tortions in both phenyl derivatives can be explained by repulsion between the space-demanding phenyl groups and the axial ligands. In the [PhSiF$_4$]$^-$ anion the axial bonds are bent away 5.4° from the phenyl ring; in [Ph$_2$SiF$_3$]$^-$ the axial bonds are bent 7.5° toward the equatorial fluorine atom. Despite this distortion the F···H(ortho) distances are quite short (see above and ref 13).

The structural data that are now available for compounds of pentacoordinated silicon indicate that these compounds follow the same path of minimum energy as the isoelectronic phosphoranes when distortions from the trigonal-bipyramidal geometry are observed. The degree of distortion, however, (especially for spirobicyclic compounds) may be very different from that observed in similar phosphorus compounds.

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Supplementary Material Available: Tables of anisotropic temperature factors, positional and isotropic temperature factors for hydrogen atoms, and observed and calculated structure factors for both compounds (20 pages). Ordering information is given on any current masthead page.

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Higher Valent Manganese Chemistry. Synthetic, Structural, and Solution Studies on [Mn(catecholate)$_3$]$^{n-}$ (n = 2, 3) Complexes

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The complexes (Et$_3$NH)$_2$[Mn(Cat)$_3$] and K$_2$[Mn(3,5-(t-Bu)$_2$Cat)$_3$]·6CH$_3$CN (Cat = catecholate) have been synthesized, and the latter has been characterized by X-ray diffraction (trigonal system, space group $R\bar{3}$, a = 14.760 (9) Å, c = 50.752 (32) Å, Z = 6, final R = 6.9%, final R_w = 7.1%). The [Mn(3,5-(t-Bu)$_2$Cat)$_3$]$^{2-}$ anion has crystallographic threefold symmetry with short Mn–O bond lengths (1.922 (3) and 1.891 (3) Å) and no evidence of either dynamic or static Jahn–Teller distortion. The electron paramagnetic resonance spectrum of the [Mn(Cat)$_3$]$^{2-}$ ion at 77 K is characteristic of a d^3 system with large zero-field splitting. The magnetic behavior of K$_2$[Mn(3,5-(t-Bu)$_2$Cat)$_3$]·6CH$_3$CN is fully consistent with that expected for a simple d^3 system. The present structural, magnetic susceptibility, and magnetic resonance results establish that these essentially identical chelates are tris(catecholate)manganese(IV) rather than (semiquinone)bis(catecholate)manganese(III) complexes. The present structural results also show that the "bite distance" of catechol (2.58 Å) is too short to offer a regular octahedral environment to Mn(IV). This fact has a pervasive influence on the chemistry of the system. It causes trigonal compression of the Mn(IV) ion and thereby gives rise to the large zero-field splitting observed. In the Mn(III)–catechol system, it actually determines the solution chemistry. Because Mn(III) is even larger than Mn(IV) and has either two or four elongated bonds (by the Jahn–Teller theorem), three catechol ligands cannot span all six coordination sites in a chelating fashion. The short bite distance of catechol therefore effectively prevents formation of [Mn$^{\text{III}}$(Cat)$_3$]$^{3-}$. Moreover, the difficulty of forming a tris complex of Mn(III) with a catechol-like ligand may contribute significantly to stabilization of [Mn(3,5-(t-Bu)$_2$Cat)$_3$]$^{2-}$ as tris(catecholate)manganese(IV) instead of (semiquinone)bis(catecholate)manganese(III).

Introduction

Relatively little is known of the chemistry of the higher valence states of manganese,[2] although Mn(III) and Mn(IV) are thought to play a central role in photosynthetic oxygen evolution.[3] Recent EXAFS results on chloroplasts and Mn(III) and Mn(IV) model compounds support this long-held presumption.[4] However, for relatively few Mn(III) or Mn(IV) complexes are either the electronic or the molecular structures known, and in particular the factors that determine their redox potentials are not well understood. In large part this is because few ligands are presently known that can complex these ions without being oxidized by them.

One ligand with remarkable ability to stabilize high oxidation states is catechol (o-dihydroxybenzene). Complexes of catechol with, e.g., Fe(III),[5] V(V),[6] Ti(IV),[7] and even Ce(IV)[8] are all extremely stable, and recently the Mn(IV)–catecholate complex [Mn(3,5-(t-Bu)$_2$Cat)$_2$(py)$_2$] (Cat = catecholate) has been reported.[9] Coordinated catechol can also be oxidized to the o-semiquinone, which is itself a good ligand.[10] A wide variety of metal semiquinone complexes have been prepared in the last 5 years, in particular by Razuvaev and Pierpont, Hendrickson, and their co-workers. The area has been reviewed,[10] and theoretical studies on V, Cr, and Fe quinone–semiquinone–catecholate complexes have recently been published.[11,12]


catecholate semiquinone

Recently Sawyer and co-workers reported that reaction of manganic acetate with 3,5-di-*tert*-butylcatechol and 3,5-di-*tert*-butyl-o-benzoquinone in the presence of base gave a deep

