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The First Sideways-Bonded Peroxo Complex for a Tetraaminecobalt(III) Species

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Cobalt(II) salts react with H_2O_2 in the presence of 2 equiv of tetramethylethylenediamine (tmen) to produce a stable sideways bonded mononuclear peroxo complex $[Co(tmen)_2O_2]ClO_4$ which has been characterized chemically and by a single crystal X-ray determination. This is the first such tetraaminecobalt(III) complex, indeed, the first for any tetraaminemetal ion complex. The mononuclear peroxo complex can also be synthesized by O_2^{2-} anation of *cis*-$[Co(tmen)_2(OH_2)_2]^{3+}$. This reaction is reversed in acid, and this offers the potential to develop Co(III) catalyzed oxidation reactions.

Air is usually a good enough oxidant to raise cobalt(II) salts, in the presence of amines under neutral to slightly basic conditions, up to the cobalt(III) state.[1,2] The immediate product is commonly the characteristic brown, bridging peroxo complex containing the entity $[(amine)_5Co(III)-O_2^{2-}-Co(III)(amine)_5]^{4+}$ or $[X(amine)_4Co(III)-O_2^{2-}-Co(III)(amine)_4X]^{m+}$ ($X = Cl^-$ or OH_2). Such a reaction occurs with $CoCl_2$ and ethylenediamine, for example, and the intermediate brown $[Cl(en)_2CoO_2Co(en)_2Cl]Cl_2$ complex is decomposed by HCl to yield the well-known *trans*-$[Co(en)_2Cl_2]Cl$ complex and H_2O_2.

Pure O_2 and H_2O_2 are sometimes used as oxidants when the $(amine)_nCo(III)/Co(II)$ potential is too high, or Co(III) starting materials such as $Na_3[Co(OCO_2)_3]$ or *trans*-$[Co(py)_4Cl_2]Cl$ are employed to make Co(III) complexes.[1,2] $[Co(tmen)_2Cl_2]Cl$ is prepared by the latter routes, because O_2 does not oxidize Co(II) plus tmen.[3,4] However, H_2O_2 does react with Co(II)/tmen, but curiously, the usual peroxo bridging dinuclear species is not formed. Rather, with use of the ClO_4^- salt, red-brown crystals of composition $[Co(tmen)_2O_2]ClO_4 \cdot 2H_2O$ are produced in good yield.[5] The same complex was derived (quantitatively) by treating *cis*-$[Co(tmen)_2(OH_2)_2]^{3+}$ with H_2O_2.[5]

The single crystal X-ray structure (Figure 1) revealed the mononuclear sideways bonded peroxo complex.[6] The prominent structural features are the small bite angles for the tmen five-membered rings, 83.2°, a feature of tmen complexes which is becoming the norm, the O−O bond length (1.457 Å) which is typical for a sideways bonded peroxide, and the distortion from octahedral geometry arising from the triangular CoO_2 moiety with a small bite angle of 45.7°. The geometry of the complex could also be described as distorted trigonal bypyramidal, if the center of the chelating peroxo ligand is regarded as a monodentate entity (trigonal plane bond angles 131°, 131°, and 98°). The complex nonetheless has the spectroscopic properties of a diamagnetic, octahedral cobalt(III) complex. Despite having two tmen ligands in cis positions, there is none of the strain apparent in the tris complex, $[Co(tmen)_3]^{3+}$, manifested in elongated C(tert)−C(tert) and Co−N bonds, and pronounced trigonal twisting.[4]

Ancilliary ligands such as phosphines or arsines were required for Co(III) to bind O_2^{2-} as a three-membered ring

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(5) The diaqua complexes *cis*-$[Co(tmen)_2(OH_2)_2]NO_3(ClO_4)_2$ and *cis*-$[Co(tmen)_2(OH_2)_2](ClO_4)_3$ were prepared as described elsewhere (ref 3). Addition of a fifth volume of 32% H_2O_2 (excess) to a saturated aqueous solution of the diaqua complex followed by a fifth volume of 5 M $NaClO_4$ yielded pink crystals of $[Co(tmen)_2O_2]ClO_4 \cdot 2H_2O$ essentially quantitatively. The same complex was obtained by addition of H_2O_2 (excess) to a solution of $Co(ClO_4)_2 \cdot 6H_2O$ in water containing tmen·$2HNO_3$ (2 equiv) and NaOH (2 equiv). The crystals were recrystallized twice from water by careful addition of 5 M $NaClO_4$. Yield: 65%. Anal. Calcd for $CoC_{12}H_{36}N_4ClO_8$: C, 31.4; H, 7.9; N, 12.2; Cl, 7.7. Found: C, 31.4; H, 8.0; N, 12.2; Cl, 7.8%.

