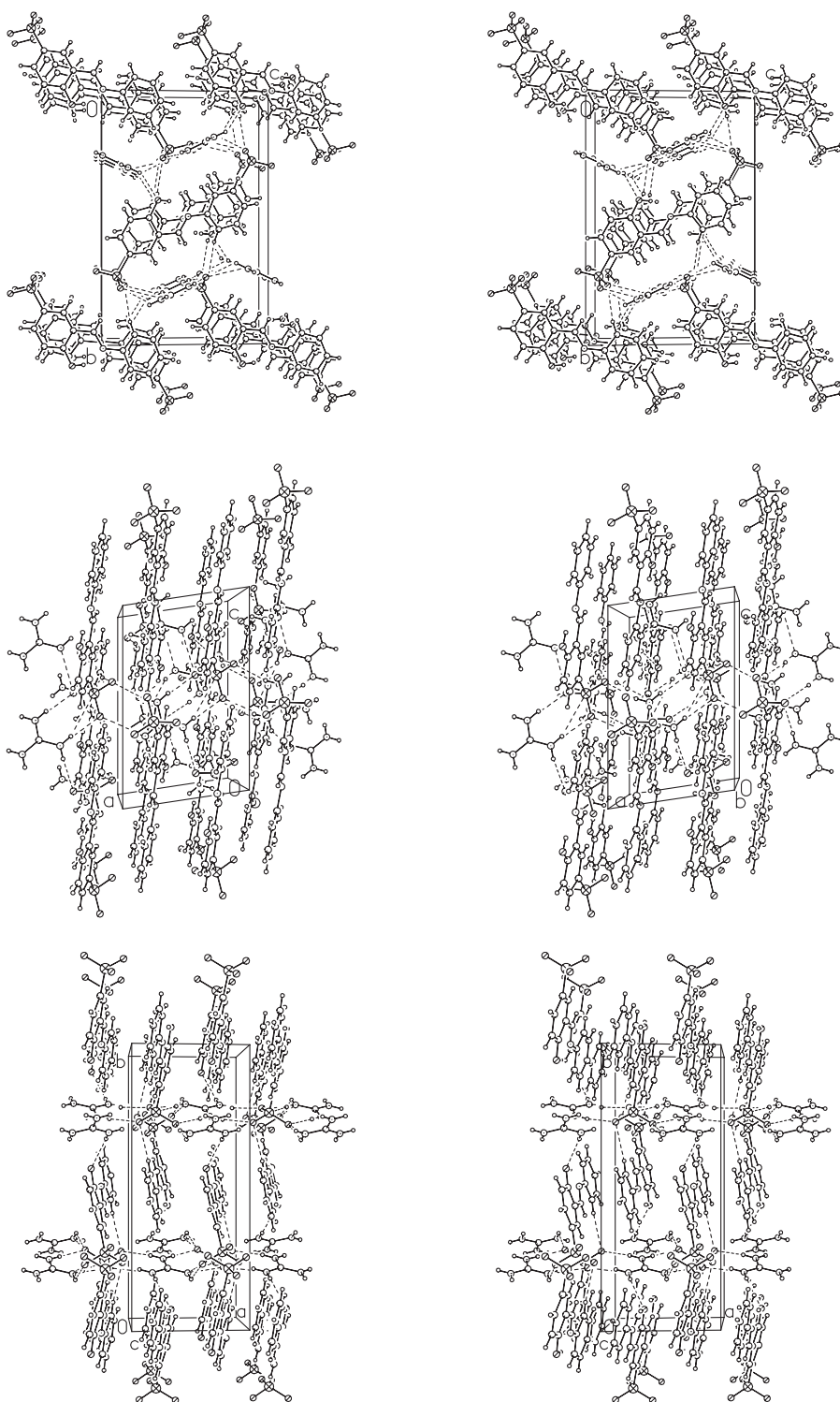
guanidinium N-phenylsalicylidene sulfonate. However, the crystal structure is an example of a “Ward lattice”. The details of the crystal structure are given in Appendix II.