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(1) Department of Chemistry, Brandeis University, Waltham, MA 02254.
(2) Levason, W.; McAuliffe, C. A. *Coord. Chem. Rev.* **1972**, *7*, 353–84.
(3) Radmer, R.; Cheniae, G. *Top. Photosynth.* **1977**, *2*, 303–48. Livorness, J.; Smith, T. D. *Struct. Bonding (Berlin)* **1982**, *48*, 1–44.
(4) Kirby, J. A.; Robertson, A. S.; Smith, J. P.; Thompson, A. C.; Cooper, S. R.; Klein, M. P. *J. Am. Chem. Soc.* **1981**, *103*, 5529–7.
(5) Raymond, K. N.; Isied, S. S.; Brown, L. D.; Fronczek, F. R.; Nibert, J. H. *J. Am. Chem. Soc.* **1976**, *98*, 1767–74.
(6) Cooper, S. R.; Koh, Y. B.; Raymond, K. N. *J. Am. Chem. Soc.* **1982**, *104*, 5092–102.
(7) Borgias, B.; Koh, Y. B.; Cooper, S. R.; Raymond, K. N., submitted for publication.
(8) Sofen, S. R.; Cooper, S. R.; Raymond, K. N. *Inorg. Chem.* **1979**, *18*, 1611–6.
(9) Lynch, M. W.; Hendrickson, D. N.; Fitzgerald, B. J.; Pierpont, C. G. *J. Am. Chem. Soc.* **1981**, *103*, 3961–3.
(10) Pierpont, C. G.; Buchanan, R. M. *Coord. Chem. Rev.* **1981**, *38*, 45–87.
(11) Gordon, D. J.; Fenske, R. F. *Inorg. Chem.* **1982**, *21*, 2907–15.
(12) Gordon, D. J.; Fenske, R. F. *Inorg. Chem.* **1982**, *21*, 2916–23.

blue complex.[13-15] While this compound was not isolated in pure form, preliminary studies on the complex generated in situ suggested the complex to be $[Mn(3,5\text{-}(t\text{-}Bu)_2Cat)_3]^{2-}$. In a dichotomy reminiscent of the oxidation-state ambiguity of metal dithiolene complexes, $[Mn(3,5\text{-}(t\text{-}Bu)_2Cat)_3]^{2-}$ could be formulated as either a Mn(IV)–catecholate or as a Mn(III)–semiquinone complex. For tris(catecholato) complexes of *tri*valent first-row ions the M(III)–catecholate/M(II)–semiquinone "crossover point" occurs after Fe. For the *tetra*valent ions the crossover point should move to the left in the periodic table, in which case the Mn(IV) complex might be near this "crossover point". Thus a reasonable case could be made for either formulation of the electronic structure of $[Mn(3,5\text{-}(t\text{-}Bu)_2Cat)_3]^{2-}$.

To address this question and gain further insight into the chemistry of manganese in its higher oxidation states, we have examined this system more closely. Our structural, magnetic, and EPR results show that $[Mn(3,5\text{-}(t\text{-}Bu)_2Cat)_3]^{2-}$ and $[Mn(Cat)_3]^{2-}$ are better considered as Mn(IV)–tris(catecholate) rather than Mn(III)–semiquinonebis(catecholate) complexes.[16] In the course of our investigation we observed that Mn(III) (alone among the trivalent ions of Ti, V, Cr, Mn, and Fe) is extremely reluctant to form a tris(catecholato) complex, a striking exception that demanded explanation. The results reported here indicate that the singular difficulty of forming $[Mn^{III}(Cat)_3]^{3-}$ comes from the short bite distance of catechol, because of which this ligand is unable to span the elongated coordination axes of the Jahn–Teller-distorted Mn(III) ion.

Experimental Section

Degassed solutions and standard Schlenk and syringe techniques were used throughout. Catechol and $Mn(acac)_3$ (acac = acetylacetonate) were recrystallized from benzene; Et_3N was distilled from BaO, CH_3CN from calcium hydride, and CH_2Cl_2 from P_4O_{10}. Manganese was determined spectrophotometrically as MnO_4^-, as described by Vogel.[17]

