Conclusions

The solution chemistry of iron(III) having a set of ligands similar to those provided by lactoferrin is analogous to the chemistry of iron(III) in the transferrins with regard to reactivity, spectroscopic, and electrochemical considerations. It is unclear as to whether the model systems or the proteins represent more structurally constrained situations with respect to the iron(III) coordination geometry, though the protein active sites appear to be more rhombically distorted than the models, as judged by the three *g* values observed in the high-spin ESR spectrum of the diiron(III) proteins. The cyanide adducts of the model compounds closely resemble the low-spin cyanide adduct of transferrin, illustrating the susceptibility of at least one of the two iron(III) sites to cyanide adduction and the subsequent disruption of its "native" coordination. The wavelength and molar absorptivity of the tyrosinate-to-iron(III) charge-transfer band are individually mimicked by the substituted bidentate phenolate ligands, demonstrating the utility of using ligands isostructural with amino acid residues. The quite negative redox potential of diferric transferrin precludes simple noncooperative reduction via endogenous reducing agents in vivo. The irreversible electrochemical reduction of the model complexes at quite negative potentials is related to the intrinsic stability of these iron(III) complexes with this given set of ligands and reiterates the stability of the iron(III) atom in the lactoferrin active site.

Acknowledgment. We thank Drexel University for support.

Supplementary Material Available: Listings of anisotropic thermal parameters, additional bond angles, and least-squares planes (9 pages); a table of observed and calculated structure factors (17 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry, Carnegie Mellon University,
4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213

Chromium(V)-Oxo Complexes of Macrocyclic Tetraamido-*N* Ligands Tailored for Highly Oxidized Middle Transition Metal Complexes: A New ^{18}O-Labeling Reagent and a Structure with Four Nonplanar Amides

Terrence J. Collins,*[1a] Carla Slebodnick, and Erich S. Uffelman[1b]

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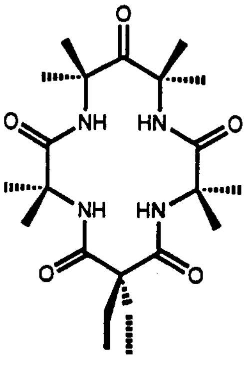
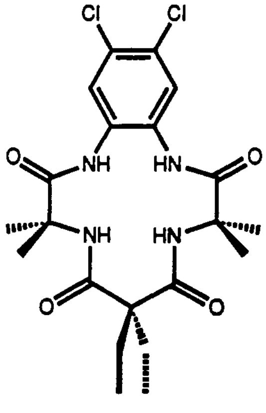
Two chromium(V)-oxo complexes, $[(CH_3)_4N][Cr(O)(\eta^4\text{-}\mathbf{1})]$ and $[(CH_3)_4N][Cr(O)(\eta^4\text{-}\mathbf{2})]$, have been synthesized and characterized by X-ray crystallography and IR and EPR spectroscopies. Because exchange of the oxo ligand with water is slow, the easily synthesized, stable, crystalline ^{18}O-labeled diperoxide $(CH_3)_2(H^{18}O^{18}O)CCH_2CH_2C(^{18}O^{18}OH)(CH_3)_2$ was prepared and used to conveniently synthesize ^{18}O-labeled oxo complexes in high yields. The bonding of the two unique oxidation-resistant macrocyclic tetraamides to chromium is compared. The structural and EPR properties are consistent with a chromium-centered radical in each case and suggest that a chromium(V) oxidation state assignment is equally appropriate whether the ancillary ligand is the innocent $[\eta^4\text{-}\mathbf{1}]^{4-}$ or the potentially noninnocent $[\eta^4\text{-}\mathbf{2}]^{4-}$. Both oxo complexes contain nonplanar amide groups. The distortions in $[Cr(O)(\eta^4\text{-}\mathbf{1})]^-$ are more marked, and it is a unique species in containing four distinctly nonplanar amides. The discovery of these unusual structural parameters expands the class of nonplanar amides arising from ring constraint.