## 7.2.2 *Guanidinium 5,5'-Salendisulfonic Acid Bimetallic Materials*

### 7.2.2.1 *The Copper-Manganese Complex*

5,5'-Salendisulfonic acid (dss), manganese (II) acetate, copper (II) acetate, and guanidinium (gd) acetate were mixed to produce a solid to which we assign the molecular composition:  $\text{Mn}_3[\text{Cu}(\text{dss})]_3(\text{gd})_4(\text{OAc})_4$ , based on quantitative and qualitative analysis. The molecular composition was determined from the copper-manganese, copper-sulfur, manganese-sulfur, sulfur-nitrogen, and carbon-nitrogen ratios. The copper to manganese ratio is 1.2:1.0. From the manganese-sulfur and the copper-sulfur ratios, disulfonate to metal ratios of 0.9:1.0 and 1.1:1.0 are obtained, respectively. The guanidinium to disulfonate ratio is 1.4:1.0, as determined from the nitrogen to sulfur ratio. Using these ratios the molecular formula of the complex was determined. Furthermore, the analytical data indicate that the purity of the desired material is approximately 90%. The magnetic and analytical data suggest that the observed impurity is an antiferromagnetic copper complex, given the excess of copper to manganese. The relative amount of this impurity is dependent on the reaction stoichiometry.



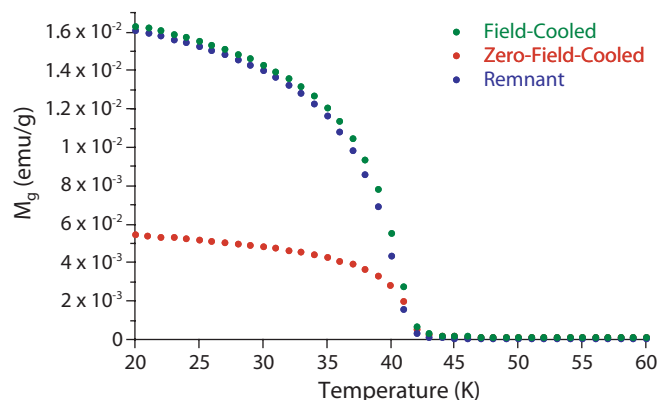


**Figure 7.4:** Stereo views of the guanidinium N-phenylsalicylidene sulfonate crystal structure as viewed along each of the principle crystallographic axes.

Using the optimal reaction stoichiometry described in the Methods section, we can reproducibly prepare large quantities of the copper-manganese complex whose materials we will now describe. All efforts at crystallization or further purification failed. As such, we feel there is value in reporting the intriguing magnetic behaviors of this material and several derivatives at this time, in the hope that it will spur further work.

Qualitative analysis of the copper-manganese complex indicated that the copper is bound to the salen ligand. Free copper in solution can be detected by the formation of a precipitate upon addition of either potassium iodide or potassium thiocyanate (Svehla, 1996). Addition of potassium iodide or potassium thiocyanate to the copper-manganese complex did not result in precipitation, indicating that the copper is tightly bound by the salen ligand.

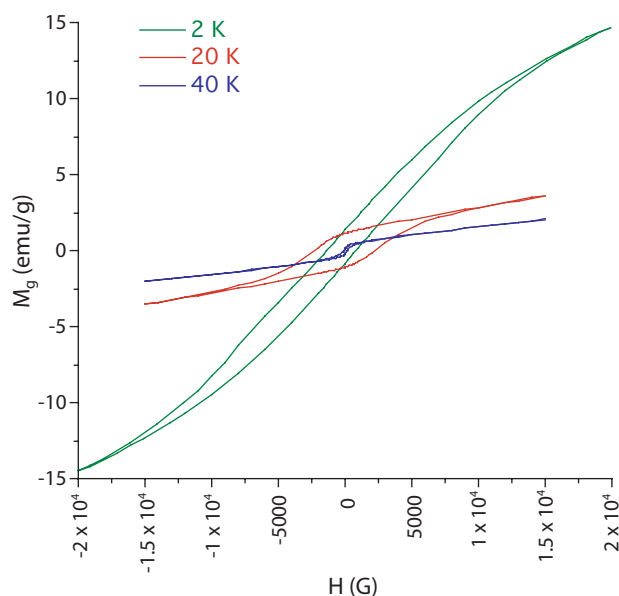
On the face of it, the magnetic behavior of the copper-manganese complex appears to be ferromagnetic with a critical temperature of 42.4 K. Figure 7.5 shows field-cooled, zero-field-cooled, and remnant magnetization measurements collected with a 1 gauss magnetic field. The data suggest that the material orders ferromagnetically with a relatively high ordering temperature for a molecular magnetic material. Although in a small number of cases high temperature ferromagnetic ordering has been achieved, most molecular magnetic materials order ferromagnetically only below 10 K (Kahn, 1993; Turnbull et al., 1996).



**Figure 7.5:** Field-cooled, zero-field-cooled, and remnant magnetization as a function of temperature for the copper-manganese complex.

