Chapter 2

Introduction

Pioneering work by Groves and coworkers has led to widespread interest in the reactivity of oxo-metal complexes of porphyrins and other macrocycles.[1,2] Nowadays, it is generally accepted that the catalysis of oxygen-atom transfer by chromium, manganese, iron, and ruthenium porphyrins involves oxo-metal species as key intermediates, reminiscent of the mechanism of action of cytochrome P450.[3] Moreover, similar mechanisms and intermediates have been proposed for many other types of catalytic oxidations.[4] Remarkably, even after years of research on porphyrins containing the aforementioned four metals, only oxochromium(IV) and dioxoruthenium(VI) derivatives have been fully characterized.[5,6]

With one carbon less and one NH proton more, corroles are close relatives of porphyrins.[7] They have received much less attention, [8] mainly because simple synthetic routes have not been available until recently. In addition, until 1993 all reported derivatives lacked aryl substituents in the meso position, which greatly diminished the possibilities for catalytic applications. Indeed, catalysis by metal corroles was first reported only after a novel procedure for the preparation of triaryl derivatives was discovered.[9– 11]

We have initiated a systematic investigation of the coordination chemistry of tris(pentafluorophenyl)corrole, H_3(tpfc).[12] One particular goal is the isolation of oxo-metal complexes, since corroles are known to be superior to porphyrins in stabilizing high oxidation states,[13] with the oxochromium(V) and chloroiron(IV) complexes as relevant examples.[12,14-16] We report here the synthesis of the first triarylcorrolato chromium complex, (tpfc)Cr(O); the structure and spectroscopic properties of this chromium(V) species provide a framework for discussion of the stabilization of high oxidation states by corroles.

Experimental Section

Synthesis

[tpfc]Cr(O) (**2**): A boiling solution of 79.6 mg (0.1 mmol) H_3[tpfc] [9] in 50 mL toluene was treated with aliquots of 5-10 mg chromium hexacarbonyl at 15 min intervals for 3 h. As the reaction proceeds (TLC), the color changes from deep purple (reactant) to blood red (product). Flash chromatography (Silica, 12% CH_2Cl_2/hexanes, collection of the first red fraction), followed by recrystallization from minimum CH_2Cl_2 yields 65.3 mg (75.8 %) **2**. ESI-MS: 861.5 [M^-]; UV-Vis (λ_{max} (nm), logε): 402 (4.91), 556 (4.10), 702 (2.73); SQUID: 1.72 μ_B (50 to 300K).

Structure

Single crystals suitable for X-ray crystallography were obtained by dissolving **2** in CH_2Cl_2 with a slight excess of triphenylphosphine oxide, layered with methanol, left for slow evaporation to a small volume, followed by cooling to -20 °C. The tiny crystals that formed were redissolved in minimum CH_2Cl_2, followed by slow evaporation to half the volume and slow cooling to -20 °C for several days. *Crystal data* for **2**, $2[(C_{37}H_8CrF_{15}N_4O)\cdot(CH_2Cl_2)]$: triclinic, *P*1, purple-red, a = 14.3325(14), b = 15.7474(15), c = 17.2641(16) Å, $\alpha = 108.241(2)^\circ$, $\beta = 109.212(2)^\circ$, $\gamma = 92.414(2)^\circ$, V = 3448.5(6) Å^3, T = 98(2)K, Z = 2, R1=0.0611 (wR2 = 0.0877) for all unique data, GOF =

1.746. Disorder in the two CH_2Cl_2 molecules in the asymmetric unit does not appear to affect the rest of the structure. [22]

Spectroscopy

EPR spectra were obtained on a Bruker EMX ER 082 spectrometer. UV-Vis spectra were measured using an HP 8452 spectrometer.

Electrochemistry

Volammetric measurements were made on a CHI660 workstation with a normal three-electrode configuration: glassy carbon working electrode; Ag/AgCl reference electrode; and a Pt-wire auxiliary electrode. Samples were 2-5 mM [tpfc]Cr(O) in 0.1 M $(Bu_4N)(PF_6)/CH_2Cl_2$ solution at ambient temperature.