Preparation of Compounds. $K_2[Mn(3,5\text{-}(t\text{-}Bu)_2Cat)_3]\cdot 6CH_3CN$. To a solution of 3,5-di-*tert*-butylcatechol (0.70 g, 3.2 mmol) and KOH (0.38 g, 6.8 mmol) in 10 mL of MeOH was added $Mn(acac)_3$ (0.35 g, 1.0 mmol) to give a deep green solution. Removal of the MeOH under reduced pressure gave a reddish brown oil, which was dissolved in 4 mL of CH_3CN and filtered to yield a brown solution. Upon addition of I_2 (0.10 g, 0.4 mmol) the solution became blue and then green as it deposited deep blue crystals of $K_2[Mn(3,5\text{-}(t\text{-}Bu)_2Cat)_3]\cdot 6CH_3CN$, which were filtered and washed with CH_3CN; yield 0.53 g (51%). Anal. (Galbraith Laboratories, Knoxville, TN) Calcd for $C_{54}H_{78}N_6O_6K_2Mn$: C, 62.34; H, 7.56; N, 8.08; Mn, 5.28. Found: C, 62.12; H, 7.65; N, 7.62; Mn, 5.89. Infrared data (Nujol mull, KBr plates; cm^{-1}): 3400 b, 2258 m, 1662 m, 1588 w, 1548 m, 1438 s, 1412 s, 1370 ms, 1326 m, 1282 s, 1262 m, 1238 s, 1205 m, 1178 w, 1106 w, 1028 m, 982 s, 920 w, 890 w, 872 w, 850 m, 828 m, 812 m, 764 w, 750 s, 692 m, 654 m, 619 s, 608 sh, 566 m, 542 m, 506 m, 458.

$(Et_3NH)_2[Mn(cat)_3]$. Catechol (0.35 g, 3.18 mmol) was dissolved in a solution of 15 mL of Et_2O and 0.5 mL of Et_3N, and to the resulting clear solution was added $Mn(acac)_3$ (0.35 g, 1.0 mmol) in 7 mL of CH_3CN to give a blue solution. Addition of benzoquinone (0.06 g, 0.56 mmol) gave a deep blue solution, which was cooled in an ice bath, filtered, and washed with 4:1 v/v CH_3CN–Et_2O and then pure Et_2O to afford the product as large dark blue needles (0.17 g), which were dried under vacuum. Anal. (Galbraith Laboratories, Knoxville, TN) Calcd for $C_{30}H_{44}N_2O_6Mn$: C, 61.74; H, 7.60; N, 4.80; Mn, 9.41. Found: C, 61.76; H, 7.57; N, 4.66; Mn, 9.03. X-ray powder pattern (Å, intensity): 28.26 (vs), 25.513 (m), 22.420 (m), 20.581 (m), 18.504 (s), 16.809 (s), 14.894 (w), 13.829 (s), 13.521 (w), 12.898 (m), 11.542 (m), 11.160 (m), 10.737 (w), 9.580 (m), 8.400 (w), 8.031 (w), 7.791 (w), 6.761 (w), 6.341 (w). Infrared data (KBr pellet; cm^{-1}): 3400 vb, 2810 w, 2588 m, 2575 m, 2526 w, 2508 m, 2495 m, 1478 sh, 1468 s, 1464 sh, 1398 w, 1395 w, 1388 m, 1330 w, 1262 sh, 1246 vs, 1212 m, 1206 m, 1158 m, 1090 m, 1026 m, 1012 m, 864 m, 798 s, 730 s, 644 s, 626 s, 618 s, 514 s, 408 s, 368 m.

Table I. Crystallographic Data for $K_2[Mn(3,5\text{-}(t\text{-}Bu)_2Cat)_3]\cdot 6CH_3CN$

mol wt	1040.40
space group	$R\bar{3}$
a, Å	14.760 (9)
c, Å	50.752 (32)
V, $Å^3$	9575.3
d_{calcd}, g/cm^3	1.08
Z	6
λ	Mo Kα (0.710 69 Å)
$F(000)$	3330
μ, cm^{-1}	3.71
cryst size, mm	0.55 × 0.45 × 0.30
reflcns collected	6737
unique data with $F > 3\sigma(F)$	1838
2θ range, deg	3–42
final R, %	6.9
final R_w, %	7.1
GOF[a]	1.730
no. of variables	208

[a] The goodness of fit is defined as $[w(|F_o| - |F_c|)^2/n_o - n_v)]^{1/2}$, where n_o and n_v denote the numbers of data and variables, respectively.

Physical Measurements. Optical and infrared spectra were measured on a Perkin-Elmer 559A spectrophotometer and a Perkin-Elmer 683 grating spectrometer, respectively. The complexes decompose gradually in CH_3CN solution, thereby precluding precise extinction coefficient measurements, although the decomposition could be slowed by addition of a trace of Et_3N. Solid-state magnetic susceptibilities were measured at 10 kG with an SHE Model 805 variable-temperature susceptometer and Model 868 susceptometer control system. Six determinations were made at each temperature and the data averaged. The susceptibility data were corrected for molecular diamagnetism by use of Pascal's constants ($\chi_M^{dia} = -6.47 \times 10^{-4}$ cm^3/mol)[18] and fitted to the Curie–Weiss expression $\chi = C/(T - \Theta)$ by linear least squares. Tables of experimental magnetic susceptibility data are available as supplementary material. Solution magnetic moments were determined by the NMR method with use of a concentric NMR tube.[19-22] Electron paramagnetic resonance spectra were measured with a Varian E-9 spectrometer, with diphenylpicrylhydrazyl radical as g standard (2.0037). Quartz flat cells were used for fluid solutions in polar solvents, while cylindrical quartz tubes were used for frozen solutions in polar solvents and all measurements in solvents with low dielectric loss. Electrochemical measurements were performed with a Princeton Applied Research (PAR) Model 175 programmer in conjunction with a PAR Model 170 potentiostat and Model 179 digital coulometer. In all cases 0.1 M tetraethylammonium perchlorate was used as supporting electrolyte. Neither complex exhibited either reversible or quasi-reversible behavior in CH_3CN or dimethyl sulfoxide at either a Pt or hanging-mercury-drop electrode. X-ray powder patterns were determined with Cu Kα radiation (1.5418 Å) with a Ni filter on a 114.83 mm diameter Debye–Scherrer camera. Intensities were estimated visually from Kodak NST-90 No-Screen X-ray film.