Introduction

The scarcity of highly oxidized middle and later transition metal complexes[2] challenges chemists to develop ligand complements compatible with oxidizing metal centers. An objective of our program in this area[3a] is to understand how the structural and electronic properties of specifically designed ancillary ligand complements affect the properties of new metal-oxo species. One aspect of this interrelationship arises when one wishes to contribute new species to the very small class of highly oxidized middle and later first row transition metal complexes. In such cases it is important to consider the possibility of ligand noninnocence, the ability of a ligand to become part or all of the redox-active site of the complex. Here we describe two unique macrocyclic tetraamido-*N* ligands, the innocent H_4-**1** and potentially noninnocent H_4-**2**,[3b] where the dichlorophenylenediamide unit is a possible site of oxidation in highly oxidized complexes. We have examined these ligands, which are remarkably resistant to oxidative decomposition, by comparing the chromium(V)-oxo complexes. Although there are significant differences in the structures of the two ligands, the relevant structural properties and the EPR spectra of the five-coordinate monoanionic chromium(V)-oxo complexes indicate that the assignment of the +V oxidation state to the chromium center is equally appropriate in both cases. In addition,



H_4-1



H_4-2

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[1] (a) Dreyfus Teacher-Scholar, 1986-1990; Alfred P. Sloan Research Fellow, 1986-1989. (b) California Institute of Technology. Current address: Department of Chemistry, Carnegie Mellon University.

[2] For comprehensive discussions, see: (a) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley-Interscience: New York, 1988. (b) Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401-1449. (c) Sheldon, R. A.; Kochi, J. K. *Metal Catalyzed Oxidations of Organic Compounds*; Academic Press: New York, 1981. For a review of chromium(V) coordination chemistry see: (d) Mitewa, M.; Bontchev, P. R. *Coord. Chem. Rev.* **1985**, *61*, 241-272.

[3] (a) For initial reference, see: Anson, F. C.; Christie, J. A.; Collins, T. J.; Coots, R. J.; Furutani, J. J.; Gipson, S. L.; Keech, J. T.; Krafft, T. E.; Santarsiero, B. D.; Spies, G. H. *J. Am. Chem. Soc.* **1984**, *106*, 4460-4472. (b) For a discussion of the terms "innocent" and "noninnocent", see: Anson, F. C.; Collins, T. J.; Richmond, T. G.; Santarsiero, B. D.; Toth, J. E.; Treco, B. G. R. T. *J. Am. Chem. Soc.* **1987**, *109*, 2974-2979.

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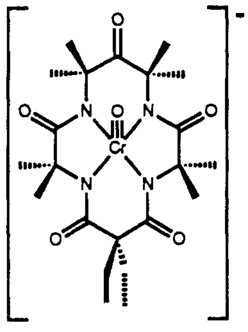
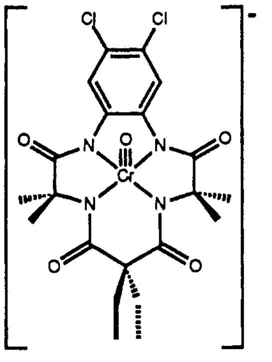
both complexes are structurally significant in containing distinctly nonplanar amide groups. The anion $[Cr(O)(\eta^4\text{-}\mathbf{1})]^-$ is an unprecedented case with four such groups. We also describe here the first use of a new ^{18}O-labeling reagent for synthesizing oxo complexes that either are not water stable or do not readily exchange their oxo ligand with water.



$[Cr(O)(\eta^4\text{-}1)]^-$



$[Cr(O)(\eta^4\text{-}2)]^-$

Experimental Section

Materials. All solvents and reagents were reagent grade (Aldrich) except for THF (Aldrich, Sureseal), $CrCl_2$ (Alfa), and $^{18}O_2$ (EG & G Mound Applied Technologies) and were used as received.

Physical Measurements. ^1H and ^{13}C NMR spectra were recorded at 300 and 75.45 MHz, respectively, on an IBM NR/300 FT-NMR spectrometer. ^1H and ^{13}C NMR data are reported in δ vs $(CH_3)_4Si$ with the solvent $CDCl_3$ as the internal standard. EPR spectra were recorded on a Bruker ER300 spectrometer. Infrared data were obtained on a Nicolet 5DXB FT-IR spectrometer. Crystal structures were solved by Crystalytics Co., Lincoln, NE.