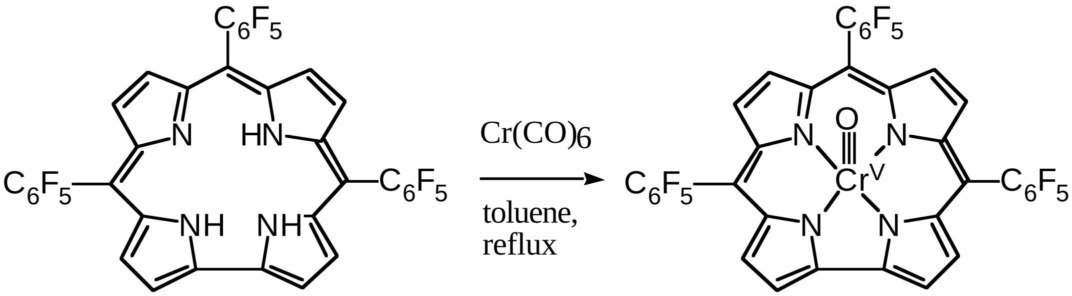
Results and Discussion

Metallation of H_3[tpfc] was achieved via aerobic reaction with chromium hexacarbonyl in toluene (Scheme 2.1): identification of the dark red product as [Tpfc]Cr(O) (**2**, note that corrolates are trianionic ligands) is based on MS, EPR spectroscopy, magnetic susceptibility, and X-ray crystallography. The Cr^V oxidation state in **2** is clearly evident by both the magnetic moment of 1.72 μ_B and by virtue of the fact that it displays a room temperature EPR spectrum. The other possible formulations can easily been ruled out: the EPR spectra of Cr^{III} complexes are very different and observable only in frozen solutions, and both the EPR and the magnetic moment are inconsistent with $[tpfc^{+\cdot}]Cr^{IV}(O)$. Complex **2** also is remarkably stable (no long-term apparent decomposition or transformation to other compounds), which accords with its low reduction potential compared to related species (Table 2.1).

The room-temperature EPR spectrum of **1** (Figure 2.1) features an isotropic signal of nine lines attributable to coupling of the unpaired electron to four ^{14}N nuclei, and there are also satellite signals due to coupling to ^{53}Cr. Such a spectrum is characteristic of d^1 Cr(V)O complexes,[17,18] but the coupling constants— which are directly related to unpaired spin densities— are unusually high for the nitrogens and low for the metal (Table 2.1).

X-ray quality crystals of **2** were obtained from CH_2Cl_2 solution. The asymmetric unit of **2** consists of two pairs of molecules with different conformations: one with a slightly domed corrole (all pyrroles bend downwards); and the other featuring a twisted corrole with one pyrrole ring bending upwards (Figure 2.2). Bond lengths and angles are virtually identical for the two conformers (Table 2.2). As there is no X-ray structure available for a Cr(V) porphyrin, we turn to (TPP)Cr(IV)O for comparison to **2**.[5a] Although the metal-oxo bonds are 1.57 Å in both complexes, the Cr-N bonds are much shorter (1.93 Å vs. 2.03 Å) and the out of plane (defined by the four nitrogens) displacement of the metal atom is much larger— 0.5616(11) Å and 0.5696(10) Å in the two molecules of **2**— than in the porphyrin complex (0.469 Å). It must be emphasized that similar metal-nitrogen bond lengths are accomodated in other metallocorroles without such large out of plane displacement of the metal, ruling out the somewhat contracted N_4 coordination core of corroles relative to porphyrins as the major reason behind this phenomenon in **2**.

Scheme 2.1. Synthesis of **2**.



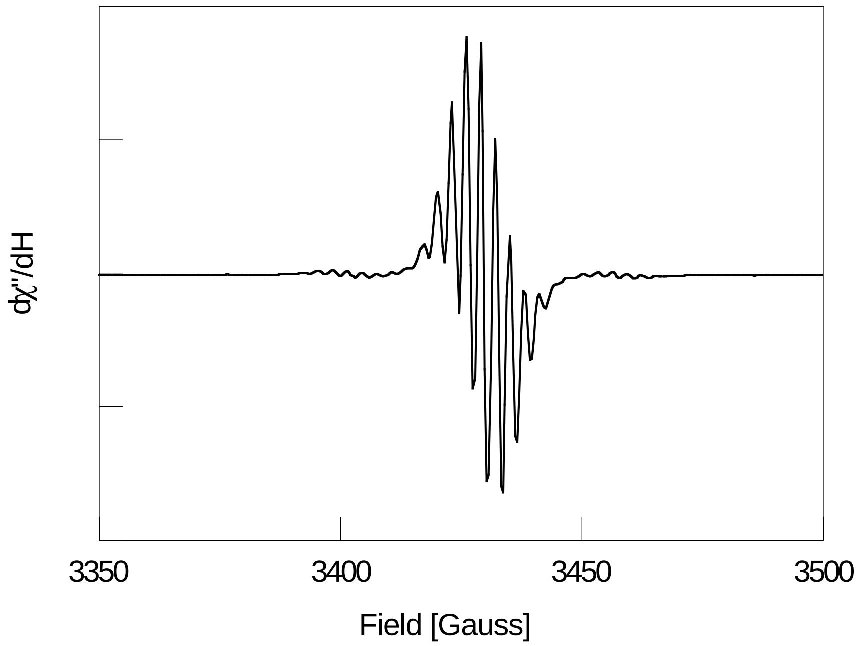
$(tpfc)H_3$ (tpfc)Cr(O), **2**

Table 2.1. EPR parameters and reduction potentials for oxochromium(V) complexes.