Structure Determination. A rhombohedral prism of $K_2[Mn(3,5\text{-}(t\text{-}Bu)_2Cat)_3]\cdot 6CH_3CN$ (dimensions 0.55 × 0.45 × 0.30 mm) with well-developed faces was sealed in a quartz capillary under

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(13) Magers, K. D.; Smith, C. G.; Sawyer, D. T. *J. Am. Chem. Soc.* **1978**, *100*, 989–91.

(14) Magers, K. D.; Smith, C. G.; Sawyer, D. T. *Inorg. Chem.* **1980**, *19*, 492–6.

(15) Earlier claims that $[Mn(3,5\text{-}(t\text{-}Bu)_2Cat)_3]^{2-}$ binds oxygen reversibly have been shown to be in error: Cooper, S. R.; Hartman, J. R. *Inorg. Chem.* **1982**, *21*, 4315–7.

(16) A preliminary account of this work has appeared: Hartman, J. R.; Foxman, B. M.; Cooper, S. R. *J. Chem. Soc., Chem. Commun.* **1982**, 583–4.

(17) Vogel, A. I. "Quantitative Inorganic Analysis", 3rd ed.; Longmans, Green and Co.: London, 1961; pp 787–8.

(18) Mulay, L. N.; Boudreaux, E. A. "Theory and Application of Molecular Diamagnetism"; Wiley: New York, 1976.

(19) Reilly, C. A.; McConnell, H. M.; Meisenheimer, R. G. *Phys. Rev.* **1955**, *98*, 264.

(20) Klein, M. P.; Holder, B. E. *Phys. Rev.* **1955**, *98*, 265.

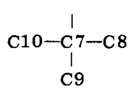
(21) Evans, D. F. *J. Chem. Soc.* **1959**, 2003–5.

(22) Bartle, K. D.; Jones, D. W.; Maricic, S.; *Croat. Chem. Acta* **1968**, *40*, 227–40.

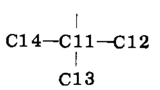
Table II. Atom Coordinates (×10^4) and Temperature Factors (Å × 10^3) for $K_2[Mn(3,5\text{-}(t\text{-}Bu)_2Cat)_3]\cdot 6CH_3CN$

atom[a]	x	y	z	U[b]
Mn	0	0	2491 (1)	36 (1)
K(1)	0	0	3167 (1)	56 (1)
K(2)	0	0	1830 (1)	67 (1)
O(1)	1196 (2)	530 (2)	2709 (1)	42 (2)
O(2)	832 (2)	1215 (2)	2277 (1)	46 (2)
C(1)	1928 (4)	1514 (4)	2635 (1)	39 (2)
C(6)	2820 (4)	2119 (4)	2786 (1)	44 (2)
C(2)	1724 (4)	1902 (4)	2405 (1)	43 (2)
C(5)	3533 (4)	3134 (4)	2706 (1)	50 (2)
C(4)	3308 (4)	3513 (4)	2479 (1)	55 (3)
C(3)	2415 (4)	2930 (4)	2323 (1)	48 (3)
C(7)	2202 (5)	3381 (4)	2074 (1)	71 (3)
C(11)	4511 (4)	3806 (4)	2878 (1)	64 (3)
C(8)	3042 (6)	4548 (5)	2030 (2)	121 (4)
C(12)	5218 (6)	4866 (6)	2758 (2)	151 (5)
C(13)	4158 (6)	3987 (7)	3150 (2)	144 (6)
C(9)	2207 (6)	2772 (6)	1827 (1)	108 (4)
C(10)	1143 (5)	3305 (6)	2094 (2)	107 (5)
C(14)	5106 (5)	3241 (6)	2927 (2)	130 (5)
N(1)	−1843 (5)	−519 (5)	3462 (1)	117 (4)
Ac(1)	−2538 (5)	−782 (5)	3597 (1)	78 (3)
Me(1)	−3449 (5)	−1135 (5)	3763 (1)	94 (4)
N(2)	1535 (8)	202 (9)	1455 (2)	215 (8)
Ac(2)	2030 (7)	853 (8)	1323 (2)	116 (6)
Me(2)	2679 (6)	1674 (6)	1153 (2)	120 (5)

