J|A|C|S
COMMUNICATIONS

Why the Chromyl Bond Is Stronger Than the Perchromyl Bond in High-Valent Oxochromium(IV,V) Complexes of Tris(pentafluorophenyl)corrole

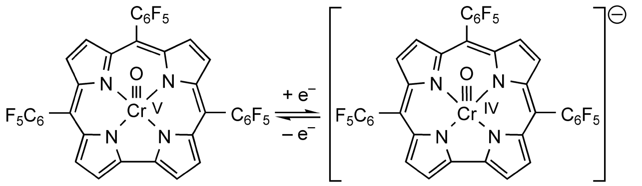
Roman S. Czernuszewicz,*,† Vicky Mody,† Arkadiusz Czader,† Michał Gałęzowski,‡ and Daniel T. Gryko*,‡

Department of Chemistry, University of Houston, Houston, Texas 77204-5003, and Institute of Organic Chemistry of the Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland

Received July 30, 2009; E-mail: Roman@uh.edu; daniel@icho.edu.pl

The coordination chemistry of corroles[1] has attracted considerable attention because of the uncertain electronic structure of these complexes and their possible applications in catalysis and oxygen atom transfer (OAT) reactions.[2,3] In particular, complexes of chromium,[4] manganese,[5] and iron[6] have been studied extensively, mainly by Gross and co-workers. After a long dispute, it was concluded that one-electron oxidation in these complexes is often corrole- rather than metal-centered.[7] Meier-Callahan et al.[4b] have reported that a neutral product of aerobic metalation of 5,10,15-tris(pentafluorophenyl)corrole (tpfpc) with $Cr(CO)_6$, that is, the oxochromium(V) (perchromyl) complex $(tpfpc)Cr^{V}O$ (**1**) (Scheme 1), can easily be transformed into complexes containing chromium in +3 and +4 formal oxidation states as well as into the perchromyl corrole π-cation radical $[(tpfpc^{\bullet})Cr^{V}O]^{+}$. It was also determined that the catalytic reactivity of **1** in the OAT reaction $Cr^{V}O + PPh_3 \rightarrow Cr^{III} + OPPh_3$ is markedly increased in acetonitrile solution, which was attributed to the formation of an oxochromium(IV) (chromyl) ionic species $[(tpfpc)Cr^{IV}O]^{-}$ (**2**) (Scheme 1).[4c] This intriguing observation prompted us to perform a more detailed investigation of this system using for the first time resonance Raman (RR) spectroscopy as a probe of the molecular structure of high-valent oxochromium(IV,V) corroles.

Scheme 1



The Soret-excited RR spectrum of **1** in CS_2 solution displayed a rich array of distinctive metallocorrole vibrational bands in the 900−1600 cm^{-1} region,[8] with the strongest polarized features at 986, 1080, 1372, 1507, 1545, and 1582 cm^{-1} (Figure 1a). The polarized band at 986 cm^{-1} is due to the stretching mode of the perchromyl bond, $\nu(Cr^{V}O)$, because it downshifted to 946 cm^{-1} upon incorporation of ^{18}O into the oxo ligand (Figure 2a).[9] A simple Hooke's law calculation predicts $\nu(Cr^{V}O)$ to appear at ~943 cm^{-1} upon $^{18}O \rightarrow {}^{16}O$ exchange. It also gives a force constant of 7.00 mdyn/Å for the perchromyl moiety (Table 1), which is indicative[8,10] of a $Cr^{V}{\equiv}O$ triple bond in **1**. The key RR experiment involved dissolution of **1** in CH_3CN. During RR data acquisition (see Figure S-1 in the Supporting Information), we noted that new polarized bands gradually emerged at 992, 1002, 1331, 1536, and 1561 cm^{-1} and that the 1002 cm^{-1} band dominated the final spectrum (Figure 1b). These spectral changes did not depend on the incident laser power used (20−300 mW). When a small grain of solid PPh_3 was added, the 1002 cm^{-1} peak instantly intensified and then very slowly weakened (Figure S-2), suggesting that the newly formed species (**2**) apparently reacted with PPh_3 to give $OPPh_3$.

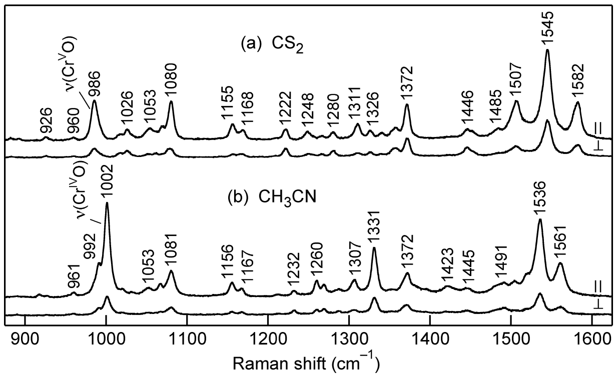


Figure 1. RR spectra for parallel (||) and perpendicular (⊥) scattering of **1** (~1 mM) dissolved in (a) CS_2 and (b) CH_3CN, excited at 413.1 nm.