	(tpfc)Cr(O)	[(tmp)Cr(O)]$^+$	[(salen)Cr(O)]$^+$
g_{iso}	1.986	1.982	1.978
$A_{^{53}Cr}$ (mT)	1.64	1.79	1.94
$A_{^{14}N}$ (mT)	0.30	0.26	0.22
$E_{1/2}$ (Cr^{V}/Cr^{IV})	0.11[a]	0.76[a]	0.47[b]

[a] vs. Ag/AgCl. [b] quasi-reversible

Figure 2.1. EPR spectrum of **2** in CH_2Cl_2 at room temperature.


dχ''/dH
3350
3400
3450
3500
Field [Gauss]

But, the combination of a long Cr-O bond, short Cr-N bonds, and large out of plane displacement of the metal is also found in one of the very stable tetraamido Cr(V)O complexes reported by Collins and coworkers (the corresponding values are 1.569(2), 1.913(3), and 0.60 Å).[19] Interestingly, Cr-O is much shorter (1.545(2) Å) and the Cr-N bonds are much longer (1.969 and 1.991 Å) in the more reactive salen complex.[18,20]

The structural and spectroscopic data for **2** provide a good starting point for discussion of the experimentally observed stabilization of high oxidation states by corroles. It is unlikely that ligand π donation is a major contributor to such stabilization in a molecule with both electron withdrawing substituents and an unfavorable geometry for dπ overlap. Unusually strong σ(N)–>dσ(Cr) bonding must occur to account for the spin densities on the Ns (large) and Cr (small) as well as the short Cr-N bond length. [21] Interestingly, with the Cr atom almost 0.6 Å out of the N_4 plane, the σ(N) orbitals also can interact with the π-system of the Cr-O moiety. This σ(N)–>π(Cr=O) interaction undoubtedly contributes to lengthening the Cr=O bond.

Our results clearly demonstrate that σ(N)-donation is a major factor in the stabilization of high oxidation states by corroles. The effect is enormous, considering the 0.75 V difference in the Cr^{V}/Cr^{IV} redox couple of **2** relative to a porphyrin with much more electron donating aryl substituents (the difference for the Fe^{IV}/Fe^{III} couple with similar ligands is 1.09 V).[13] The possible role of this type of strong σ(N)-donation on the reactivity of oxo-metal corroles is currently under investigation.

Figure 2.2. Structure of the twisted conformer of **2**.

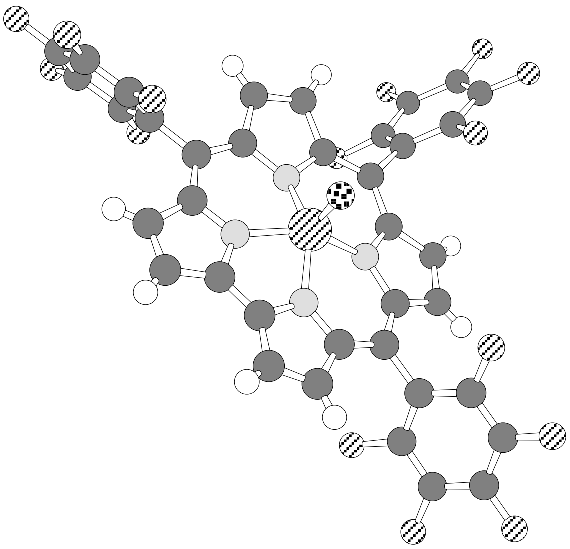


Table 2.2. Selected bond lengths (Å) and angles (˚).

domed conformer		twisted conformer	
Cr-O	1.5700(17)	Cr-O	1.5713(17)
Cr-N_1	1.936(2)	Cr-N_1	1.943(2)
Cr-N_2	1.9425(19)	Cr-N_2	1.943(2)
Cr-N_3	1.927(2)	Cr-N_3	1.929(2)
Cr-N_4	1.936(2)	Cr-N_4	1.927(2)
N_1-Cr-N_3	145.53(9)	N_1-Cr-N_3	144.84(8)
N_2-Cr-N_4	145.35(9)	N_2-Cr-N_4	145.03(8)

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