[a] Phenyl carbon atoms are numbered 1–6 beginning with that bonded to O1. The *tert*-butyl groups



$$\begin{array}{c} | \\ C10{-}C7{-}C8 \\ | \\ C9 \end{array}$$



$$\begin{array}{c} | \\ C14{-}C11{-}C12 \\ | \\ C13 \end{array}$$

are bonded to C3 and C5, respectively. The acetonitrile group N1-Ac1-Me1 is coordinated to K1 and similarly for the second acetonitrile (which is coordinated to K2). [b] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

nitrogen atmosphere. The crystal was mounted and centered on a Nicolet R3 diffractometer with a graphite-crystal monochromator. The unit cell parameters (Table I) and orientation matrix were determined from the setting angles of 20 reflections with $2\Theta > 20°$ (Mo Kα (0.71069 Å) radiation). A data set ($0\bar{k}\bar{l}$ to hkl) with $3° \leq 2\theta \leq 42°$ was collected by use of the θ–2θ scan technique, with an angular range of 1.1° on either side of the Mo Kα_1–MoKα_2 doublet with a variable scan rate of from 2.00 to 30°/min. Four standard reflections (0,0,10; 701; 070; 004) were measured every 122 reflections as orientation and intensity standards. No decomposition was observed during data collection.

The data were corrected for Lorentz and polarization effects, but no absorption correction was applied owing to the small variation in transmission coefficients and the low linear absorption coefficient (3.71 cm^{-1}). The systematic absences (hkl, $h + k + l \neq 3n$) and diffraction symmetry ($\bar{3}$) were consistent with the space groups $R3$ and $R\bar{3}$. After averaging of the 6764 reflections collected (agreement between equivalent reflections 3.66%) the 1838 unique reflections with $F > 3\sigma(F)$ were used to calculate a sharpened Patterson map, from which the positions of the manganese and potassium ions were determined. Subsequent cycles of difference Fourier maps and least-squares refinement revealed the remaining atoms (including some of the hydrogen atoms) and established $R\bar{3}$ as the correct space group. In subsequent cycles the hydrogen atoms were included at the calculated positions with isotropic thermal parameters but were not refined. Calculations were performed with the Nicolet SHELXTL Crystallographic Package programs on a Nova 3 minicomputer. Atomic scattering factors were obtained from the usual source.[23] Block-diagonal least-squares refinement with anisotropic temperature factors for all non-hydrogen atoms converged to a final $R = 6.9\%$, $R_w = 7.1\%$, where the functions minimized during refinement were $R = \sum(||F_o| - |F_c||)/\sum|F_o|$ and $R_w = \sum(w^{1/2}|F_o| - |F_c|)/\sum w^{1/2}F_o$, where $w = 1/(\sigma^2F + 0.001F^2)$. The final goodness of fit (GOF = $[\sum w(|F_o| - |F_c|)^2/(n_o - n_v)]^{1/2}$, where n_o is the number of observations and n_v is the number of variable parameters) was 1.805 for 1838 observations and 208 parameters. No correction for extinction was applied. The final difference map showed no peak greater than 0.4 e/Å^3. Data collection parameters and atomic positional parameters are collected in Tables I and II, respectively. Tables of observed and calculated structure factors, as well as all bond distances and angles, are available as supplementary material.

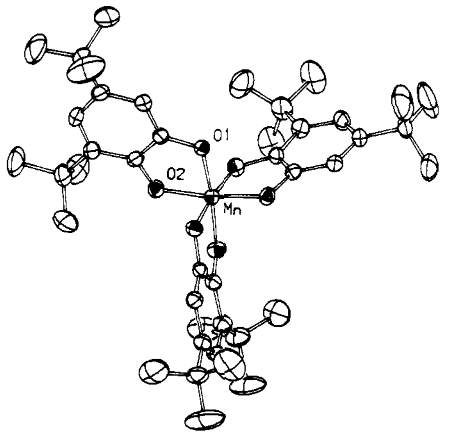


Figure 1. ORTEP drawing of $K_2[Mn(3,5\text{-}(t\text{-}Bu)_2Cat)_3]\cdot 6CH_3CN$. The individual atoms are drawn at 35% probability contours of the thermal motion. Hydrogen atoms are omitted for clarity.

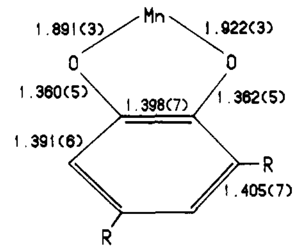


Figure 2. Schematic diagram of bond lengths in the $[Mn(3,5\text{-}(t\text{-}Bu)_2Cat)_3]^{2-}$ anion.