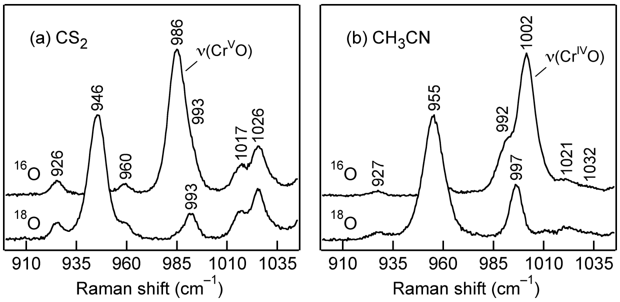


Figure 2. RR spectra of **1** (~1 mM) in (a) CS_2 and (b) CH_3CN before (^{16}O) and after (^{18}O) exchange with $H_2{}^{18}O$, excited at 413.1 nm.

To establish that these new RR marker bands represent chromyl species, we prepared the salt $[(tpfc)Cr^{IV}O](Co^{III}Cp_2)$ (**3**) by reacting **1** with $Co^{II}Cp_2$ (cobaltocene),[4c] recorded its 900−1600 cm^{-1} RR spectra in the solid state (as a KCl pellet) and in solution (CS_2 and CH_3CN), and examined the isotope shifts of the dominant bands near 1002 cm^{-1} by $^{18}O \rightarrow {}^{16}O$ substitution. Both the solid and solution spectra of **3** revealed a vibrational pattern identical to that of **2** in Figure 1b (data in Table 1), which verified that the autoreduced product of **1** in CH_3CN is indeed a chromyl corrole anion (Scheme 1). As shown in Figure 2b and Figure S-3, the 1002 cm^{-1} band of $[Cr^{16}O]$-**2** in CH_3CN shifted to 955 cm^{-1} in the $[Cr^{18}O]$-**2** spectrum.[11] This RR observation unequivocally identifies the 1002 cm^{-1} band as the stretching vibration of the chromyl bond, $\nu(Cr^{IV}O)$ and demonstrates for the first time that the reduced $Cr^{IV}{\equiv}O$ group vibrates with considerably *higher* frequency than its one-electron-oxidized $Cr^{V}{\equiv}O$ counterpart. More importantly,

---

† University of Houston.
‡ Polish Academy of Sciences.

10.1021/ja906393r CCC: $40.75

it indicates a strengthened metal−oxo bond and/or a decrease in bond length upon Cr^{5+}/Cr^{4+} reduction. As described above, reduction of **1** to **2** also influences the internal vibrational modes of the corrole macrocycle (Figure 1), with some of these high-frequency modes being downshifted by 8−19 cm^{-1} in CH_3CN (Table 1).

Table 1. Vibrational and DFT Data for (tpfpc)Cr≡O Complexes[a]

	$[Cr^{V}O]$-**1**	$[Cr^{IV}O]$-**2**	$[Cr^{IV}O]$-**3**[b]
	Carbon Disulfide		
$\nu(Cr^{16}O)$	985.9		1001.7
$\nu(Cr^{18}O)$	946.4		954.6
F_{CrO}	7.00		7.23
ν(Corrole)	1507, 1545, 1582		1537, 1562
	Acetonitrile		
$\nu(Cr^{16}O)$	982.7	1001.6	1001.9
$\nu(Cr^{18}O)$	943.1	954.9	954.7
F_{CrO}	6.96	7.23	7.23
ν(Corrole)[c]	1508, 1544, 1580	1536, 1561	1536, 1561
	DFT in Vacuum		
d(Cr−O)	1.5660	1.5649	
$d(Cr-N_P)_{ave}$	1.9476	1.9721	
$d(N_P\cdots N_P)_{ave}$	3.7098	3.7506	
Cr(oop)[d]	0.579	0.597	
$\nu(Cr^{16}O)$	1058.0	1069.4	

[a] ν = stretching mode in cm^{-1}; F = harmonic force constant in mdyn/Å; d = distance in Å. [b] Solid **3** (KCl pellet) gave $\nu(Cr^{16}O)$ = 1005 cm^{-1} and F_{CrO} = 7.28 mdyn/Å. [c] Corrole Cr oxidation state marker bands. [d] Out-of-plane (defined by the four N_P atoms) displacement of the Cr ion (Å).