Synthesis of $[(CH_3)_4N][Cr(O)(\eta^4\text{-}2)]$ and $[Ph_4P][Cr(O)(\eta^4\text{-}2)]$. H_4-**2** (0.114 g) was dissolved in dry, deoxygenated THF (18 mL), and *tert*-butyllithium in pentane (0.62 mL, 1.7 M solution) was added to the frozen solution under nitrogen. Anhydrous $CrCl_2$ (0.050 g) was added under nitrogen just before the THF finished thawing (−108 °C). As the suspension warmed to room temperature, a bright yellow precipitate (presumably a Cr(II) complex) collected on the flask walls. After the contents were stirred at room temperature (30 min), *tert*-butyl hydroperoxide (0.70 mL, 3.0 M in 2,2,4-trimethylpentane) was added. A dark brown solution developed rapidly with concomitant disappearance of the yellow precipitate. $Li[Cr(O)(\eta^4\text{-}\mathbf{2})]$ was obtained in 75% isolated yield. Analytically pure $[Ph_4P][Cr(O)(\eta^4\text{-}\mathbf{2})]$ was obtained (0.082 g, 38.8% yield from starting ligand) by dissolving the Li^+ salt in water, adding aqueous $[Ph_4P]Cl$, isolating the precipitate, and washing the precipitate with ether and pentane. Anal. Calcd for $[Ph_4P][Cr(O)(\eta^4\text{-}\mathbf{2})]$: C, 61.78; H, 5.03; N, 6.41; P, 3.54. Found: C, 61.84; H, 5.09; N, 6.39; P, 3.47. Electronic spectrum of $[Ph_4P][Cr(O)(\eta^4\text{-}\mathbf{2})]$ (CH_3CN; values in parentheses are molar absorptivities in $M^{-1}\,cm^{-1}$): 316 (9.9×10^3), 356 (5.6×10^3), ≈512 nm (shoulder) ($\approx 8.6 \times 10^2$). In a similar preparation, the $[(CH_3)_4N]^+$ salt was obtained by adding excess aqueous $[(CH_3)_4N][Cl]$ to aqueous $Li[Cr(O)(\eta^4\text{-}\mathbf{2})]$. The water was removed in vacuo, and a CH_3CN/CH_2Cl_2 solution of the residue was treated with pentane to precipitate the LiCl and excess $[(CH_3)_4N][Cl]$. Large brown parallelepipeds, characterized by X-ray analysis (Figure 1), were obtained by evaporation from CH_3CN.

Synthesis of $[(CH_3)_4N][Cr(O)(\eta^4\text{-}1)]$ and $[Et_4N][Cr(O)(\eta^4\text{-}1)]$. These analogues were prepared in a similar fashion by metathesizing aqueous $Li[Cr(O)(\eta^4\text{-}\mathbf{1})]$ with aqueous $[(CH_3)_4N][Cl]$ and $[Et_4N][F]$, respectively, and X-ray-quality crystals of $[(CH_3)_4N][Cr(O)(\eta^4\text{-}\mathbf{1})]$ were obtained by diffusion of pentane into an acetonitrile/dichloroethane solution (Figure 2). Electronic spectrum of $[Et_4N][Cr(O)(\eta^4\text{-}\mathbf{1})]$ (CH_3CN; values in parentheses are molar absorptivities in $M^{-1}\,cm^{-1}$): 316 (8.8×10^3), 460 (3.2×10^3), ≈550 nm (shoulder) ($\approx 1.9 \times 10^3$).

Synthesis of $(CH_3)_2(H^{18}O^{18}O)CCH_2CH_2C(^{18}O^{18}OH)(CH_3)_2$. The synthesis of $(CH_3)_2(HOO)CCH_2CH_2C(OOH)(CH_3)_2$ was first reported in 1951.[4] The title compound was produced by using a method adapted from Rust's synthesis of the unlabeled material.[5] 2,4-Dimethylhexane (8.7 mL) was added to a glass bomb (123 mL), and the system was subjected to three freeze/pump/thaw/degas cycles. $^{18}O_2$ gas (96.9% ^{18}O, 0.5% ^{17}O, 2.6% ^{16}O) was added to the evacuated bomb to bring the total pressure to 27–29 psi (25 °C). The sealed bomb was placed in a silicone oil bath and heated (116–120 °C, 17 h). After the bomb had cooled to room temperature, air was admitted at ambient pressure (the pressure inside had dropped below room pressure). Upon standing, the reaction mixture separated into two phases—the lower phase being oily product and the upper phase being primarily unreacted hydrocarbon. (It is essential to run the reaction at low hydrocarbon conversion in order to obtain satisfactory yields of dihydroperoxide.) The contents of the bomb were washed into a flask with CH_2Cl_2 and CH_3CN, and the solvents were removed under reduced pressure. The waxy solid residue was washed twice with a CH_2Cl_2 (5 mL)/pentane (15 mL) mixture and then washed twice with pentane (10 mL). The resulting white powder was dried under reduced pressure, giving analytically pure material (0.309 g). This peroxide has shown no decomposition after months of storage at room

