The *cis*-Dioxomolybdenum(v) Radical Anion, $[\{HB(Me_2C_2N_3)_3\}MoO_2(SPh)]^-$

Zhiguang Xiao, Robert W. Gable, Anthony G. Wedd* and Charles G. Young*

School of Chemistry, University of Melbourne, Parkville, Victoria 3052, Australia

Reaction of $[CoCp_2]$ ($Cp^- = \eta^5$-cyclopentadienyl) with $[\{HB(Me_2tz)_3\}Mo^{VI}O_2(SPh)]$ [$HB(Me_2tz)_3^-$ = hydrotris(3,5-dimethyl-1,2,4-triazol-1-yl)borate] in toluene results in the formation of green, air-sensitive, paramagnetic crystals of $[CoCp_2][\{HB(Me_2tz)_3\}Mo^VO_2(SPh)]\cdot C_7H_8$, in which the structure of the Mo^V radical anion [Mo–O(1)/(2) 1.742(9) Å, O(1)–Mo–O(2) 112.1(4)°] differs significantly from that of the Mo^{VI} analogue [Mo–O(1) 1.702(4) Å, Mo–O(2) 1.698(3) Å, O(1)–Mo–O(2) 103.9(2)°].

EPR studies of monomeric *cis*-$[Mo^VOS]^+$, *cis*-$[Mo^VO(SH)]^{2+}$ and *cis*-$[Mo^VO(OH)]^{2+}$ complexes have provided evidence for the presence of such centres during turnover of xanthine oxidase and sulfite oxidase.[1–5] Complexes containing the *cis*-$[Mo^VO_2]^+$ centre have also been generated and characterised by EPR spectroscopy.[2–5] Recently, we reported the isolation of oxygen-sensitive $[CoCp_2][\{HB(Me_2pz)_3\}MoO_2(SPh)]$ [$HB(Me_2pz)_3^-$ = hydrotris(3,5-dimethylpyrazol-1-yl)borate anion] and EPR and IR evidence for the presence of a monomeric dioxo-Mo^V radical anion;[2] the growth of X-ray quality crystals was prevented by decomposition in solution. We report here the isolation and characterisation of $[CoCp_2][\{HB(Me_2tz)_3\}MoO_2(SPh)]\cdot C_7H_8$ **1** [$HB(Me_2tz)_3^-$ = hydrotris(3,5-dimethyl-1,2,4-triazol-1-yl)borate] and its X-ray crystal structure, the first reported for any d^1 *cis*-dioxo-Mo^V complex. While *cis*-$[MoO_2]^{n+}$ species are numerous for the d^0 configuration,[6] only two structurally characterised six-coordinate *cis*-$[MO_2]^{n+}$ complexes are known for d^n ($n > 0$), *viz.* $[Re^VO_2(py)_2(bipy)]^+$[7,8] and $[Os^{VI}O_2(MeCO_2)_3]^-$.[9]

The dioxo-Mo^{VI} complexes *cis*-$[LMoO_2(SPh)]$ [L = $HB(Me_2pz)_3^-$, $HB(Pr^ipz)_3^-$ = hydrotris(3-isopropylpyrazol-1-yl)borate or $HB(Me_2tz)_3^-$ **2**[†]] undergo reversible one-electron electrochemical reductions to generate dioxo-Mo^V anions; the same anions are formed upon cobaltocene reduction of the dioxo-Mo^{VI} complexes. Reaction of **2** [$E_{1/2}$(MeCN) = −0.52 V *vs.* SCE] with cobaltocene in toluene leads to the rapid precipitation of green, microcrystalline **1**.[†] The compound is extremely air-sensitive and reacts with oxygen to give the starting material **2** in high yield. The anion is also trapped by the electrophilic reagent Me_3SiCl as $[\{HB(Me_2tz)_3\}MoO(OSiMe_3)(SPh)]$.