(6) Crystal data: $[Co(tmen)_2O_2]ClO_4 \cdot 2H_2O$, $M = 458.82$, monoclinic, space group $C2/c$, dark red block crystal ($0.30 \times 0.20 \times 0.12$ mm^3), $a = 11.108(3)$ Å, $b = 18.6362(6)$ Å, $c = 10.4397(2)$ Å, $\beta = 105.488(2)$°, $V = 2082.69(10)$ Å^3, $Z = 4$, $D_c = 1.463$ Mg m^{-3}, $\mu = 0.996$ mm^{-1}, 295 K, 18449 reflections measured, 2397 independent, Nonius KappaCCD diffractometer, Mo Kα ($\lambda = 0.71070$ Å), $\omega-2\theta$ scans, θ_{max} 27.59°. The structure was solved by heavy-atom methods and refined by full-matrix least-squares procedures based on F. Non-H atoms were refined with anisotropic displacement parameters. H atoms were refined positionally. Refinement with 173 parameters converged at $R = 0.035$, $R_w = 0.041$ for 1888 reflections with $I > 3\sigma(I)$

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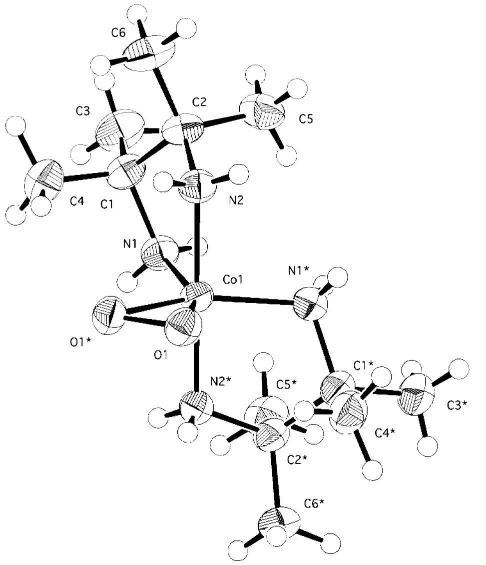

Figure 1. ORTEP diagram of $[Co(tmen)_2O_2]^+$ showing 30% thermal ellipsoids. Asterisks indicate atoms generated by crystallographic 2-fold symmetry. The Δ enantiomer is arbitrarily depicted. Principal bond lengths (Å) and angles (deg) are the following: O1−O1* 1.457(3), Co1−O1 1.875(2), Co1−N1 1.988(2), Co1−N2 1.956(2), C1−C2 1.551(3), O1−Co1−O1* 45.70(8), N2−Co1−N1 83.22(8), N1−Co1−N1* 97.4(1).

chelate.[7,8] A number of such complexes are known for a range of transition metal ions, but none previously involving a saturated ligand backbone such as a set of amines.[9] Johnson and Geldard[10] have described the synthesis and characterization (but no X-ray structure) of a mononuclear tetra-N-donor peroxocobalt(III) complex which spectroscopically seems to be an authentic side-on peroxo ion and which comes closest to ours, but the donors are unsaturated imines. Sideways bonded dioxygen is also known for the cobalt complexes of the facially capping tridentate N-donor ligands Tp^R (monoanionic substituted tris(pyrazoyl)hydridoborate), which have imine donors.

The complex has the stoichiometry $Co(TpR)O_2$ (uncharged); i.e., it is either a Co(III) peroxo or a Co(II) superoxo species The dioxygen is side-on rather than the usual bent structure for a d^7 M^{n+} complex, and there are a number of other unusual aspects of the chemistry of these complexes attributable to the special properties of these ligands.[11] The complex is paramagnetic, and while the Co(II)−superoxide description seems more appropriate, alternative views of the bonding and oxidation state descriptions have been presented more recently.[12]

The crystalline peroxo complex is stable indefinitely under ambient conditions, and despite the normal lability of tmen−Co(III) complexes,[3] the species remains intact in solution. However, it reacts completely with excess $HClO_4$ within 30 s to yield the *cis*-$[Co(tmen)_2(OH_2)_2]^{3+}$ complex, as shown by ^1H and ^{13}C NMR spectroscopy and using an authentic sample of the independently synthesized and known[3] cis-diaqua complex in deuterated media. On a larger scale, the liberated H_2O_2 was treated with excess I^- and the resultant I_2 titrated against $S_2O_3^{2-}$ to confirm 0.985 equiv of generated H_2O_2. Also, as demonstrated by NMR studies, reaction of the diaqua complex with excess H_2O_2 yielded >90% peroxo complex, together with a little protonated free ligand, established by adding an authentic specimen[3] to the NMR tube. The acid catalyzed release of H_2O_2 is not instantaneous, and a green complex can be rapidly crystallized by adding cold 70% $HClO_4$ to a saturated aqueous solution of the peroxo species. This species proved insufficiently stable to characterize. It reverted to the starting material on washing with alcohol and ether, and presumably, it was a protonated peroxo species. We have been unable to obtain crystals suitable for X-ray structural analysis to ascertain the detailed structure.

The peroxo complex reacts readily with SO_2 to afford a sulfato species. Normally, a chelated sulfato species would result, but the isolated material appears to be *trans*-$[Co(tmen)_2(OH_2)(OSO_3)]ClO_4$.[13] This is a reaction typical of side-on peroxo complexes[9] and attests to the structural characterization.