The observed behavior of the ν(CrO) stretch upon conversion of $[Cr^{V}O]$-**1** to $[Cr^{IV}O]$-**2** is in striking accord with the correlation that Czernuszewicz et al.[10c] originally recognized between $\nu(M^{IV}O)$ frequencies and the d orbital occupancy in a series of high-valent metalloporphyrin oxides of Ti^{IV} (d^0), V^{IV} (d^1), Cr^{IV} (d^2), Mn^{IV} (d^3), and Fe^{IV} (d^4) (Figure 3). This empirical correlation, recently verified by density functional theory (DFT),[12] predicts well that the metal−oxo stretching frequency should increase as the number of d electrons increases from d^1 (V^{IV}, Cr^{V}) to d^2 (Cr^{IV}).

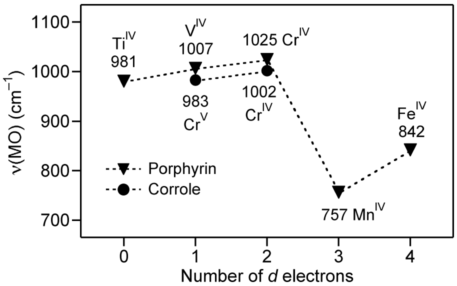


Figure 3. Variation in ν(MO) frequency for oxo complexes of M(IV) (M = Ti, V, Cr, Mn, Fe) porphyrins (ref 10b, c) and Cr(IV,V) corroles (this work).

To examine the changes in structure and vibrational frequencies for oxochromium(IV,V) corroles, we performed DFT calculations on $(tpc)Cr^{V}O$ and $[(tpc)Cr^{IV}O]^-$, where tpc is 5,10,15-triphenylcorrole (see the Supporting Information). The DFT-optimized structures (Table 1 and Table S-1) agree well with available $(tpfpc)Cr^{V}O$ (**1**)[4a] and $(TPP)Cr^{IV}O$ (TPP = tetraphenylporphyrin) X-ray crystallographic data.[13] The computed Cr^{V}≡O bond distance, 1.5660 Å, is in perfect agreement with the value of 1.5700(17) Å reported for a domed conformer of **1**.[4a] The corresponding Cr^{IV}≡O distance, 1.5649 Å, is slightly shorter, following a larger out-of-plane displacement of the Cr^{4+} ion (0.597 Å vs 0.579 Å for Cr^{5+}) and a longer average $Cr^{IV}-N_P$ (1.9721 Å) than $Cr^{V}-N_P$ (1.9476 Å) distance. Although the computed vibrational frequencies of 1058.0 and 1069.4 cm^{-1} for $\nu(Cr^{V}O)$ and $\nu(Cr^{IV}O)$, respectively, are overestimated, as is usually the case with DFT, they do reproduce the observed upshift in ν(CrO) upon Cr^{5+}/Cr^{4+} reduction remarkably well (Table 1).

In summary, we have found that the conversion of oxo−Cr^{V} **1** to oxo−Cr^{IV} **2** occurs without much effort in acetonitrile solution, which we attribute to a very low reduction potential[4b] and the ability of acetonitrile to solvate the anions. This reduction leads to the formation of the chromyl bond, which is actually stronger than the perchromyl bond, as demonstrated by RR and DFT data. To the extent that the π-bond order is actually higher for Cr^{IV}≡O than for Cr^{V}≡O, the oxygen atom of the former should both be more electrophilic and have more unpaired electron density than the latter. Such an electronic change is expected to destabilize a π-antibonding orbital of Cr≡O,[14] which would then lead to the more stable (tpfpc)Cr≡O ← :PPh_3 charge-transfer intermediate required for an efficient OAT reaction.[15] This observation has significant implications for the use of high-valent oxochromium corrolates as OAT agents.

Acknowledgment. This work was supported financially by the Robert A. Welch (R.S.C.) and Volkswagen (D.T.G.) Foundations.