Compound **1** was characterised by microanalysis and by electrochemical, EPR, IR and X-ray crystallographic studies. Cyclic voltammetry at glassy carbon in acetonitrile reveals three chemically reversible waves assignable to the **2**/**1** (−0.52 V), $[CoCp_2]^+/[CoCp_2]$ (−0.94 V) and $[CoCp_2]/[CoCp_2]^-$ (−1.88 V) couples. The room temperature EPR spectrum of **1** in dichloromethane exhibits a very broad signal with g = 1.922, $a(^{95,97}Mo) = 40.0 \times 10^{-4}\ cm^{-1}$, $W_{1/2}$ = 1.9 mT. At 77 K, the complex exhibits a highly anisotropic spectrum in frozen dichloromethane with $g_x = 1.995$, $g_y = 1.937$ and $g_z = 1.845$. The EPR spectra are uniquely characteristic of a dioxo-Mo^V anion; similar EPR properties were observed previously for electrogenerated complexes.[1–5] Complex **1** is stable in solution and does not undergo protonation by adventitious water. The IR spectrum of **1** exhibits bands typical of $[CoCp_2]^+$ and the tridentate N-donor and PhS^- ligands on molybdenum. As well, strong bands assignable to the $\nu_s(MoO_2)$ and $\nu_{as}(MoO_2)$ vibrations are observed at 877 and 777 cm^{-1}. These assignments have been confirmed by IR studies of ^{18}O-labelled $[CoCp_2][LMoO_2(SPh)]$ complexes.

The structures of **1** and **2** have been determined by X-ray crystallography.[‡] The structure of the $[\{HB(Me_2tz)_3\}Mo^VO_2(SPh)]^-$ anion in **1** is shown in Fig. 1; the structure of complex **2** is closely related to that of the anion in **1**. Both complexes contain a facially tridentate triazolylborate ligand and mutually *cis* oxo and benzenethiolate ligands. They both exhibit a distorted octahedral geometry; the principal distortions result from disparate Mo–O and Mo–N distances and associated angles. The Mo atoms are displaced from the mid-point of the equatorial plane defined by O(1), O(2), N(21) and N(31), towards the oxo ligands. The Mo–O(1) and Mo–O(2) bond distances in **1** [1.742(9) Å] are significantly longer than the corresponding bonds of **2** [1.700(6) Å] and the median distance of structurally characterised oxo-Mo complexes (1.694 Å).[10] Notably, the O(1)–Mo–O(2) angle in **1** [112.1(4)°] is increased considerably relative to that in **2** [103.9(2)°]. This is associated with an increase in the N(11)–Mo–S angle in **1** [168.9(4)°] relative to that in **2** [152.7(1)°] and a conspicuous canting of the triazole planes about the Mo···B vector in **1**. The modest increase in the Mo–O bond distance in **1** compared to **2** is consistent with a principally non-bonding metal-based HOMO containing the unpaired electron. The more obtuse O(1)–Mo–O(2) angle in **1** compared to **2** suggests

