Molecular Structure and Electronic Properties of Oxomolybdenum(V) Catecholate Complexes

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Introduction

Sulfite oxidase, the enzyme involved in the physiologically vital oxidation of sulfite to sulfate,[1–4] possesses a pterin-containing molybdenum cofactor and a cytochrome b_5 type heme center in each identical subunit.[5,6] We have recently[7,8] synthesized bimetallic complexes that contain both oxo–molybdenum-(V) and iron(III) porphyrin centers as simple models for the interprosthetic group interaction in sulfite oxidase. The oxo–Mo(V) center is stabilized by the tridentate facially coordinating hydrotris(3,5-dimethyl-1-pyrazolyl)borate ligand (L)[9,10] and coordinated to a catecholate fragment which has been linked to a 10,15,20-tri-*p*-tolylporphyrin at the 5-meso carbon position. Such complexes show weak coupling between the two paramagnetic metal centers and perturbation of the Mo(V/IV) redox potential by the porphyrin moiety. In order to quantitate the effect of the substitutents on the catecholate ring on the spectral and redox properties of the LMoO(cat) center we have synthesized a series of mononuclear oxomolybdenum(V) catecholate complexes (Figure 1) and investigated their spectral and redox properties. The structure of a representative example, LMoO(catCl₄) (**2**), has been determined by X-ray crystallography. There have been several reports of mononuclear Mo-(VI) catecholate complexes,[11,12] but to our knowledge this is the first structure determination of a Mo(V) catecholate complex.

Experimental Section

Materials. Substituted catechols were purchased either from Sigma or Aldrich Chemical Co. and used as received. Solvents were purified as previously described.[10] Tetraethylammonium perchlorate was prepared by the literature method.[13]

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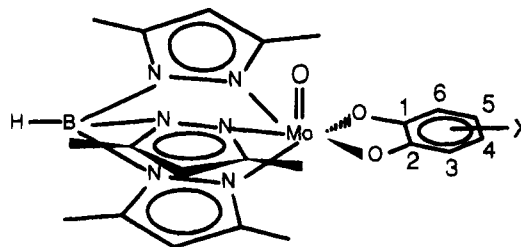
X = H	1
X = Cl₄	2
X = 3,5- tBu	3
X = 3- CHO	4
X = 4-CHO	5
X = 4-OH	6
X = 3-OH	7

Figure 1. LMoO(cat) compounds used in this study.

Physical Measurements. IR and UV–vis spectra were obtained by standard methods as described earlier.[10] Cyclic voltammetry was performed using a BAS CV-50W system with a normal three-electrode configuration.[14] Electron paramagnetic resonance (EPR) spectra were obtained with a Bruker ESP 300E spectrometer; the frequency was measured by a Systron Donner 6530 frequency counter.

Preparation of Compounds. Compounds **1**, **6** and **7** have been reported earlier.[10,15] All the compounds were prepared from (ethyleneglycolato)(hydrotris-(3,5-dimethyl-1-pyrazolyl)borato)oxomolybdenum(V)[10] (**8**) and the appropriate catechol in toluene at elevated temperature, purified by column chromatography, recrystallized from dichloromethane–hexane (1:1), and isolated in high yield (~80%). Representative examples gave satisfactory elemental analysis and all compounds gave low resolution mass spectra for the parent ion (Table SI).[16] Rectangular dark green crystals of **2** suitable for X-ray structure determination[17] were obtained by slow evaporation of an acetonitrile solution.

Results and Discussion

Crystal and Molecular Structure of 2. An ORTEP drawing and the atom labelling scheme for **2** are presented in Figure 2. Selected bond distances and angles appear in Table 1. The details of the structure determination and complete atomic parameters appear in the supplementary material. The molecule exhibits distorted octahedral geometry. The tridentate tris-(pyrazolylborate) ligand occupies one face of the distorted octahedron; the terminal oxo group and the two oxygens of the catechol ring occupy the other three mutually cis coordination sites. The Mo=O and Mo–N distances agree with those for related Mo(V) complexes.[10,18,19] The catechol ligand is not coplanar with the molybdenum atom. The angle between the plane defined by Mo, O1, O2 and the plane containing O1, O2, C1 and C2 is 18.4(2)°. This deformation is probably due to non bonded interaction between the C36 methyl group and atoms C1 and C2 of the catechol ligand. The C36···C1 and