Table III. Bond Distances for $K_2[Mn(3,5\text{-}(t\text{-}Bu)_2Cat)_3]\cdot 6CH_3CN$ (Å)

Mn–O1	1.891 (3)	C2–C3	1.403 (6)
Mn–O2	1.922 (5)	C3–C4	1.405 (7)
O1–C1	1.361 (6)	C4–C5	1.392 (8)
O2–C2	1.362 (5)	C5–C6	1.392 (8)
C1–C2	1.398 (7)	C6–C1	1.391 (6)

Table IV. Bond Angles for $K_2[Mn(3,5\text{-}(t\text{-}Bu)_2)_3]\cdot 6CH_3CN$ (deg)

O(1)–Mn–O(2)	85.2 (1)	C(1)–C(2)–C(3)	120.2 (4)
Mn–O(1)–C(1)	111.0 (3)	C(1)–C(6)–C(5)	119.7 (5)
Mn–O(2)–C(2)	110.8 (3)	C(2)–C(3)–C(4)	116.5 (5)
O(1)–C(1)–C(2)	116.7 (4)	C(5)–C(4)–C(3)	124.1 (4)
O(1)–C(1)–C(6)	121.7 (4)	C(6)–C(1)–C(2)	121.5 (4)
O(2)–C(2)–C(1)	114.8 (4)	C(6)–C(5)–C(4)	117.9 (4)
O(2)–C(2)–C(3)	125.0 (5)		

Results

Description of the Structure. The structure of $K_2[Mn(3,5\text{-}(t\text{-}Bu)_2Cat)_3]\cdot 6CH_3CN$ consists of an array of $(CH_3CN)_3K^+$-*cis*-$Mn(3,5\text{-}(t\text{-}Bu)_2Cat)_3^{2-}$–$K^+(CH_3CN)_3$ units along the 3-fold (c) axis of the unit cell. Each Mn ion is coordinated by six catechol oxygen atoms (Figure 1) in an arrangement with a twist angle of 51.8°, yielding a complex that is much closer to octahedral (60°) than to trigonal-prismatic geometry (0°). The 3,5-di-*tert*-butylcatechol ligands are in a cis arrangement (i.e., the three *tert*-butyl groups adjacent to a catechol oxygen atom are on the same side of the complex) as required by the crystallographic 3-fold symmetry of the complex. Steric interactions between these cis

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(23) Cromer, D. T.; Waber, J. T "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

tert-butyl groups slightly force apart the oxygen atoms adjacent to them and cause the three Mn–O bond lengths on one side of the molecule (1.922 (3) Å) to be longer than the three on the other side (1.891 (3) Å) (see Tables III and IV and Figure 2). The O–Mn–O bite angle is 85.2°, a typical value for a catechol complex.

The bond distances in $[Mn(3,5\text{-}t\text{-}Bu)_2Cat)_3]^{2-}$ are more consistent with a Mn(IV)–catecholate formulation than a Mn(III)–semiquinone. In general, the Mn–O distances of typical Mn(III) complexes are significantly longer than those found for the $[Mn(3,5\text{-}(t\text{-}Bu)_2Cat)_3]^{2-}$ ion. For example, in $Mn^{III}(acac)_3$ and $Mn^{III}(trop)_3$ (tetragonal form; trop = tropolonate) the Mn–O distances are 1.95 and 2.00[24] and 1.94 and 2.13 Å,[25] respectively. Both of these complexes are axially distorted owing to the Jahn–Teller effect, as expected for high-spin d^4 ions. Severely rhombically distorted manganese(III) complexes exist that have Mn–O bond lengths as short as those in $[Mn(3,5\text{-}(t\text{-}Bu)_2Cat)_3]^{2-}$, but such complexes simultaneously have Mn–O bonds that are much longer than those above. For example, the Mn–O distances of $Mn^{III}(trop)_3$ (orthorhombic form), $Mn^{III}(ox)_3{}^{3-}$,[26] and $Mn^{III}(mal)_3{}^{3-}$ [27] range from 1.94 to 2.05, 1.91 to 2.07, and 1.92 to 2.04 Å, respectively (ox and mal denote oxalate and malonate, respectively). Since $[Mn(3,5\text{-}(t\text{-}Bu)_2Cat)_3]^{2-}$ lacks either a tetragonal or an orthorhombic distortion, the bond length data militate against a Mn(III)–semiquinone formulation.

Another point favoring the Mn(IV)–catecholate formulation is that there is no evidence for a Jahn–Teller distortion of $[Mn(3,5\text{-}(t\text{-}Bu)_2Cat)_3]^{2-}$, as would be expected for a Mn(III)–semiquinone complex. (The trigonal distortion of the complex does not reflect static Jahn–Teller distortion because such distortion does not life the degeneracy of the e_g (in O_h) orbitals). While in principle $[Mn(3,5\text{-}(t\text{-}Bu)_2Cat)_3]^{2-}$ could undergo dynamic Jahn–Teller distortion or static distortion coupled with disorder in the unit cell, the thermal parameters of the oxygen atoms do not support either suggestion. They are neither unusually large nor elongated along the Mn–O vectors, as would be expected in either of the above cases.[28]

