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Stabilization of High-Valent Metals by Corroles: Oxo[tris(pentafluorophenyl)corrolato]chromium(V)

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The aerobic reaction of $Cr(CO)_6$ with tris(pentafluorophenyl)corrole (H_3(TpFPC)) in toluene gives the dark red oxochromium(V) compound (TpFPC)Cr(O), which has been characterized by X-ray crystallography, electrochemistry, and EPR spectroscopy. Short Cr−N (1.927−1.943 Å) bonds as well as relatively large ^{14}N and small ^{53}Cr coupling constants suggest that $\sigma(N \rightarrow Cr)$ donation is responsible for the unusual stability of chromium(V) in this complex. The $Cr^{V/IV}$ reduction potential (0.11 V vs Ag/AgCl) is 0.65 V below that of oxo(tetramesitylporphinato)chromium(V).

Introduction

Pioneering work by Groves and co-workers 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] However, 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 positions, 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(TpFPC).[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, (TpFPC)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.

Results and Discussion

Metalation of H_3(TpFPC) was achieved via an aerobic reaction with chromium hexacarbonyl in toluene (Scheme 1). Identification of the dark red product as (TpFPC)Cr(O) (**1**; note that corrolates are trianionic ligands) is based on MS, EPR, and magnetic susceptibility measurements and on the results of X-ray

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(1) (a) Groves, J. T.; Kruper, W. J. *J. Am. Chem. Soc.* **1979**, *101*, 7613. (b) Groves, J. T.; Haushalter, R. C.; Nakamura, M.; Nemo, T. E.; Evans, B. J. *J. Am. Chem. Soc.* **1981**, *103*, 2884.

(2) Meunier, B. In *Metalloporphyrin Catalyzed Oxidations*; Montanary, F., Casella, L., Eds.; Kluwer Academic: Dordrecht, The Netherlands, 1994; Chapter 1.

(3) Ortiz de Montellano, P. R. *Cytochrome P450: Structure, Mechanism, and Biochemistry*, 2nd ed.; Plenum Press: New York, 1995.

(4) Shilov, A. E.; Shul'pin, G. B. *Chem. Rev.* **1997**, *97*, 2879.

(5) (a) Groves, J. T.; Kruper, W. J., Jr.; Haushalter, R. C.; Butler, W. M. *Inorg. Chem.* **1982**, *21*, 1363. (b) Lai, T.-S.; Zhang, R.; Cheung, K.-K.; Kwong, H.-L.; Che, C.-M. *J. Chem. Soc., Chem. Commun.* **1998**, 1583.

(6) (a) A preliminary X-ray structure of an oxoiron(IV) porphyrin: Schappacher, M.; Weiss, R.; Montielmontoya, R.; Trautwein, A. X.; Tabard, A. *J. Am. Chem. Soc.* **1985**, *107*, 3736. (b) EXAFS of an oxomanganese(IV) porphyrin: Ayougou, K.; Bill, E.; Charnock, J. M.; Garner, C. D.; Mandon, D.; Trautwein, A. X.; Weiss, R.; Winkler, H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 343. (c) An oxomanganese(V) porphyrin: Jin, N.; Groves, J. T. *J. Am. Chem. Soc.* **1999**, *121,* 2923.

(7) Sessler, J. L.; Weghorn, S. J. *Expanded, Contracted & Isomeric Porphyrins*; Pergamon: London, 1997; Chapter 1.

(8) A computer search of article titles, keywords, and abstracts in the ISI database for 1998 produced 1143 hits for "porphyrin" but only 10 for "corrol".

(9) (a) Gross, Z.; Galili, N.; Saltsman, I. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 1427. (b) Gross, Z.; Galili, N.; Simkhovich, L.; Saltsman, I.; Botoshansky, M.; Bläser, D.; Boese, R.; Goldberg, I. *Org. Lett.* **1999**, *1*, 599. (c) Tris(pentafluorophenyl)corrole is now commercially available (Strem Chemicals). (d) Triphenylcorrole has just been reported: Paolesse, R.; Jaquinod, L.; Nurco, D. J.; Mini, S.; Sagone, F.; Boschi, T.; Smith, K. M. *J. Chem. Soc., Chem. Commun.* **1999**, 1307.

(10) Paolesse, R.; Licoccia, S.; Fanciullo, M.; Morgante, E.; Boschi, T. *Inorg. Chim. Acta* **1993**, *203*, 107.

(11) Gross, Z.; Simkhovich, L.; Galili, N. *J. Chem. Soc., Chem. Commun.* **1999**, 599.