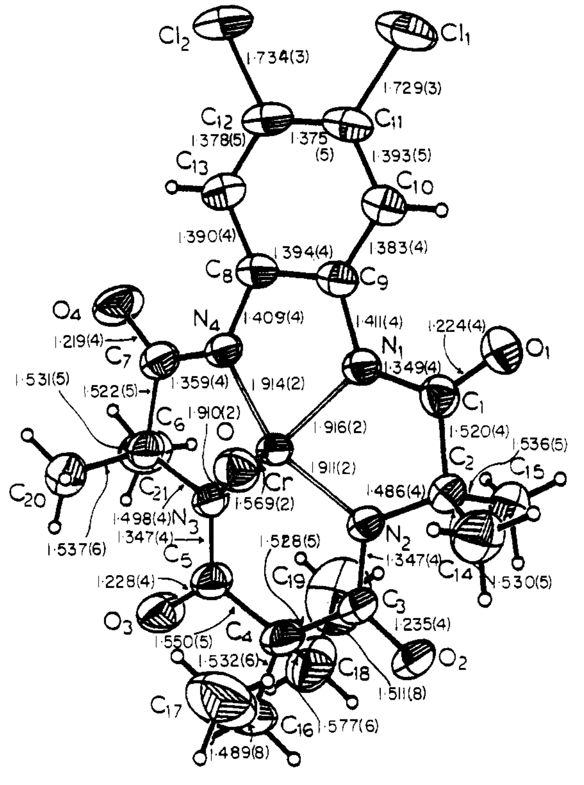


Figure 1. Molecular structure of $[Cr(\eta^4\text{-}\mathbf{2})]^-$. ORTEP drawing with all non-hydrogen atoms drawn to encompass 50% of electron density.

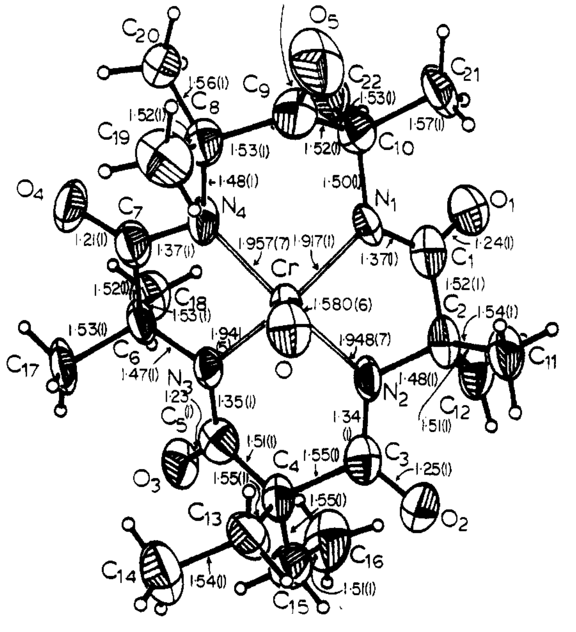


Figure 2. Molecular structure of $[Cr(\eta^4\text{-}\mathbf{1})]^-$. ORTEP drawing with all non-hydrogen atoms drawn to encompass 50% of electron density.

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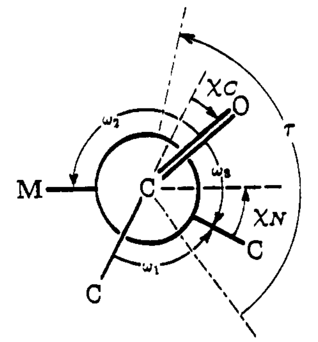

Figure 3. Dunitz amide nonplanarity parameters.

temperature. Anal. Calcd for $C_8H_{18}{}^{96.9\%\ 18,\ 0.5\%\ 17}O_4$: C, 51.66; H, 9.75. Found: 51.80; H, 9.64. ^{1}H NMR ($CDCl_3$) (ppm): 8.09 (s, 2 H, OOH), 1.65 (s, 4 H, $-CH_2-$), 1.20 (s, 12 H, $-CH_3$). ^{13}C NMR (broad-band decoupled, $CDCl_3$) (ppm): 82.5 (COOH), 31.0 ($-CH_2-$), 24.2, ($-CH_3$).