The vis−UV spectrum is typical for a $Co^{III}N_4O_2$ chromophore (ϵ_{max}(527 nm) 107, (ϵ_{max}(422 nm) 136 M^{-1} cm^{-1}; CH_3CN), despite the distortion from octahedral geometry evident from the crystal structure (Figure 1). Also, strong charge transfer absorptions are observed at 244 and 197 nm (H_2O), while a sharp O−O stretch is observed in the IR (KBr disk) at 861 cm^{-1}. For Me_2SO-d_6 as solvent, the ^{13}C NMR spectrum shows the expected two C(tert) (δ 62.1, 59.1 ppm) and four CH_3 resonances (δ 23.0, 23.8, 25.4, 26.3 ppm) characteristic of the C_2 symmetry for the *cis*-CoN_4X_2 species, while the ^1H NMR spectrum shows four NH doublets (5.41, 3.72, 3.25, 1.16 ppm) and four methyl singlets (1.33, 1.28, 0.97, 0.81 ppm). The NH resonances are unusually sharp compared to corresponding NH signals of unsubstituted ethylenediamine species, no doubt due to the absence of CH−NH coupling, and minimal quadrupolar ^{14}N broadening. The geminal NH coupling (J_{HH} ca. 5 Hz) has now become clear. One of the four NH doublets, likely to be one of the two axial NH protons, is at very high field (δ 1.16 ppm), indicating unusual shielding by virtue of its proximity over the center of the π system comprising the triangular CoO_2 moiety (Figure 2).

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[13] The pink-brown peroxo complex becomes purple on trituration as a thin paste in SO_2(aq) (6% w/v). It was recrystallized from water/$NaClO_4$. The tmen complexes are unusually labile, and the ^1H and ^{13}C NMR spectra were indicative of a species having the symmetry of the *trans*-$[Co(tmen)_2(OS(CD_3)_2)(OSO_3)]ClO_4$ complex in solution. In Me_2SO-d_6, this product slowly reverts to a purple complex having *cis*-$[Co(tmen)_2X_2]$ symmetry, likely containing chelated sulfate. Both species tested positive for SO_4^{2-} (Ba^{2+}). Trans complex data follow. ^1H NMR (Me_2SO-d_6): δ 5.19 d, 3.78 d, NH, 1.20, 1.10 s, CH_3. ^{13}C NMR (Me_2SO-d_6): δ 24.4, 24.0 (CH_3), 61.2 (tert C). Chelatedata follow. ^1H NMR: δ 6.43 d, 5.27 d, 4.49 d, 4.01 d, NH.; 1.30 s, 1.20 s, 1.10 s, 1.08 s, CH_3. ^{13}C NMR (Me_2SO-d_6): δ 26.1, 26.0, 23.7, 23.3 (CH_3), 65.7, 61.2 (tert C).

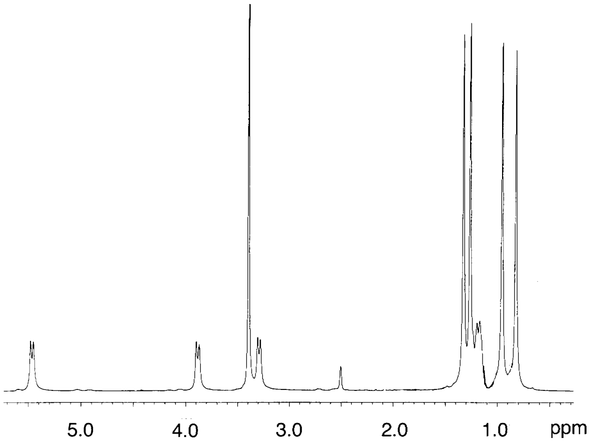

Figure 2. Proton NMR spectrum for $[Co(tmen)_2O_2]ClO_4 \cdot 2H_2O$ in Me_2SO-d_6. The central spike arises from lattice water.

The synthesis for the peroxocobalt(III) complex by two independent methods is novel, and the stoichiometry for these reactions appears to be

$$2Co(II)^{2+} + 3H_2O_2 \rightarrow 2Co(III){-}O_2^{+} + 2H_2O + 2H^{+}$$

$$Co(III){-}OH_2^{3+} + H_2O_2 \rightarrow Co(III){-}O_2^{+} + H_2O + 2H^{+}$$

The second reaction is reversible and clearly controlled by pH. If the Co(III) peroxo complex can be shown to be an effective oxidant, as has $[Co(CN)_5O_2H]^{3-}$ for example,[14] the system could well be constructed to be catalytic. The same may prove true for their arsine analogues[7,8] for which peroxide addition is also reversible. A particular advantage of the Co−tmen system is that the complexes are unusually labile (engendered by the tmen ligand), and that these amine ancillary ligands are not readily oxidized while the arsine (and phosphine) analogues are. Mirza et al. have detailed the conditions necessary for effective catalysis in these metal ion/H_2O_2 systems,[14] and on the basis of these criteria, there is clear potential for the present *cis*-$[Co(tmen)_2O_2]^{+}$ ion.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org. This material also available from the Cambridge Crystallographic Data Centre, CCDC 217508. [Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, U.K. (Fax: +44-1223-336033. E-mail: deposit@ccdc.cam.ac.uk or www: http//www.ccdc.cam.ac.uk.)]

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