Similarly, the C–O and C–C bond lengths found for the catechol moiety also indicate the Mn(IV)–catecholate formulation as the more appropriate. Metal–catecholates generally have C–O bond lengths of 1.34–1.36 Å (cf. $[Cr(Cat)_3]^{3-}$; 1.349 (5) Å;[5] $Fe(Cat)_3{}^{3-}$, 1.349 (3) Å;[5] $Ce(Cat)_4{}^{4-}$, 1.353 (6) Å[8]). By comparison, metal–semiquinone complexes have C–O distances of approximately 1.28 Å (e.g. $Cr(3,5\text{-}(t\text{-}Bu)_2\text{-}o\text{-}BzSQ)_3$, d(C–O) = 1.285 (8) Å;[29] BzSQ = benzosemiquinone). The C–O bond lengths in $[Mn(3,5\text{-}(t\text{-}Bu)_2Cat)_3]^{2-}$ average 1.362 (5) Å and are clearly more typical of a metal–catecholate complex than of a metal–semiquinone complex. In addition, the catechol rings do not exhibit the elongation in C1–C2 bond length that is characteristic of semiquinones:[10] rather, the C1–C2 distance (1.398 (7) Å) is typical of coordinated catecholates (1.40 Å) (cf. 1.44 Å in coordinated semiquinones).[10] The closest comparison with the present work is the structural report of Hendrickson, Pierpont, and co-workers[9] on $Mn^{IV}(3,5\text{-}(t\text{-}Bu)_2Cat)_2(py)_2$, which has a Mn–O distance of 1.853 (2) Å and a C–O distance of 1.349 (4) Å. In summary, the C–C and C–O and Mn–O bond length criteria clearly indicate that $[Mn(3,5\text{-}(t\text{-}Bu)_2Cat)_3]^{2-}$ is a Mn(IV)–tris(catecholate) complex.

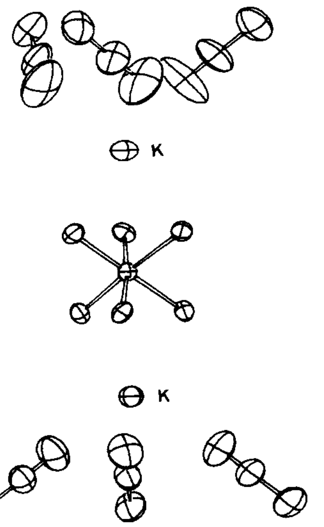

Figure 3. ORTEP drawing of the coordination environment of the potassium ions (comprising three catechol oxygen atoms and three acetonitrile nitrogen atoms about each potassium; see text). The catechol carbon atoms have been omitted for clarity. The individual atoms are drawn at 35% probability contours of the thermal motion.

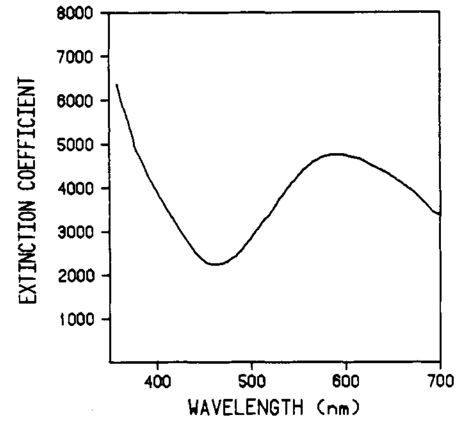

Figure 4. Optical spectrum of $[Mn(Cat)_3]^{2-}$ in CH_2Cl_2.

Examination of the coordination environment about the potassium ions (Figure 3) reveals the origin of the stability of the $K_2[Mn(3,5\text{-}(t\text{-}Bu)_2Cat)_3]\cdot 6CH_3CN$ lattice and explains the low solubility of the salt. Each potassium ion is coordinated on one side to three catechol oxygen atoms at 2.77 Å (average) and on the other to three acetonitrile nitrogen atoms at 2.85 Å (average). The coordination about the potassium ion is reminiscent of that in crown ether complexes.[30] Coordination of the catechol oxygen atoms to a potassium ion indicates that they retain considerable Lewis basicity even though coordinated to the strongly Lewis acidic Mn(IV) ion.[31]

Analysis of a number of structures of tris(bidentate) complexes by Raymond and co-workers has shown that the twist angle ϕ is related to the ligand bite b (where b is the ratio of the separation between chelate donor atoms to the metal donor atom distance) by $\phi = -73.95 + 94.10b$.[5] Consistent with previous results on catecholate complexes,[5,32] the trigonal twist

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[24] Fackler, J. P., Jr.; Avdeef, A. *Inorg. Chem.* **1974**, *13*, 1864–75.

[25] Avdeef, A.; Costamagna, J. A.; Fackler, J. P., Jr. *Inorg. Chem.* **1974**, *13*, 1854–63.

[26] Lis, T.; Matuszewski, J. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1980**, *B36*, 1938–40.

[27] Lis, T.; Matuszewski, J.; Jezowska-Trzebiatowska, B. *Acta Crystallogr. Sect. B: Struct. Crystallogr. Cryst. Chem.* **1977**, *B33*, 1943–6.