X-ray Data Collection and Structure Refinement of [$(CH_3)_4N$][Cr(O)(η^4-1)] and [$(CH_3)_4N$][Cr(O)(η^4-2)]. Crystal Data. Single crystals of [$(CH_3)_4N$][Cr(O)(η^4-**1**)] at 20 ± 1 °C are orthorhombic, space group $P2_12_12_1$-D_2^4 (No. 19), with a = 9.210 (3) Å, b = 16.352 (4) Å, c = 19.957 (5) Å, V = 3005 (2) Å^3, and Z = 4 formula units (d_{calcd} = 1.240 g cm^{-3}; μ_a(Cu K$\bar{\alpha}$) = 3.5 mm^{-1}). A total of 2557 independent absorption-corrected reflections having 2θ(Cu K$\bar{\alpha}$) < 120.0° (the equivalent of 0.65 limiting Cu K$\bar{\alpha}$ spheres) were collected on a computer-controlled Nicolet autodiffractometer using θ–2θ scans and Ni-filtered Cu K$\bar{\alpha}$ radiation. Single crystals of [$(CH_3)_4N$][Cr(O)(η^4-**2**)] at 20 ± 1 °C are monoclinic, space group $P2_1/C$-C_{2h}^5 (No. 14), with a = 12.414 (2) Å, b = 7.878 (1) Å, c = 30.673 (5) Å, β = 93.39 (1)°, V = 2994.6 (9) Å^3, and Z = 4 formula units (d_{calcd} = 1.352 g cm^{-3}; μ_a(Mo K$\bar{\alpha}$) = 0.59 mm^{-1}). A total of 5488 independent reflections having 2θ(Mo K$\bar{\alpha}$) < 50.7° (the equivalent of 0.80 limiting Cu K$\bar{\alpha}$ spheres) were collected on a computer-controlled Nicolet autodiffractometer using full (0.9° wide) ω scans and graphite-monochromated Mo K$\bar{\alpha}$ radiation. The structures were solved by using direct methods techniques with the Nicolet SHELXTL software package as modified at Crystalytics Co. The resulting structural parameters have been refined to convergence (R_1(unweighted, based on F) = 0.054 for 1634 independent reflections for [$(CH_3)_4N$][Cr(O)(η^4-**1**)] and R_1(unweighted, based on F) = 0.040 for 3700 independent reflections for [$(CH_3)_4N$][Cr(O)(η^4-**2**)]) by using counter-weighted cascade block-diagonal least-squares techniques and a structural model that incorporated anisotropic thermal parameters for non-hydrogen atoms and isotropic thermal parameters for all hydrogen atoms. The methyl groups were included in the refinement as idealized sp^3-rigid rotors. The remaining hydrogen atoms were fixed at idealized sp^2- or sp^3-hybridized positions with a C–H bond length of 0.96 Å. The Cr≡O unit of [$(CH_3)_4N$][Cr(O)(η^4-**2**)] is disordered in the lattice, being 95% "above" the macrocycle (Cr and O) and 5% below it (Cr′ and O′). Oxygen atom O′ was refined isotropically.

Results

The syntheses of the chromium(V)–oxo complexes proceed in good yields. Obtaining the ^{18}O-labeled oxo complexes was an important goal. Both oxo complexes are stable in water, and the [$N(CH_3)_4$]$^+$ salts show no decomposition after standing as solutions in water for many weeks. Exchange of the ^{16}O-oxo ligand with ^{18}O-labeled water is very slow under these conditions. The ^{18}O-oxo labeled complexes can be conveniently synthesized in high yields by employing the easily synthesized 2,5-bis(hydroper[$^{18}O_2$]oxy)-2,5-dimethylhexane, which can be isolated as an analytically pure crystalline solid and stored in the crystalline form for periods of many months at room temperature without observable decomposition. The $\nu_{Cr\equiv{}^{16}O}$ band of [$(CH_3)_4N$][Cr(O)(η^4-**2**)] at 982 cm^{-1} is found at 944 cm^{-1} in the ^{18}O-labeled analogue. The $\nu_{Cr\equiv{}^{16}O}$ stretch of [$(CH_3)_4N$][Cr(O)(η^4-**1**)] at 982 cm^{-1} is shifted by ^{18}O-labeling to 941 cm^{-1}.

Table I. Dunitz Amide Nonplanarity Parameters for Complex Anions

amide	angle	$\bar{\tau}$, deg	χ_N, deg	χ_C, deg
[Cr(O)(η^4-**1**)]$^-$	$N_1C_1O_1$	−17.35	−12.4	−3.5
[Cr(O)(η^4-**1**)]$^-$	$N_2C_3O_2$	28.45	24.0	0.6
[Cr(O)(η^4-**1**)]$^-$	$N_3C_5O_3$	16.0	10.9	5.7
[Cr(O)(η^4-**1**)]$^-$	$N_4C_7O_4$	−7.85	−25.0	0.7
[Cr(O)(η^4-**2**)]$^-$	$N_1C_1O_1$	−9.21	−3.14	0.76
[Cr(O)(η^4-**2**)]$^-$	$N_2C_3O_2$	−12.79	−16.74	−2.32
[Cr(O)(η^4-**2**)]$^-$	$N_3C_5O_3$	14.39	19.54	3.90
[Cr(O)(η^4-**2**)]$^-$	$N_4C_7O_4$	9.51	3.15	−0.86
[Co(η^4-**1**)]$^-$	$N_1C_1O_1$	4.65	16.17	2.49
[Co(η^4-**1**)]$^-$	$N_2C_3O_2$	9.96	11.61	0.87
[Co(η^4-**1**)]$^-$	$N_3C_5O_3$	6.68	5.46	5.91
[Co(η^4-**1**)]$^-$	$N_4C_7O_4$	−22.31	−23.82	−0.60
[Mn(O)(η^4-**2**)]$^-$	$N_1C_1O_1$	−6.42	−2.69	0.50
[Mn(O)(η^4-**2**)]$^-$	$N_2C_3O_2$	−16.97	−23.27	−2.49
[Mn(O)(η^4-**2**)]$^-$	$N_3C_5O_3$	10.46	16.77	1.61
[Mn(O)(η^4-**2**)]$^-$	$N_4C_7O_4$	10.68	0.90	0.56