Supporting Information Available: Experimental details, DFT results, and additional spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Erben, C.; Will, S.; Kadish, K. M. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: New York, 2000; Vol. 2, p 233. (b) Gryko, D. T.; Fox, J. P.; Goldberg, D. P. *J. Porphyrins Phthalocyanines* **2004**, *8*, 1091.
(2) (a) Ghosh, A.; Steene, E. *J. Inorg. Biochem.* **2002**, *91*, 423. (b) Walker, F. A.; Licoccia, S.; Paolesse, R. *J. Inorg. Biochem.* **2006**, *100*, 810.
(3) (a) Simkhovich, L.; Mahammed, A.; Goldberg, I.; Gross, Z. *Chem.—Eur. J.* **2001**, *7*, 1041. (b) Gross, Z.; Simkhovich, L.; Galili, N. *Chem. Commun.* **1999**, 599. (c) Mahammed, A.; Gross, Z. *J. Am. Chem. Soc.* **2005**, *127*, 2883.
(4) (a) Meier-Callahan, A. E.; Gray, H. B.; Gross, Z. *Inorg. Chem.* **2000**, *39*, 3605. (b) Meier-Callahan, A. E.; Di Bilio, A. J.; Simkhovich, L.; Mahammed, A.; Goldberg, I.; Gray, H. B.; Gross, Z. *Inorg. Chem.* **2001**, *40*, 6788. (c) Mahammed, A.; Gray, H. B.; Meier-Callahan, A. E.; Gross, Z. *J. Am. Chem. Soc.* **2003**, *125*, 1162. (d) Golubkov, G.; Gross, Z. *Angew. Chem., Int. Ed.* **2003**, *42*, 4507. (e) Edwards, N. Y.; Eikey, R. A.; Loring, M. I.; Abu-Omar, M. M. *Inorg. Chem.* **2005**, *44*, 3700.
(5) (a) Gross, Z.; Golubkov, G.; Simkhovich, L. *Angew. Chem., Int. Ed.* **2000**, *39*, 4045.
(6) (a) Simkhovich, L.; Goldberg, I.; Gross, Z. *Inorg. Chem.* **2002**, *41*, 5433. (b) Simkhovich, L.; Gross, Z. *Inorg. Chem.* **2004**, *43*, 6136. (c) Stavitski, E.; Berg, A.; Ganguly, T.; Mahammed, A.; Gross, Z.; Levanon, H. *J. Am. Chem. Soc.* **2004**, *126*, 6886. (d) Joseph, C. A.; Ford, P. C. *J. Am. Chem. Soc.* **2005**, *127*, 6737.
(7) (a) Ye, S.; Tuttle, T.; Bill, E.; Simkhovich, L.; Gross, Z.; Thiel, W.; Neese, F. *Chem.—Eur. J.* **2008**, *14*, 10839. (b) Roos, B. O.; Veryazov, V.; Conradie, J.; Taylor, P. R.; Ghosh, A. *J. Phys. Chem. B* **2008**, *112*, 14099.
(8) Czernuszewicz, R. S.; Mody, V.; Zareba, A. A.; Zaczek, M. B.; Gałezowski, M.; Sashuk, V.; Grela, K.; Gryko, D. T. *Inorg. Chem.* **2007**, *46*, 5616.
(9) All of the complexes (∼1 mM) were easily labeled with ^{18}O in the oxo group by solution in dry solvents (∼0.5 mL) and exposure to pure $H_2{}^{18}O$ (97 atom % ^{18}O, ∼20 μL) under a dry N_2 atmosphere.
(10) (a) Mandimutsira, B. S.; Ramdhanie, B.; Todd, R. C.; Wang, H.; Zareba, A. A.; Czernuszewicz, R. S.; Goldberg, D. P. *J. Am. Chem. Soc.* **2002**, *124*, 15170. (b) Czernuszewicz, R. S.; Spiro, T. G. In *Inorganic Electronic Structure and Spectroscopy*; Solomon, E. I., Lever, A. B. P., Eds.; Wiley-Interscience: New York, 1999; Vol. 1, p 353. (c) Czernuszewicz, R. S.; Su, Y. O.; Stern, M. K.; Macor, K. A.; Kim, D.; Groves, J. T.; Spiro, T. G. *J. Am. Chem. Soc.* **1988**, *110*, 4158. (d) Gross, Z. *Angew. Chem., Int. Ed.* **2008**, *47*, 2337. (e) Jin, N.; Ibrahim, M.; Spiro, T. G.; Groves, J. T. *J. Am. Chem. Soc.* **2007**, *129*, 12416.
(11) The observed ^{18}O shift (−47 cm^{-1}) is larger than that expected for a diatomic Cr−O stretch (−43 cm^{-1}) because of kinematic coupling with a nearby corrole macrocycle vibration at 997 cm^{-1} (see Figure S-3).
(12) Czernuszewicz, R. S.; Czader, A. *J. Porphyrins Phthalocyanines* **2006**, *10*, 256.
(13) Groves, J. T.; Kruper, W. J., Jr.; Haushalter, R. C.; Butler, W. M. *Inorg. Chem.* **1982**, *21*, 1363.
(14) Fuji, H.; Yoshimura, T.; Kamada, H. *Inorg. Chem.* **1997**, *36*, 1122.
(15) Ostovic, D.; Bruice, T. C. *Acc. Chem. Res.* **1992**, *25*, 314.

JA906393R