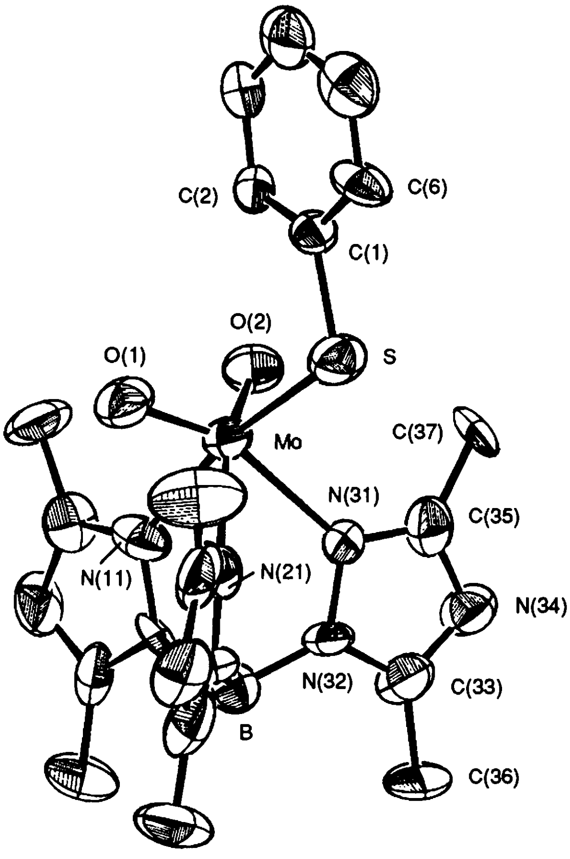

Fig. 1 Structure of the anion of **1**. The numbering of atoms in the rings containing N(11) and N(21) parallels that shown for the ring containing N(31). Selected bond lengths (Å): Mo–O(1) 1.742(9), Mo–O(2) 1.742(9), Mo–N(11) 2.277(11), Mo–N(21) 2.410(12), Mo–N(31) 2.334(10), Mo–S 2.442(4). Selected angles (°): O(1)–Mo–O(2) 112.1(4), O(1)–Mo–S 96.3(4), O(1)–Mo–N(11) 90.1(5), O(1)–Mo–N(21) 84.3(5), O(1)–Mo–N(31) 157.7(5), O(2)–Mo–S 95.5(4), O(2)–Mo–N(11) 90.4(5), O(2)–Mo–N(21) 161.6(5), O(2)–Mo–N(31) 87.5(5), S–Mo–N(11) 168.9(4), S–Mo–N(21) 90.7(4), S–Mo–N(31) 91.9(4), N(11)–Mo–N(21) 80.9(6), N(11)–Mo–N(31) 78.9(5), N(21)–Mo–N(31) 75.0(5).

some repulsion between the d^1 electron and the Mo=O π-electrons. With the exception of the Mo–N(31) bonds of **1** and **2**, the Mo–N distances of **1** are significantly longer than their counterparts in **2**. A noticeable *trans*-influence is associated with the terminal oxo ligands in both **1** and **2**. The Mo–S distance [2.442(4) Å] and Mo–S–C(1) angle [110.5(6)°] of **1** are slightly larger than those of **2** [2.398(2) Å and 105.6(2)°, respectively]. The orientation of the phenyl group in **1** [Mo–S–C(1)–C(2) torsion angle −12.9(3)°, *cf.* 63.5(5)° for **2**] appears to be dictated primarily by the position of the neighbouring $[CoCp_2]^+$ counterions. Each of the two Mo=O units of the anion is directed towards the Co atoms of separate $[CoCp_2]^+$ counterions.

The highly anisotropic EPR signals characteristic of these and other $[Mo^VO_2]^+$ centres have not been observed in any molybdenum-containing enzyme but the conjugate acid $[Mo^VO(OH)]^{2+}$ has been implicated in the turnover of sulfite oxidase and nitrate reductase.[1] While we have not observed the involvement of the dioxo–Mo^V complexes in any two-electron oxygen atom transfer reactions they are clearly susceptible to one-electron redox reactions and attack by electrophiles such as H^+[2] and $SiMe_3^+$.

The financial assistance of the Australian Research Council is gratefully acknowledged.

Received, 22nd December 1993; Com. 3/07520F

Footnotes

† *Syntheses.* $[\{HB(Me_2tz)_3\}MoO_2X]$, X = Br: dichloromethane (70 cm^3) was added to a mixture of $K\{HB(Me_2tz)_3\}$ (11.6 g, 34.2 mmol) and $[MoO_2Br_2(Me_2SO)_2]$ (15.0 g, 34.1 mmol) and the mixture stirred for one day. The yellow suspension was reduced in volume and the crude product isolated by filtration. The complex was purified by Soxhlet extraction using dichloromethane, yield 7.8 g, 45%.

X = SPh **2**: a solution of $[\{HB(Me_2tz)_3\}MoO_2Br]$ (1.0 g, 2.0 mmol) in dry, deoxygenated dichloromethane (20 cm^3) was treated (simultaneously) with triethylamine (1.0 cm^3, 7.0 mmol) and benzenethiol (0.42 cm^3, 4 mmol) and the mixture stirred for 2 h. The complex was isolated by column chromatography (silica–tetrahydrofuran, in air), yield 0.93 g, 88%. Crystals were grown by slow diffusion of *n*-hexane into a toluene solution of the compound.