Noteworthy structural features include the following: (i) For [$(CH_3)_4N$][Cr(O)(η^4-**2**)] and [$(CH_3)_4N$][Cr(O)(η^4-**1**)], the Cr≡O bond lengths are 1.569 (2) and 1.580 (6) Å, respectively, typical for the chromium(V)–oxo triple bond.[6] (ii) For [$(CH_3)_4N$][Cr(O)(η^4-**2**)], the four nitrogens lie in a plane (largest deviation 0.0006 Å) with the chromium located 0.60 Å above the mean plane, nearly equidistant from all four nitrogens. The entire chelate system remains virtually planar. For [$(CH_3)_4N$][Cr(O)(η^4-**1**)], the four nitrogens alternate 0.12 Å above and below their mean plane, and the chromium sits 0.58 Å above the mean plane. (iii) A remarkable feature of the structures of these chromyl complexes is the strong distortions found for the amido-*N* ligands (Table I, Figure 3). The distortions are more pronounced for [$(CH_3)_4N$][Cr(O)(η^4-**1**)] than for [$(CH_3)_4N$][Cr(O)(η^4-**2**)]. There are two other structures of complexes of the tetraamide macrocycles, [$(CH_3)_4N$][Co(η^4-**1**)][7a] and [$(CH_3CH_2)_4N$][Mn(O)(η^4-**2**)],[7b] and the Dunitz amide nonplanarity parameters[8] for these species are also included in Table I. For the metal–oxo complexes, the amido-*N* nonplanarity arises from ring strain

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(6) For structurally characterized Cr(V) oxo complexes produced from molecular oxygen, see parts a and b; for the other structurally characterized Cr(IV), Cr(V), and Cr(VI) oxo complexes see parts c–m: (a) Morse, D. B.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1988**, *110*, 8234–8235. (b) Herberhold, M.; Kremnitz, W.; Razavi, A.; Schöllhorn, H.; Thewalt, U. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 601–602. (c) Gahan, B.; Garner, D. C.; Hill, L. H.; Mabbs, F. E.; Hargrave, K. D.; McPhail, A. T. *J. Chem. Soc., Dalton Trans.* **1977**, 1726–1729. (d) Palmer, K. J. *J. Am. Chem. Soc.* **1938**, *60*, 2360–2369. Stomberg, R. *Arkiv. Kemi* **1963**, *22*, 29–47. (e) Stomberg, R.; Ainalem, I.-B. *Acta Chem. Scand.* **1968**, *22*, 1439–1451. (f) Stomberg, R. *Arkiv. Kemi* **1965**, *24*, 111–131. (g) Krumpolc, M.; Deboer, B. G., Roček, J. *J. Am. Chem. Soc.* **1978**, *100*, 145–153. (h) Srinivasan, K.; Kochi, J. K. *Inorg. Chem.* **1985**, *24*, 4671–4679. (i) Groves, J. T.; Kruper, W. J., Jr.; Haushalter, R. C.; Butler, W. M. *Inorg. Chem.* **1982**, *21*, 1363–1368. (j) Budge, J. R.; Gatehouse, B. M. K.; Nesbit, M. C.; West, B. O. *J. Chem. Soc., Chem. Commun.* **1981**, 370–371. (k) McGinnety, J. A. *Acta Crystallogr., Sect. B* **1972**, *B28*, 2845–2852. (l) Amirthalingam, V.; Grant, D. F.; Senol, A. *Acta Crystallogr., Sect. B* **1972**, *B28*, 1340–1345. (m) Stensland, B.; Kierkegaard, P. *Acta Chem. Scand.* **1970**, *24*, 211–220.