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(14) The reference electrode was a silver/ silver chloride electrode [Ag/AgCl]; a BAS Model MF-2012 graphite electrode was used as the working electrode, and a platinum wire served as the counter electrode. All potentials were internally referenced against the ferrocenium/ferrocene ion couple and expressed with respect to the saturated calomel electrode, SCE.
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(16) Representative characterization for **2**. Anal. Calcd for C₂₁H₂₂N₆O₃Cl₄BMo: C, 38.49; H, 3.36; N, 12.83; Cl, 21.69. Found: C, 39.73; H, 3.86; N, 12.19; Cl, 22.35. MS: 518.49 [MP]⁺. IR: *v*-(MoO) 945 cm⁻¹.
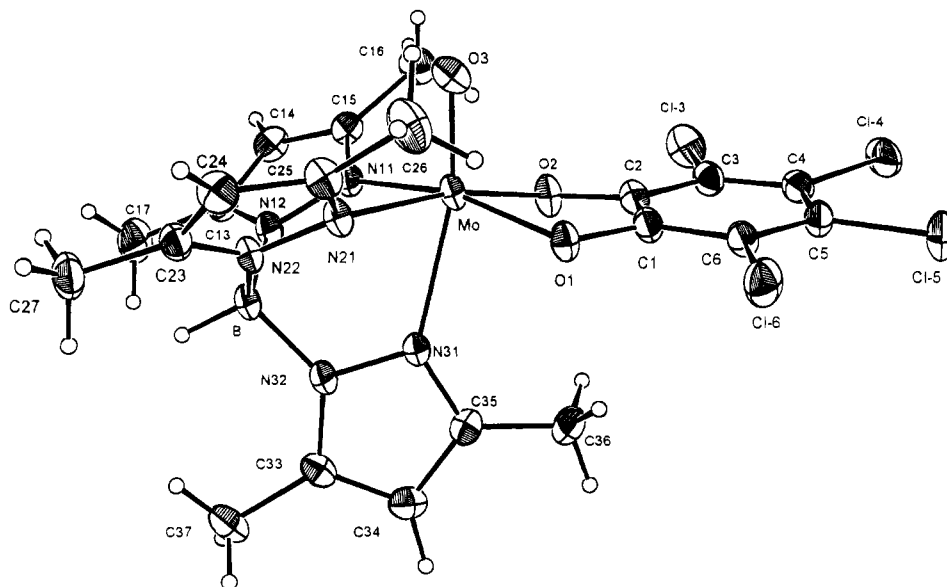
Figure 2. Perspective view and atom labeling scheme of **2**. Atoms are shown as 30% probability ellipsoids; hydrogen atoms have been made arbitrarily small for clarity.

Table 1. Selected Bond Parameters of **2**

	Bond Lengths		
Mo−O1	1.994(2)	Mo−N11	2.123(3)
Mo−O2	1.978(3)	Mo−N21	2.156(3)
Mo−O3	1.675(3)	Mo−N31	2.327(3)
O1−C1	1.354(4)	O2−C2	1.340(4)
C1−C2	1.401(5)		

	Bond Angles (deg)		
O1−Mo−O2	80.1(1)	O1−Mo−O3	102.1(1)
O1−Mo−N11	163.2(1)	O1−Mo−N21	96.7(1)
O1−Mo−N31	86.7(1)	O2−Mo−O3	101.3(1)
O2−Mo−N11	92.1(1)	O2−Mo−N21	169.4(1)
O2−Mo−N31	90.7(1)	O3−Mo−N11	94.0(1)
O3−Mo−N21	89.2(1)	O3−Mo−N31	166.1(1)
N11−Mo−N21	88.3(1)	N11−Mo−N31	78.6(1)
N21−Mo−N31	79.0(1)		

C36···C2 contact distances of 3.32 and 3.41 Å, respectively, are substantially less than the estimated van der Waals contact between a methyl group and an aromatic ring (3.7 Å).[20] The O1−Mo−N21 (96.7(1)°) and O2−Mo−N11 (92.1(1)°) angles differ by 4.6° (46σ), and the O3−Mo−N11 and O3−Mo−N21 angles differ by 4.8° (48σ).