1 A solution of $[CoCp_2]$ (0.09 g, 0.47 mmol) in dry deoxygenated toluene (5 cm^3) was added to a stirred solution of **2** (0.14 g, 0.26 mmol) in toluene (5 cm^3). The green precipitate was filtered off, washed with toluene and vacuum dried (yield, 0.17 g, 90%). Correct microanalyses were obtained. In a second reaction, single crystals of X-ray diffraction quality were obtained by dissolving the precipitated product by dropwise addition of a minimum of carefully dried (activated Al_2O_3) acetonitrile, followed by cooling at −20 °C for 3 days.

‡ *Crystal data* for **1**: $C_{35}H_{42}BCoMoN_9O_2S$, $M = 818.5$, orthorhombic, space group *Pbca* (No. 61), $a = 17.695(3)$, $b = 19.490(3)$, $c = 21.925(4)$ Å, $U = 7561.4$ Å^3, $F(000) = 3368$, $Z = 8$, $D_c = 1.438$ g cm^{-3}, $\mu(Mo\text{-}K\bar{\alpha}) = 8.35\ cm^{-1}$. At convergence, $R = 0.067$ and $R_w = 0.067$ for the 2269 observed reflections $[I \geqslant 2.5\ \sigma(I)]$.

Crystal data for **2**: $C_{18}H_{24}BMoN_9O_2S$, $M = 537.3$, orthorhombic, space group $P2_12_12_1$ (No. 19), $a = 7.9302(13)$, $b = 16.627(2)$, $c = 17.543(2)$ Å, $U = 2313.1$ Å^3, $F(000) = 1096$, $Z = 4$, $D_c = 1.543$ g cm^{-3}, $\mu(Mo\text{-}K\bar{\alpha}) = 6.53\ cm^{-1}$. At convergence, for the preferred absolute configuration, $R = 0.039$ and $R_w = 0.045$ for the 3681 observed reflections $[I \geqslant 2\ \sigma(I)]$.

Intensity data were collected using an Enraf-Nonius CAD-4MachS single-crystal X-ray diffractometer using the ω–2θ scan method; absorption corrections were applied. The structures were refined using full-matrix least squares (SHELX-76), with anisotropic thermal parameters applied to each of the non-hydrogen atoms. For **2** all the hydrogen atoms were observed in the difference map and were constrained at geometrical estimates; no hydrogen atoms were included in the model for **1**. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

References

1. J. H. Enemark and C. G. Young, *Adv. Inorg. Chem.*, 1993, **40**, 1; C. G. Young and A. G. Wedd, in *Molybdenum Enzymes, Cofactors and Models*, ed. E. I. Stiefel, D. Coucouvanis and W. E. Newton, *ACS Symp. Ser.*, 1993, **535**, 70.
2. Z. Xiao, C. G. Young, J. H. Enemark and A. G. Wedd, *J. Am. Chem. Soc.*, 1992, **114**, 9194.
3. R. J. Greenwood, G. J. Wilson, J. R. Pilbrow and A. G. Wedd, *J. Am. Chem. Soc.*, 1993, **115**, 5385.
4. G. L. Wilson, R. J. Greenwood, J. R. Pilbrow, J. T. Spence and A. G. Wedd, *J. Am. Chem. Soc.*, 1991, **113**, 6803.
5. D. Dowerah, J. T. Spence, R. Singh, A. G. Wedd, G. L. Wilson, F. Farchione, J. H. Enemark, J. G. Kristofzski and M. Bruck, *J. Am. Chem. Soc.*, 1987, **109**, 5655.
6. E. I. Stiefel, in *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, Oxford, 1987, ch. 36.5, p. 1375.
7. R. L. Blackburn, L. M. Jones, M. S. Ram, M. Sabat and J. T. Hupp, *Inorg. Chem.*, 1990, **29**, 1791.
8. M. S. Ram and J. T. Hupp, *Inorg. Chem.*, 1991, **30**, 130.
9. T. Behling, M. V. Caparelli, A. C. Skapski and G. Wilkinson, *Polyhedron*, 1982, **1**, 840.
10. A. G. Orpen, L. Brammer, F. H. Allen, O. Kennard, D. G. Watson and R. Taylor, *J. Chem. Soc., Dalton Trans.*, 1989, S1.