The data of Figure 7.5 for the copper-manganese complex are as expected for a ferromagnetic material. In all cases the data show an abrupt transition around 42 K. Fitting the remnant magnetization near the critical temperature to a power law gives a critical temperature ( $T_c$ ) of 42.4 K and a critical exponent ( $\beta$ ) of 1.48. As expected for a ferromagnet, the zero-field-cooled magnetization is always lower than the field-cooled magnetization, since in this temperature range the applied magnetic field is too weak to move the domain walls.

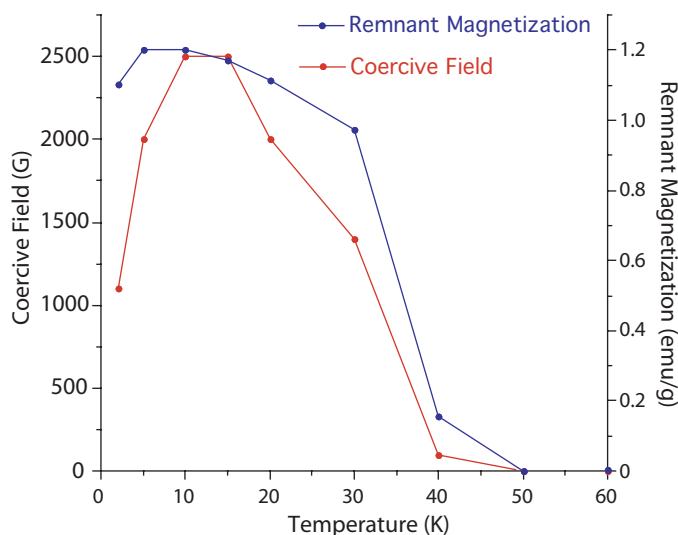
In addition to exhibiting ferromagnetic field-cooled, zero-field-cooled, and remnant magnetic behavior, the copper-manganese complex also exhibits significant hysteresis, Figure 7.6. The copper manganese complex is a “hard” magnetic material and exhibits coercive fields of up to 2,500 G coupled with large remnant magnetizations. The magnitude of the observed values for coercive field and remnant magnetization are not atypical for molecular magnetic materials.



**Figure 7.6:** Hysteresis loops for the copper-manganese complex at 2 K, 20 K and 40 K.

The hysteresis data for the copper-manganese complex, however, exhibit unusual temperature dependence. The coercive field and remnant magnetization vary greatly with temperature (Figure 7.7). These changes are accompanied by changes in the shape of the hysteresis curve as can be seen in Figure 7.6. These findings indicated that a simple ferromagnetic model is not sufficient to describe the magnetic behavior of the copper-manganese complex.

Preliminary analysis of the temperature-dependent susceptibility data for the copper-manganese complex was in agreement with the previous suggestion of ferromagnetic behavior with a critical temperature around 42 K. The plot of the susceptibility temperature product, Figure 7.8, indicates a ferromagnetic ordering at around 42 K, followed by long range antiferromagnetic ordering at low temperature.

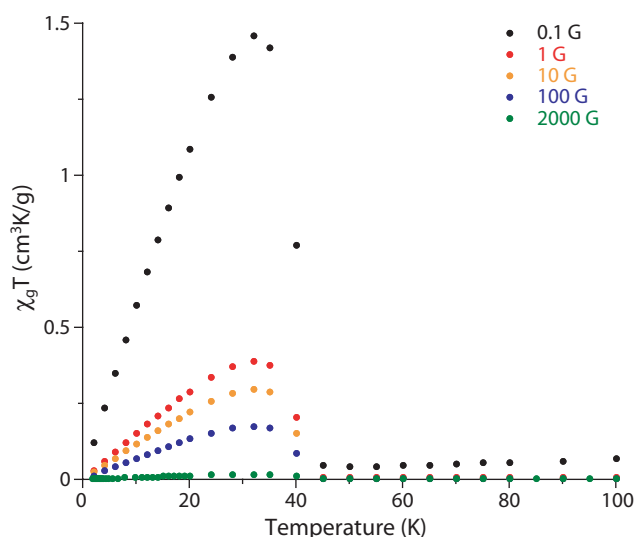


**Figure 7.7:** The temperature dependence of the coercive field and remnant magnetization of the copper-manganese complex is shown.

However, further analysis of the copper-manganese complex revealed that its susceptibility shows unusual field dependence (Figure 7.9). The copper-manganese complex exhibits increasing magnetic susceptibility as a function of decreasing magnetic field. This behavior is the exact opposite of the behavior typically observed for ferromagnetic materials. Close examination of the magnetic data suggest that magnetic responses observed for the copper-manganese complex are those of a frustrated magnetic material.