The average Mo−O(catechol) distance is 1.986(3) Å, slightly longer than the average Mo−O(phenolato) distance of 1.940-(3) Å in the corresponding bis-phenoxy complexes.[18,19] The average Mo(V)−O(cat) length in **2** falls within the range of Mo(VI)−O lengths (2.014(5)−1.956(5) Å) for structurally characterized mononuclear monooxo−Mo(VI)(cat) species.[11,12]

(17) Crystal data for compound **2** ($C_{21}H_{22}N_6O_3Cl_4BMo$): dark green prismatic (size: 0.23 × 0.33 × 0.56 mm), triclinic, $P\bar{1}$(No 2), $a = 10.5822(7)$ Å, $b = 11.5035(11)$ Å, $c = 11.8638(7)$ Å, $\alpha = 81.603-(7)°$, $\beta = 65.548(5)°$, $\gamma = 84.685(7)°$, $V = 1299.8(2)$ Å^3, $Z = 2$, d(calc) = 1.674 g cm^{-3}, d(obs) = 1.672 g cm^{-3}, μ(Mo Kα) = 9.4 cm^{-1}, $T = 23 \pm 1$ °C; 4915 total refections (4560 unique) with $2\theta \le 50°$-(max) of which 3981 with $I > 3\sigma(I)$ were used in the refinement. Final $R = 0.037$ and $R_w = 0.055$. Calculations were done on a VAX computer using MolEN.
(18) Chang, C. S. J.; Pecci, T. J.; Carducci, M. D.; Enemark, J. H. *Inorg. Chem.* **1993**, *32*, 4106−4110.
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The C−O distances in **2** (1.354(4) and 1.340(4) Å) are consistent with the catecholato formulation.[21]

Spectroscopy. All compounds exhibit the characteristic infrared bands of the hydrotris(3,5-dimethyl-1-pyrazolyl)borate ligand ($v_{B-H} = 2536-2549$ cm^{-1}) and a strong Mo=O stretch ($v_{Mo=O} = 931-945$ cm^{-1}), with compound **3** showing the lowest frequencies for these vibrations (Table SII). The small variation of $v_{Mo=O}$ shows that the Mo=O bond order is relatively insensitive to the substituents on the catechol ring.

The colors of **1−7** range from dark green to greenish brown. Their electronic absorption spectra in toluene (Table 2) show a broad low intensity band in the 635−775 nm (13 000−16 000 cm^{-1}) region and several bands in the 274−445 nm (36 500−22 500 cm^{-1}) region. The low energy band has been assigned as the mainly $d_{xy} \rightarrow d_{xz}(d_{yz})$ transition on the basis of its energy, the magnitude of its absorption coefficient, and its pseudo-A behavior in MCD spectroscopy.[22] The intense high energy bands can most reasonably be assigned to charge transfer transitions. The low energy shoulder near 400−425 nm (23 500−25 000 cm^{-1}) can be assigned to a transition from $d_{xy} \rightarrow d_{x^2-y^2}$ transition due to its positive MCD.[22]

The X-band EPR spectra of all the compounds were measured both in frozen and fluid solution, and the EPR parameters for **1−3** were obtained by simulation (Table 3).[23] The fluid solution EPR spectra show an intense peak centered at g ~ 1.92 along with six satellite peaks characteristic of the molybdenum isotope distribution.[24] The average ⟨A⟩ value is about 40 × 10^{-4} cm^{-1}. The frozen solution EPR spectra show nearly axial g-values, however, larger rhombicity is observed in the A(^{95,97}Mo) hyperfine splitting. The EPR parameters for the most electron withdrawing (**2**) and electron releasing (**3**) substitutents are very similar to one-another, indicating that the EPR parameters are

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(23) Samples were prepared as ~1 mM solutions in toluene. Liquid nitrogen temperature was maintained using a quartz sample dewar. Simulations of the frozen solution spectra were carried out using a modified version of the program QPOW written by Professor R. L. Belford and co-workers. The $I = \frac{5}{2}$ (^{95,97}Mo isotopes, 25% abundant) and $I = 0$ (^{92,94,96,98}Mo isotopes, 75% abundant) components were simulated separately and then summed to obtain the complete spectrum.

Table 2. Electronic Spectral[a] and Cyclic Voltammetric[b] Data at 25 °C

compound	λ, nm(ϵ, M^{-1} cm^{-1})[d]	$E_{1/2}$, V (ΔE_p, mV)
	662(190)[c], 394[s] (2400),[c] 340[s] (3400),[c] 301[s] (5500),[c] 274 (13600)[c]	
1	667 (174), 445[s] (1100), 376[s] (2600), 338[s] (3600), 306[s] (5000)	−0.732 (64)
2	646 (200), 425[s] (3500), 359 (6000), 288 (16700)	−0.388 (61)
3	700 (162), 425[s] (1600), 339 (4390), 307[s] (4900), 284 (10400)	−0.832 (60)
4	646 (174), 400[s] (5100), 358 (8800)	−0.534 (88)
5	636 (178), 404[s] (4000), 358[s] (6600), 300 (23600)	−0.554 (64)
6	775 (175), 425[s] (1300), 342[s] (2400), 287 (8600)	−0.765 (68)
7	663 (191), 424[s] (2500), 385[s] (4900), 354 (6100)	−0.725 (63)

[a] In toluene. [b] In DMF, conditions: concentration, ∼0.1 mM; electrode, glassy carbon; reference measured against Ag(AgCl) and expressed with respect to SCE; supporting electrolyte, TEAP (∼0.1 M); internal calibrant, Fc⁺/Fc couple. [c] In dichloromethane. [d] Key: s = shoulder.