(12) Gross, Z.; Galili, N.; Simkhovich, L.; Saltsman, I.; Goldberg, I. *Inorg. Chem.*, in press.

(13) Van Caemelbecke, E.; Will, S.; Autret, M.; Adamian, V. A.; Lex, J.; Gisselbrecht, J.-P.; Gross, M.; Vogel, E.; Kadish, K. M. *Inorg. Chem.* **1996**, *35*, 184 and references therein.

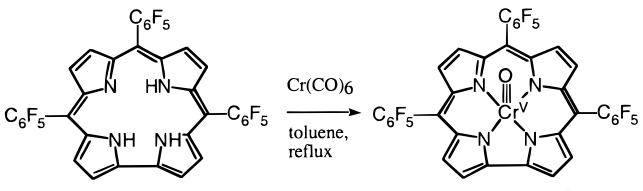
(14) Murakami, Y.; Matsuda, Y.; Yamada, S. *J. Chem. Soc., Dalton Trans.* **1981**, 855.

(15) Vogel, E.; Will, S.; Schulze Tilling, A.; Neumann, L.; Lex, J.; Bill, E.; Trautwein, A. X.; Wieghardt, K. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 731.

(16) In addition, an oxorhenium(V) corrole has been characterized: Tse, M. K.; Zhang, Z.; Mak, T. C. W.; Chan, K. S. *J. Chem. Soc., Chem. Commun.* **1998**, 1199.

10.1021/ic000180d CCC: $19.00

Scheme 1



(TpFPC)H3

(TpFPC)Cr(O),**1**

Table 1. EPR Parameters and Reduction Potentials for Oxochromium(V) Complexes

	(TpFPC)Cr(O)	$[(tmp)Cr(O)]^+$ [17]	$[(salen)Cr(O)]^+$ [18]
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}), V	0.11^a	0.76^a	0.47^b

[a] Vs Ag/AgCl. [b] Quasi-reversible.

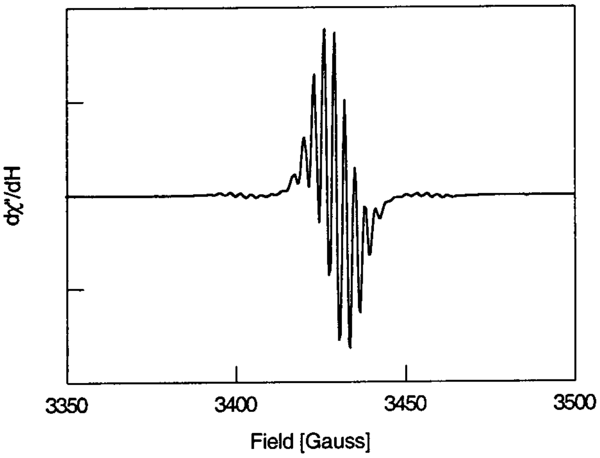


Figure 1. EPR spectrum of **1** in CH_2Cl_2 at room temperature.

crystallography. The Cr^V oxidation state in **1** is clearly evident both from 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 be ruled out: the EPR spectra of Cr^{III} complexes are very different and observable only in frozen solutions, and both the EPR spectrum and the magnetic moment are inconsistent with ($TpFPC^{\bullet+}$)Cr^{IV}(O). Complex **1** also is remarkably stable (no long-term apparent decomposition or transformation to other compounds), which accords with its low reduction potential compared to those of related species (Table 1).

The room-temperature EPR spectrum of **1** (Figure 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^VO 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 1).

X-ray-quality crystals of **1** were obtained from CH_2Cl_2 solution. The asymmetric unit of **1** consists of two pairs of molecules with different conformations: one with a slightly domed corrole (all pyrroles bend downward) and the other featuring a twisted corrole with one pyrrole ring bending upward (Figure 2). Bond lengths and angles are virtually identical for the two conformers (Table 2). As there is no X-ray structure available for a Cr(V) porphyrin, we turn to (TPP)Cr^{IV}O for comparison to **1**.[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) displacements of the metal atoms are much larger—0.5616(11) and 0.5696(10) Å—in the two molecules of **1** than in the porphyrin complex (0.469 Å). It must be emphasized that similar metal−nitrogen bond lengths are accommodated in other metallocorroles without such large out-of-plane displacements of the metals, ruling out the somewhat contracted N_4 coordination cores of corroles relative to those of porphyrins as the major reason behind this phenomenon in **1**. But, the combination of a long Cr≡O bond, short Cr−N bonds, and a large out-of-plane displacement of the metal is also found in one of the very stable tetraamido Cr^VO complexes reported by Collins and co-workers (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]