Magnetic frustration is not an experimentally well-characterized phenomenon and many different magnetic behaviors have been associated with frustration. As such, a comparison of the copper-manganese complex with several previously characterized frustrated materials has been used to assign frustration to this complex. In all cases the

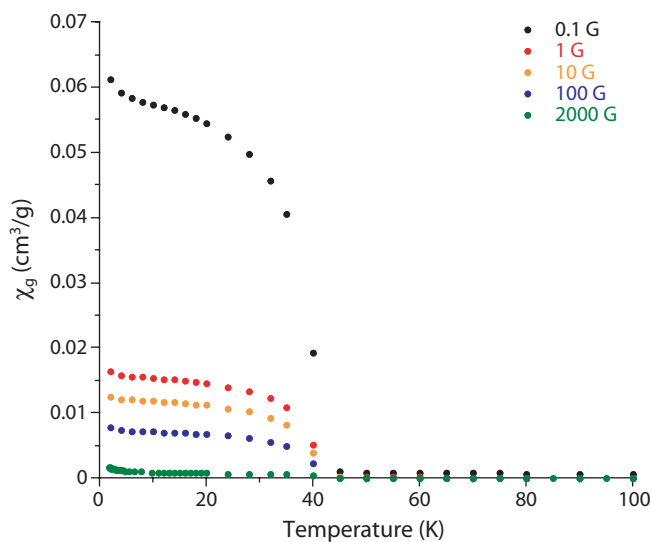
behavior exhibited by the copper-manganese complex is slightly different than the previously characterized complexes, however it should also be noted that the behavior of these frustrated compounds is not self consistent. The compounds used here for comparison are  $[\text{NH}_2(\text{CH}_2)_3\text{NH}_2](\text{VO})_3(\text{H}_2\text{O})_2(\text{PO}_4)_2$  (Soghomonian et al., 1993),  $\text{SrCr}_9\text{Ga}_3\text{O}_{19}$  (Ramirez et al., 1990),  $\text{CsNiFeF}_6$  (Alba et al., 1982),  $\text{LiNiO}_2$  (Hirakawa et al., 1985; Yamaura et al., 1996), all of which are accepted to be frustrated magnetic systems.



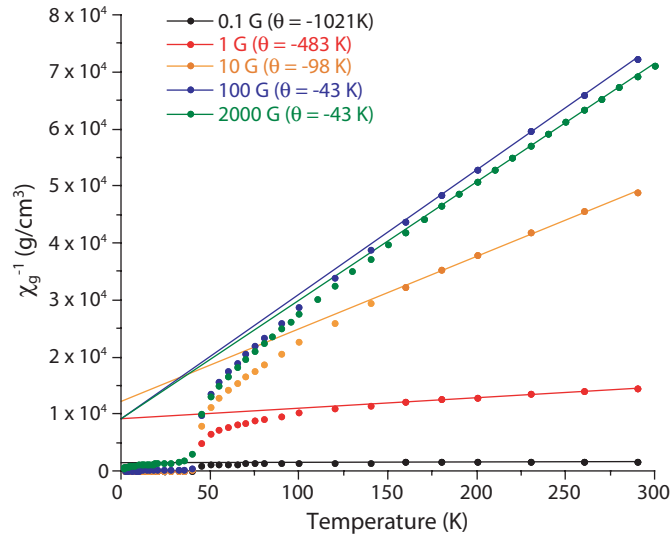
**Figure 7.8:** The susceptibility temperature product as a function of temperature for the copper-manganese complex measured at five different applied magnetic fields.

Similar field dependence of magnetic susceptibility has been observed for  $[\text{NH}_2(\text{CH}_2)_3\text{NH}_2](\text{VO})_3(\text{H}_2\text{O})_2(\text{PO}_4)_2$  (Soghomonian et al., 1993). However, this material exhibits ferromagnetic behavior at low applied magnetic fields (10 G), antiferromagnetic behavior at moderate applied magnetic fields (500 G), and paramagnetic behavior at high

applied magnetic fields (2000 G), whereas the copper-manganese complex exhibits only ferromagnetic behavior with applied magnetic fields up to 2000 G (Figure 2b).  $[\text{NH}_2(\text{CH}_2)_3\text{NH}_2](\text{VO})_3(\text{H}_2\text{O})_2(\text{PO}_4)_2$  exhibits pronounced local antiferromagnetic behavior at 50 K, which is not observed for our material, and only shows field dependant magnetization at 5.2 K. Additionally,  $[\text{NH}_2(\text{CH}_2)_3\text{NH}_2](\text{VO})_3(\text{H}_2\text{O})_2(\text{PO}_4)_2$  has a Weiss constant of +20 K as opposed to the negative Weiss constant displayed by the copper-manganese material (Figure 7.10). Nevertheless, the inverse relationship between applied magnetic field and magnetic susceptibility has been termed a hallmark of magnetic frustration (Soghomonian et al., 1993) and serves as our first line of evidence that the copper-manganese complex is a frustrated magnetic material.