Table 3. EPR Data in Toluene

compounds	g_1	g_2	g_3	$\langle g \rangle$	A_1[a]	A_2[a]	A_3[a]	$\langle A \rangle$[a]
1	1.969(1)	1.969(1)	1.920(1)	1.953(1)	34.0(3)	20.0(3)	66.24(3)	40.1(3)
2	1.969(1)	1.968(1)	1.927(1)	1.955(1)	32.0(3)	18.0(3)	68.38(3)	39.5(3)
3	1.969(1)	1.969(1)	1.919(1)	1.952(1)	30.2(3)	16.7(3)	66.06(3)	37.6(3)

[a] ×10^{-4} cm^{-1}.

primarily determined by the local coordination environment of the molybdenum center.[10] The HOMO is predominantly metal d_{xy} in character and the orbital composition is relatively unperturbed by substitution beyond the first coordination sphere.[10,22,24,25]

Electrochemistry. All complexes show a quasi-reversible one-electron reduction (Table 2).[26] This formal Mo(V/IV) reduction will place a second electron in the d_{xy} orbital that lies in the equatorial plane. Direct π interaction between d_{xy} and the oxygen $p\pi$ orbitals of the catechol ring will not be favorable and therefore inductive effects of the remote substitutents are most likely responsible for the observed potential differences, which exhibit a range of ∼450 mV for compounds **1−7**. Electron withdrawing substituents (Cl₄, **2**), lower the energy of the d_{xy} orbital and make reduction more facile; electron releasing substituents (**3**) raise the energy of the d_{xy} orbital and make reduction more difficult.[25] All the LMoO(cat) complexes are more difficult to reduce than LMoO(bdt) (bdt = benzenedithiolate) which has a reduction potential of −0.116 V under the same conditions.[27] Similar electrochemical behavior has been observed previously for substitution of sulfur for oxygen.[10,28]

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(26) The quasi reversible nature of all the couples were demonstrated by i_p/i_c = 1. The ΔE_p value ranges from 60 to 80 mV at a scan rate of 100 mV/s. Measurement of the solution rest potentials confirmed the processes were reductions. Controlled potential coulometry for compounds **1** and **2** verified the one-electron nature of the reduction waves for the complexes. The complexes were also examined for oxidative electrochemical processes. Compound **3**, which contains the most electron-releasing substituents, shows an irreversible one-electron (from current height) oxidative process near ∼1 V. None of the other complexes show oxidative waves in the DMF solvent window.

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Conclusions

Several LMo^{V}O(cat) complexes have been investigated in order to determine the sensitivity of the spectral and electrochemical properties of the oxo−Mo(V) center to remote substituents on the catecholate ligand and to provide a reference base for interpreting the perturbations of the LMo^{V}O(cat) moiety by covalently linked paramagnetic metalloporphyrin centers.[7,8] The ligand field splitting of the LMo^V(cat) center is primarily determined by the molybdenyl (Mo=O^{3+}) group[22] and the nature of the donor atoms. The HOMO is primarily d_{xy} which cannot strongly overlap with the π-orbitals of the catecholate, and therefore the EPR parameters are essentially independent of the substituents on the catecholate ligand. However, the absolute energy of d_{xy} is sensitive to inductive effects of ring substituents, and the Mo(V/IV) reduction potentials for **1−7** have a range over about 450 mV. Thus the Mo(V/IV) reduction potential should be a good probe of the electron withdrawing/releasing ability of various porphyrin and metalloporphyrin centers that are linked to the LMo^{V}O(cat) unit.

Supplementary Material Available: Tables SI and SII (mass spectral data, IR spectral data), Tables SIII−VIII (crystal data, complete bond angles and distances, positional parameters, anisotropic thermal parameters, H-atom positional parameters), Figures S1 and S2 (experimental and simulated EPR spectra for **2** and cyclic voltammograms of **1−3**) (9 pages). Ordering information is given on any current masthead page.

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