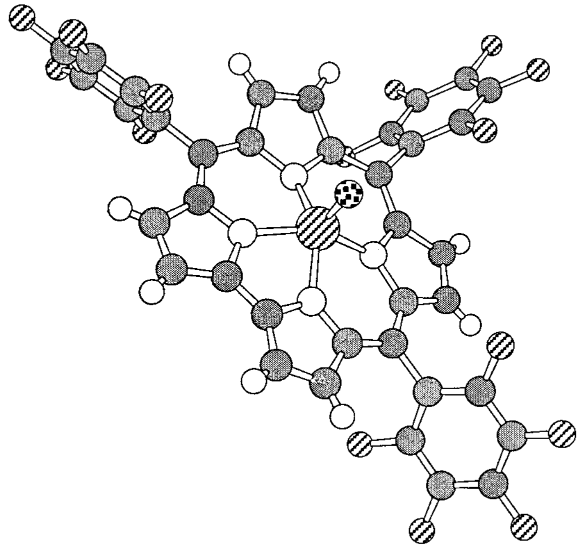


Figure 2. Structure of the twisted conformer of **1**.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1**

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)

The structural and spectroscopic data for **1** 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 N's (large) and Cr (small) as well as the short Cr−N bond length.[21] Interestingly, with the Cr atom almost 0.6 Å out

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(17) Fuji, H.; Yoshimura, T.; Kamada, H. *Inorg. Chem.* **1997**, *36*, 1122.

(18) Srinivasan, K.; Kochi, J. K. *Inorg. Chem.* **1985**, *24*, 4671.

(19) Collins, T. J.; Slebodnick, C.; Uffelman, E. S. *Inorg. Chem.* **1990**, *29*, 3433.

(20) For a discussion of the apparent anticorrelation of oxo−chromium(V) bond lengths and reactivities, see ref 17.

(21) Sunil, K. K.; Harrison, J. F.; Rogers, M. T. *J. Chem. Phys.* **1982**, *76*, 3087.

of the N_4 plane, the σ(N) orbitals also can interact with the π-system of the Cr≡O moiety. This $\sigma(N) \rightarrow \pi(Cr{\equiv}O)$ 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 0.65 V difference in the Cr^V/Cr^{IV} redox couple of **1** 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 effect of this type of strong σ(N) donation on the reactivity of oxo−metal corroles is currently under investigation.

Experimental Section

Synthesis of (TpFPC)Cr(O) (1). A boiling solution of 79.6 mg (0.1 mmol) of H_3(TpFPC)[9] in 50 mL toluene was treated with aliquots of 5−10 mg of chromium hexacarbonyl at 15 min intervals for 3 h. As the reaction proceeded (TLC), the color of the mixture changed 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 a minimum amount of CH_2Cl_2, yielded 65.3 mg (75.8%) of **1**. ESI-MS: *m*/*z* 861.5 [M^-]. UV−vis (λ_{max} (nm), log ϵ): 402 (4.91), 556 (4.10), 702 (2.73). SQUID: 1.72 μ_B (50−300 K).

Structure of 1. Single crystals suitable for X-ray crystallography were obtained by dissolving **1** in CH_2Cl_2 with a slight excess of triphenylphosphine oxide, layering with methanol, slow evaporation to a small volume, and cooling to −20 °C. The tiny crystals that formed were redissolved in a minimum quantity of CH_2Cl_2, followed by slow evaporation to half-volume and slow cooling to −20 °C for several days. Crystal data for **1**, $2[(C_{37}H_8CrF_{15}N_4O{\cdot}CH_2Cl_2)]$: triclinic, $P\bar{1}$, purple-red, $a = 14.3325(14)$ Å, $b = 15.7474(15)$ Å, $c = 17.2641(16)$ Å, $\alpha = 108.241(2)°$, $\beta = 109.212(2)°$, $\gamma = 92.414(2)°$, $V = 3448.5(6)$ Å^3, $T = 98(2)$ K, $Z = 2$, R1 = 0.0611 (*w*R2 = 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, consisting of a glassy carbon working electrode, an Ag/AgCl reference electrode, and a Pt-wire auxiliary electrode. Samples were 2−5 mM (TpFPC)Cr(O) in 0.1 M $[Bu_4N]PF_6/CH_2Cl_2$ solution at ambient temperature.

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Supporting Information Available: Tables of crystal data, structure solution and refinement details, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[22] Crystallographic data have been deposited at the CCDC, 12 Union Rd., Cambridge CB2 1EZ, U.K., and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 133553.