**Figure 7.9:** Susceptibility as a function of temperature for the copper-manganese complex. Increased susceptibility is observed as the applied magnetic field decreases.



**Figure 7.10:** Inverse susceptibility as a function of temperature for the copper-manganese complex. The observed Curie-Weiss constant decreases as a function of increasing applied magnetic field.

The main evidence for a frustrated state comes from the disparity between the expected ordering temperature as predicted by the Curie-Weiss law,  $\theta_{\text{CW}}$ , and the observed ordering temperature. The degree of frustration exhibited by a magnetic material has previously been characterized by the ratio of Weiss constant to the observed critical temperature. In this analysis if the ratio of  $\theta_{\text{CW}}$  to  $T_c$  is greater than one the material exhibits some degree of magnetic frustration.  $\text{SrCr}_9\text{Ga}_3\text{O}_{19}$  and  $\text{CsNiFeF}_6$  are thought of as strongly frustrated materials, and they exhibit  $\theta_{\text{CW}}$  to  $T_c$  ratios of 150 and 45 respectively (Alba et al., 1982; Ramirez et al., 1990). Since the copper-manganese complex shows a ferromagnetic anomaly, as opposed to the antiferromagnetic anomalies observed for  $\text{SrCr}_9\text{Ga}_3\text{O}_{19}$  and  $\text{CsNiFeF}_6$ , it is difficult to compare our  $\theta_{\text{CW}}$  to  $T_c$  ratio to those previously observed. However, if we consider the absolute value of the ratio of  $\theta_{\text{CW}}$



to  $T_c$ , the value observed at 0.1 G,  $\theta_{CW}/T_c = 24$ , is substantial compared to  $\text{LiNiO}_2$  where,  $\theta_{CW}/T_c = 3$ .

The magnitude of the ratio of  $\theta_{CW}$  to  $T_c$  is a lower estimate for the copper-manganese system, since examination of the inverse dc susceptibility of the copper-manganese complex as a function of field shows magnetic interaction at high temperatures. Fitting the magnetic data above 150 K to the Curie law gives an observed  $\theta_{CW}$  value for the complex that varies from  $-43$  K at 2000 G to  $-1021$  K at 0.1 G. Based on the observed trend in Figure 7.10, it seems likely that if the applied magnetic field were further decreased larger Weiss constants would be observed. Larger Weiss constants would give rise to a larger ratio of  $\theta_{CW}$  to  $T_c$ .