(7) (a) Collins, T. J.; Uffelman, E. S. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1509–1511. (b) Collins, T. J.; Powell, R. D.; Slebodnick, C.; Uffelman, E. S. *J. Am. Chem. Soc.* **1990**, *112*, 899–901. The other two classes are (i) cases where nonplanar amido-*N* ligands are thermodynamically favored over planar analogues accessible by isomerization at the metal center and (ii) a case where steric effects can be identified as the principal cause of nonplanarity. (c) Collins, T. J.; Coots, R. J.; Furutani, T. T.; Keech, J. T.; Peake, G. T.; Santarsiero, B. D. *J. Am. Chem. Soc.* **1986**, *108*, 5333–5339 and references therein. (d) Anson, F. C.; Collins, T. J.; Gipson, S. L.; Keech, J. T.; Krafft, T. E.; Peake, G. T. *J. Am. Chem. Soc.* **1986**, *108*, 6593–6605. (e) Collins, T. J.; Lai, T.; Peake, G. T. *Inorg. Chem.* **1987**, *26*, 1674–1677. (f) Collins, T. J.; Workman, J. M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 912–914. (g) Barner, C. J.; Collins, T. J.; Mapes, B. E.; Santarsiero, B. D. *Inorg. Chem.* **1986**, *25*, 4322–4323.

(8) (a) Dunitz, J. D.; Winkler, F. K. *J. Mol. Biol.* **1971**, *59*, 169–182. (b) Dunitz, J. D.; Winkler, F. K. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1975**, *B31*, 251–263. (c) Warshel, A.; Levitt, M.; Lifson, S. *J. Mol. Spectrosc.* **1970**, *33*, 84–99. (d) The twist angle τ and the pyramidalization terms χ_C and χ_N obtained from the primary torsion angle data ω_1, ω_2, and ω_3 as follows: $\tau = (\omega_1 + \omega_2)/2$; $\chi_N = (\omega_2 - \omega_3 + \pi) \bmod (2\pi)$; $\chi_C = (\omega_1 - \omega_3 + \pi) \bmod (2\pi)$. Here we use the modified twist angle, $\bar{\tau}$:$\bar{\tau} = \tau \bmod \pi$.[7c] $\bar{\tau}$ maximizes at ±90° and can be interpreted as the angle between the idealized positions of the pπ orbitals on C and N. The pyramidalization terms maximize at ±60°.

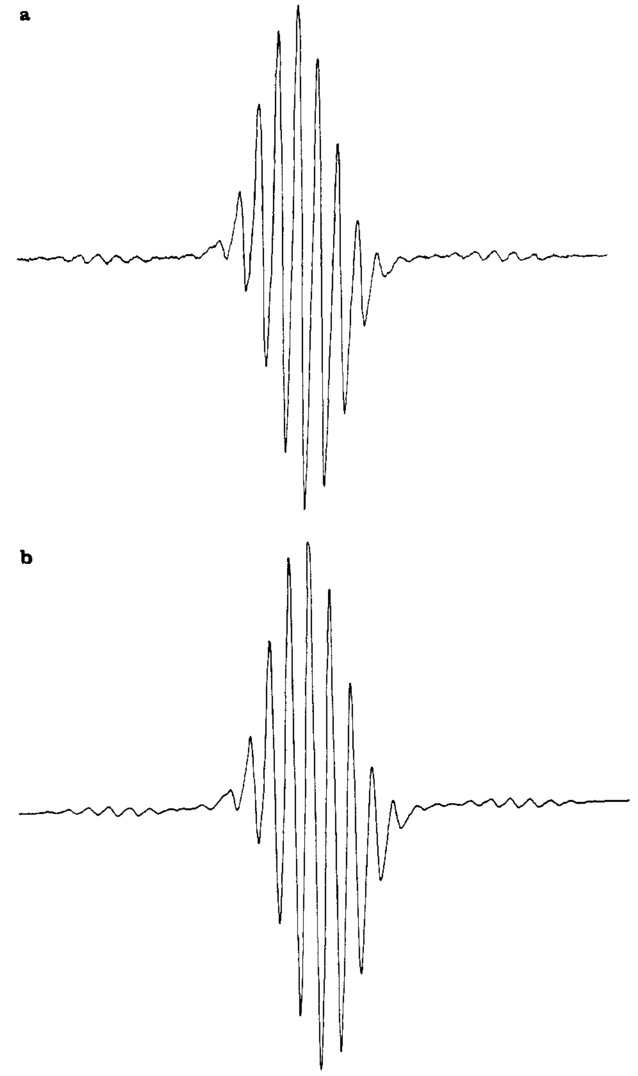

Figure 4. (a) EPR spectrum of $[Cr(\eta^4\text{-}\mathbf{1})]^-$ at 294 K, 9.34 GHz, in CH_3CN. (b) EPR spectrum of $[Cr(\eta^4\text{-}\mathbf{2})]^-$ at 292 K, 9.34 GHz, in CH_3CN.