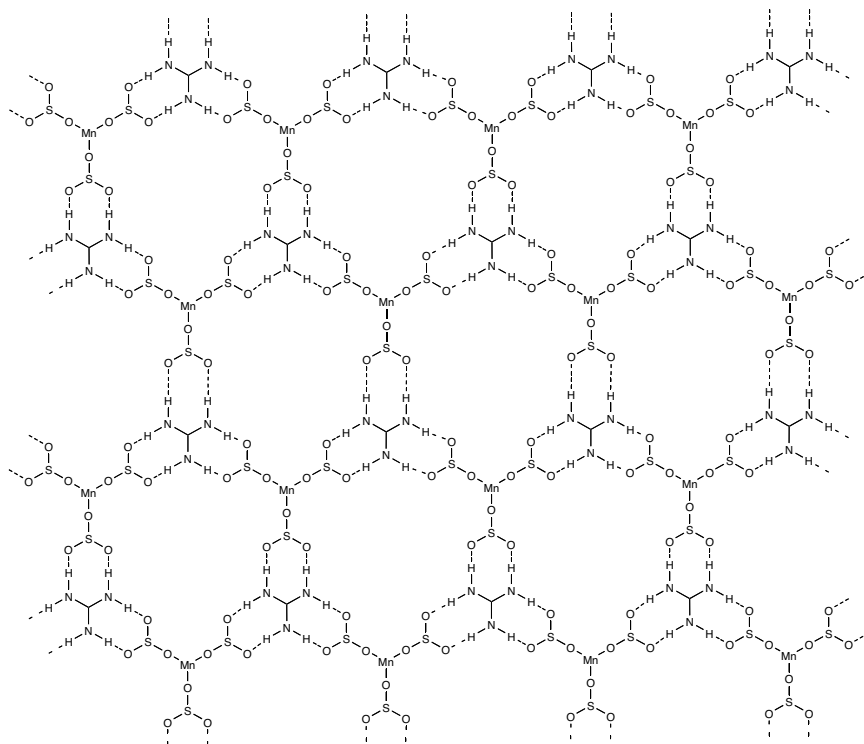
All of the known frustrated magnetic materials examined here thus far have exhibited only antiferromagnetic ordering phenomena at some applied magnetic field, however the copper-manganese complex always exhibits a ferromagnetic ordering phenomenon. In the case of  $\text{LiNiO}_2$  anomalous ferromagnetic ordering has been assigned to magnetic frustration (Hirakawa et al., 1985; Yamaura et al., 1996). However, in this case both the observed ordering and  $\theta_{CW}$  suggest ferromagnetic behavior with  $T_c$  for the complex being 5 K and  $\theta_{CW}$  being +29.5 K. Like the copper-manganese complex and  $[\text{NH}_2(\text{CH}_2)_3\text{NH}_2](\text{VO})_3(\text{H}_2\text{O})_2(\text{PO}_4)_2$ ,  $\text{LiNiO}_2$  exhibits inverse field dependence. Although the magnetic frustration observed for  $\text{LiNiO}_2$  is not identical to the frustration observed in the copper-manganese complex, it does provide precedent for anomalous ferromagnetic ordering in frustrated magnetic materials.

The observed magnetic behavior for the copper-manganese complex clearly suggests magnetic frustration resulting in an anomalous ferromagnetic ordering. The evidence for magnetic frustration is not only the disparity between the predicted and observed ordering temperatures, but also the disparity in the predicted nature of magnetic ordering. The disparity in the predicted nature of magnetic ordering may imply that this material exhibits massive frustration relative to previously reported frustrated magnetic systems.

The observation of magnetic frustration for the copper-manganese complex is not consistent with the expected magnetic behavior for the system shown in Figure 7.2. Additionally, the molecular formula that has been assigned to the copper-manganese complex lacks sufficient guanidinium to form a bridging “Ward lattice”. To form a proper “Ward lattice”, two equivalents of guanidinium are required for each equivalent of disulfonate, while the copper-manganese complex only contains 1 and 1/3 equivalents of guanidinium per equivalent of 5,5'-salendisulfonic acid. As a result it seems likely that the structure of the copper-manganese complex is modified from that of a standard “Ward lattice”.

One possible structure for copper-manganese complex, which would explain the magnetic data, is the modified “Ward lattice” shown in Figure 7.11. The proposed lattice maintains the same hydrogen-bonding pattern observed in a standard “Ward lattice”, however it contains manganese atoms in addition to guanidinium and disulfonate. In this structure the manganese atoms lie on a bridged triangular lattice that could give rise to

the observed magnetic frustration. The salen bond copper atoms would not contribute significantly to the variable temperature magnetism as is observed for compound **2**.



**Figure 7.11:** A modified “Ward lattice” that would explain the observed magnetic data for the copper manganese complex.

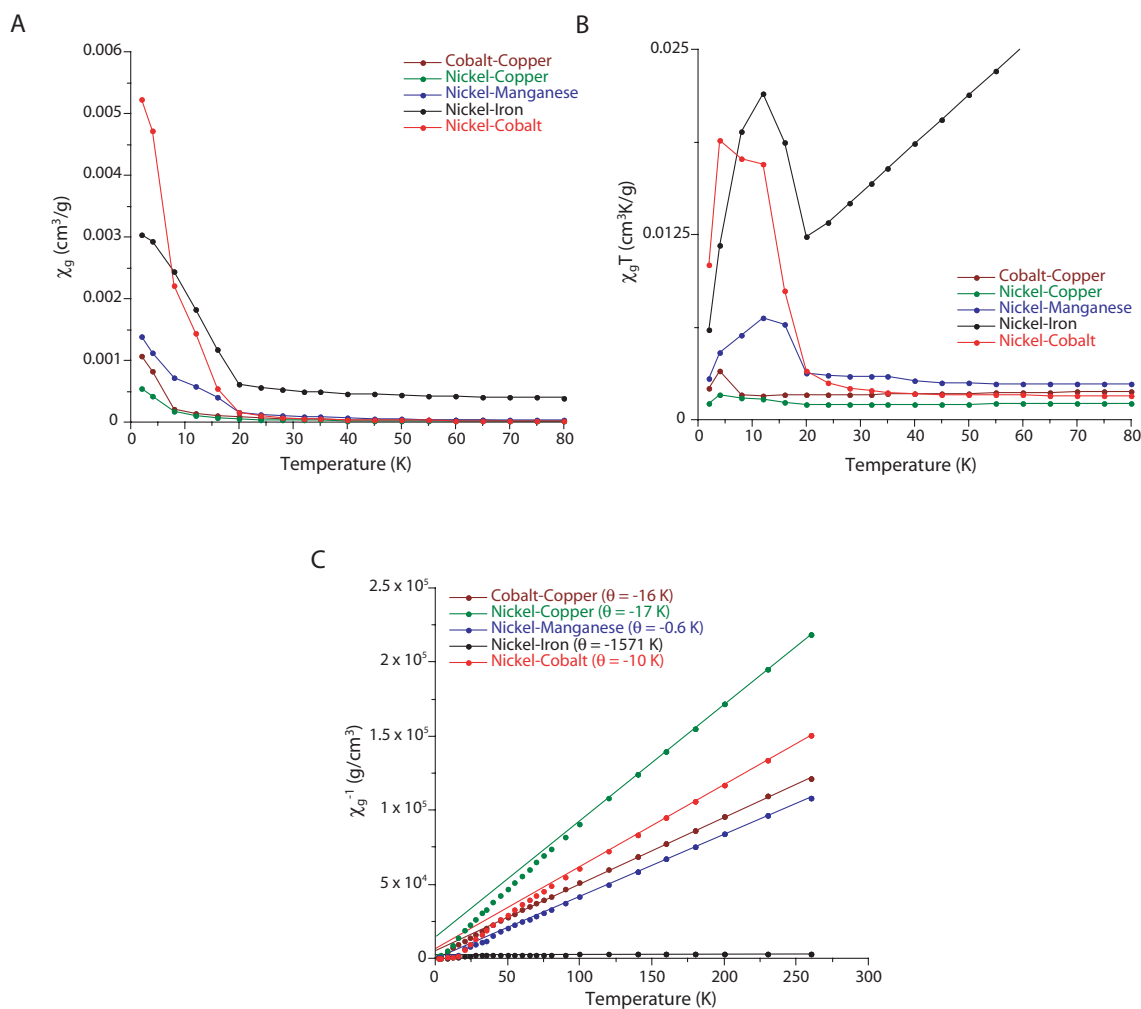
#### 7.2.2.2 Other Bimetallic Complexes

Having observed anomalous ferromagnetic ordering for the copper-manganese system, the generality of using the pillared guanidinium 5,5'-salen disulfonate lattice for the generation of frustrated magnetic materials with anomalous magnetic ordering was examined. Bimetallic complexes containing manganese-iron, cobalt-copper, cobalt-iron, iron-copper, nickel-copper, nickel-manganese, nickel-iron, nickel-cobalt, and manganese-zinc were prepared using the method described for the copper-manganese complex. Anomalous ferromagnetic ordering was observed for the cobalt-copper, nickel-copper,

nickel-manganese, nickel-iron, and nickel-cobalt complexes (Figure 7.12), while the remaining complexes exhibited antiferromagnetic ordering at low temperature.

Despite exhibiting apparent ferromagnetic ordering, the bimetallic complexes all have negative Weiss constants and thus should exhibit antiferromagnetic ordering. At 100 G all materials except the nickel-iron complex exhibit relatively small Weiss constants with values ranging from -0.6 K to -17 K, however even the copper-manganese complex exhibits a relatively small Weiss constant, -43 K, at 100 G. One would expect, based on the behavior of the copper-manganese complex, that larger Weiss constants will be observed for these complexes at low magnetic fields. The nickel-iron complex exhibits a much larger Weiss constant of -1571, however it is evident from the susceptibility temperature data that this material interacts antiferromagnetically at high temperature.

Compared to the copper-manganese complex, the anomalous ferromagnetic orderings of the other metal complexes occurs at lower temperatures. The critical temperatures for the cobalt-copper and nickel-copper complexes are around 8 K and the critical temperatures for the nickel-manganese, nickel-iron, and nickel-cobalt complexes are around 20 K. In addition to showing lower critical temperatures, the maxima in  $\chi_g T$  for these complexes are significantly reduced when compared with the copper-manganese complex. As with the critical temperature, the nickel-copper and cobalt-copper complexes show lower maxima in the susceptibility temperature product than the other three metal combinations.