induced by the inability of the macrocyles to accommodate the square-pyramidal structures without significant amide distortion. For the square-planar geometry, CPK models of $[\eta^4\text{-}\mathbf{1}]^{4-}$ indicate that this configuration may demand amide nonplanarity, and this is indeed found in $[(CH_3)_4N][Co(\eta^4\text{-}\mathbf{1})]$. However, CPK models of $[\eta^4\text{-}\mathbf{2}]^{4-}$ indicate that the square-planar geometry may be accessible without inducing significant ring strain—several structures are in progress that will elucidate this point. These results enrich the class of ring-constrained nonplanar amido-*N* ligands, one of the three known classes.[3a,7]

Discussion

The formal oxidation state of +V can be assigned to the chromium center in $[(CH_3)_4N][Cr(O)(\eta^4\text{-}\mathbf{1})]$ since $[\eta^4\text{-}\mathbf{1}]^{4-}$ is technically an innocent ligand.[3b] In $[(CH_3)_4N][Cr(O)(\eta^4\text{-}\mathbf{2})]$, other resonance structures in which electrons are transferred from the ring to the metal with a reduction of the formal oxidation state at the metal center are possible contributors to an accurate resonance hybrid. However, the degree to which the $[\eta^4\text{-}\mathbf{2}]^{4-}$ ligand is noninnocent in $[Cr(O)(\eta^4\text{-}\mathbf{2})]^-$ can be evaluated by EPR analysis. A number of Cr(V)–oxo and related complexes have been studied by this technique.[2d,9] The EPR spectrum of $[(CH_3)_4N][Cr(O)(\eta^4\text{-}\mathbf{1})]$ (Figure 4a), when compared with that for $[(CH_3)_4N][Cr(O)(\eta^4\text{-}\mathbf{2})]$ (Figure 4b), supports the contention that a formal oxidation-state assignment of +V for the chromium center is equally appropriate for both complexes. The EPR spectrum for $[(CH_3)_4N][Cr(O)(\eta^4\text{-}\mathbf{2})]$ can be interpreted as follows. The 90.45% of Cr nuclei having $I = 0$ give rise to a strong nine-line first-derivative signal at $g = 2.006$ through superhyperfine interactions with four spectroscopically equivalent nitrogen donors ($a_0 = 2.7$ G) ($2nI + 1 = 2 \times 4 \times 1 + 1 = 9$, $I = 1$ for ^{14}N and $n = 4$). In addition, a hyperfine interaction with the ^{53}Cr ($I = {}^3/_2$, 9.54%) of $A_0 = 17.9$ G gives rise to a weaker four-line feature, each component of which shows the nitrogen superhyperfine interactions. The EPR spectrum of $[(CH_3)_4N][Cr(O)(\eta^4\text{-}\mathbf{1})]$ is virtually identical. The hyperfine interaction with the ^{53}Cr is $A_0 = 17.8$ G ($g = 1.999$), and all four nitrogen donors are spectroscopically equivalent ($a_0 = 2.6$ G). These data are consistent with a chromium(V)-centered radical for both complexes.

The macrocyclic tetraamido-*N* ligand class used here is unique. In spite of the large literature of macrocyclic polyamines and Schiff bases, only one example of a complex of a macrocylic tetraamido-*N* ligand, a cyclic tetrapeptide, had been reported prior to our work.[10,11] In this classic study of copper(III) chemistry by Margerum et al.,[10] the macrocycle was shown to undergo a slow oxidation accompanied by reduction of the metal. The ligand degradation process involved β-hydrogen atoms (β to the metal). The tetraamide macrocycles described here do not possess β-hydrogens and are proving to be very resistant to oxidative decomposition, making an expanded range of middle metal–oxo and related species accessible. In addition to the chromium complexes reported here, a water-stable manganese(V)–oxo complex has been isolated and structurally characterized,[7b] as have a cobalt complex with a formal reduction potential of 1.25 V[12] (vs NHE or 0.550 V vs Fc^+/Fc) and a square-planar nickel(III) complex.[13] We are currently studying the reactions and physical properties of the oxo complexes and the broader chemistry of other complexes of the tetraamide ligands.

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Supplementary Material Available: Tables of data collection information, anisotropic thermal parameters for non-hydrogen atoms, atom coordinates for hydrogen atoms, bond lengths and angles, nonbonded distances, and torsion angles (53 pages); a listing of structure factor amplitudes (24 pages). Ordering information is given on any current masthead page.

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