**Figure 7.12:** Susceptibility (A), susceptibility temperature product (B), and Curie (C) plots for the family of frustrated magnetic material obtained with an applied magnetic field of 100 G.

The creation of a family of complexes that exhibit frustrated magnetic behavior based on the guanidinium disulfonate crystal-engineering motif indicates the resilience of this motif. Although the copper manganese material is by far the most frustrated of this family, many of the materials seem to exhibit some degree of magnetic frustration.

### 7.3 Conclusions

The creation of interesting magnetic materials using the guanidinium sulfonate organic crystal-engineering motif establishes the potential of this approach. Well-defined organic crystal engineering motifs provide ways to rigidly control spin containing units and design novel magnetic materials.

The new class of magnetic materials that has been prepared using the guanidinium sulfonate motif and 5,5'-salendisulfonic acid exhibits massive magnetic frustration. The copper-manganese material has been extensively characterized using dc magnetic analysis and displays the classic signs of magnetic frustration. Although it is difficult to quantitate the extent of frustration in this system, the copper-manganese complex seems to display significant long-range frustration. The generality of the guanidinium sulfonate motif, using 5,5'-salen disulfonic acid as a bridging sulfonate, for the formation of magnetically frustrated materials was verified by the creation of family of six different magnetically frustrated bimetallic complexes.

### 7.4 Materials and Methods

*Infrared Spectroscopy.* Infrared spectra were recorded using a Perkin Elmer Paragon 1000 FT-IR between 4000 and 500  $\text{cm}^{-1}$ . The spectra were obtained as KBr pellets.

*Elemental Analysis.* Carbon, hydrogen, nitrogen, and sulfur analysis was performed by Quantitative Technologies Inc. of Whitehouse, NJ. Copper and magnesium analysis was

performed using an Elan 5000A inductively coupled plasma mass spectrometer standardized with NIST traceable standards.

*Magnetic Measurements.* DC magnetization was measured using a Quantum Design MPMS-5 SQUID magnetometer from 1.8 to 300 K and between 0 and 5.5 T. All measurements were made on powdered samples in Delron screw-cap holders or gelatin capsules. The diamagnetic correction for the copper-manganese complex was obtained from the high temperature / high field data using the intercept of magnetic susceptibility vs. inverse temperature, as previously described and applied to the data for analysis of the susceptibility and the susceptibility temperature product (Murray et al., 1994). For other plots raw dc magnetization was used without correction.

#### *Synthesis.*

*5,5'-Salen Disulfonic Acid.* 5,5'-Salen disulfonic acid was prepared as previously described (Mukherjee and Ray, 1955).

*Metal Complexes.* Bimetallic metal complexes were prepared as described below for the Cu/Mn complex.

To a flask equipped with a reflux condenser and a stir bar was added 5,5'-salendisulfonic acid (0.250 g; 0.518 mmol), manganese (II) acetate (0.090 g; 0.518 mmol), copper (II) acetate monohydrate (0.103g; 0.518 mmol), and guanidinium acetate (0.246 g; 2.06 mmol). Distilled water (10 mL) and acetonitrile (40 mL) were added and the mixture

was allowed to reflux for 3 hours. The reaction mixture was hot filtered to give a pink/purple precipitate and a dark blue solution. The solid was washed with acetonitrile and acetone and allowed to air-dry (0.191 g). FTIR, KBr,  $\tilde{\nu}$  = IR 3406.4(vs,Broad), 3257.3(s), 3184.9(s), 3030.9(m), 2922.2(m), 2849.8(w), 1640.9(vs), 1601.4(s), 1535.0(m), 1492.1(w), 1465.8(m), 1380.8(m), 1333.6(w), 1302.9(m), 1189.8(s), 1116.3(s), 1084.5(m), 1052.8(w), 1032.1(vs), 971.3(w), 930.5(w), 898.9(w), 831.1(m), 749.7(w), 737.0(m), 697.5(m), 670.1(m), 621.3(s)  $\text{cm}^{-1}$ . XRD, Cu,  $2\theta(\text{counts/sec}) = 5.0(540), 16.9(530), 19.4(340), 20.2(320), 25.4(400), 25.7(400), 26.0(400), 32.0(400), 36.0(430)$ . Elemental analysis. Found: C, 29.82; H, 3.46; N, 11.45; S, 8.68; Cu, 9.28; Mn, 6.68.

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