[28] Aghabozorg, H.; Palenik, G. J.; Stoufer, R. C.; Summers, J. *Inorg. Chem.* **1982**, *21*, 3903–7.

[29] Sofen, S. R.; Ware, D. C.; Cooper, S. R.; Raymond, K. N.; *Inorg. Chem.* **1979**, *18*, 234–9.

[30] Dalley, N. K. In "Synthetic Multidentate Macrocyclic Compounds"; Izatt, R. M., Christensen, J. J., Eds.; Academic Press: New York, 1978; p 207.

[31] Since the original submission of this manuscript a report on $Na_2[Mn(3,5\text{-}(t\text{-}Bu)_2Cat)_3]\cdot 6CH_3CN$ has appeared: Chin, D.-H.; Sawyer, D. T.; Schaefer, W. P.; Simmons, C. J. *Inorg. Chem.* **1983**, *22*, 752–8. This compound is isostructural with $K_2[Mn(3,5\text{-}(t\text{-}Bu)_2Cat)_3]\cdot 6CH_3CN$ with small but perhaps significant differences in Mn–O bond lengths (1.874 (6) and 1.891 (6) Å, compared with the 1.891 (3) and 1.922 (3) Å values found here).

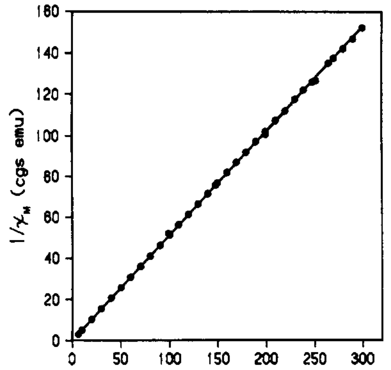

Figure 5. Magnetic behavior of $K_2[Mn(3,5\text{-}(t\text{-}Bu)_2Cat)_3]\cdot 6CH_3CN$.

of the $[Mn(3,5\text{-}(t\text{-}Bu)_2Cat)_3]^{2-}$ ion (51.8°) is 1.5° smaller than that predicted from this relation. Deviations of similar magnitude have been noted for other catechol complexes by the earlier workers.[5] Furthermore, the deviations appear to be correlated with crystal field stabilization energies.[5] For example, from d^1 to d^3 ions the deviation ($\Delta\phi$) in observed twist angle from that calculated decreases rapidly: viz, V(IV), 9.3°;[6] V(III), 3.1°;[6] Cr(III), 1.0°;[5] Mn(IV), 1.5°. This trend suggests that crystal field effects do play a significant role in determining the twist angle, as has been suggested earlier.[5]

Optical Spectra. Solutions of $(Et_3NH)_2[Mn(Cat)_3]$ in CH_3CN or CH_2Cl_2 exhibit an intense band at λ_{max} 585 nm (ϵ 4500 M^{-1} cm^{-1}, Figure 4), which causes the complex to be deep blue. This band is assigned to a catechol $\rightarrow$ Mn(IV) LMCT band on the basis of its high extinction coefficient. Similar LMCT bands have been reported for the tris(catecholate) complexes of Fe(III),[5] V(IV),[6] V(V),[6] and Ti(IV),[7] among others. No Mn(IV) d–d bands are observable owing to the intensity and breadth of this charge-transfer band. In contrast, the isoelectronic Cr(III) complex $[Cr(3,5\text{-}(t\text{-}Bu)_2Cat)_3]^{3-}$ has only d–d bands in the visible region,[29] a difference consistent with the difference in reduction potentials of Cr(III) and Mn(IV). The optical spectrum of $[Mn(3,5\text{-}(t\text{-}Bu)_2Cat)_3]^{2-}$ is essentially identical with that of $[Mn(Cat)_3]^{2-}$.

Magnetic Behavior. In the solid state $K_2[Mn(3,5\text{-}(t\text{-}Bu)_2Cat)_3]\cdot 6CH_3CN$ exhibits Curie–Weiss behavior over the region 200–6 K (C = 1.955 (5) K, Θ = –0.3 K) with a magnetic moment (corrected for diamagnetism) of 3.95 (1) μ_B ($\mu_{spin\text{-}only}$ = 3.87 μ_B for a d^3 system) (Figure 5).[33] Similar behavior is observed at room temperature for $(Et_3NH)_2[Mn(Cat)_3]$ in CH_3CN solution (μ = 3.88 μ_B) by the NMR method. Because of the large Mn–Mn separation in $[Mn(3,5\text{-}(t\text{-}Bu)_2Cat)_3]^{2-}$ (d_{min}(Mn–Mn) = 12 Å) intermolecular magnetic interaction between Mn ions is expected to be very small indeed: therefore the non-zero Weiss constant is probably attributable to zero-field splitting of the Mn(IV) ions, consistent with the EPR results (vide infra).

The magnetic behavior of $[Mn(3,5\text{-}(t\text{-}Bu)_2Cat)_3]^{2-}$ is that expected for a simple d^3 ion. There is no evidence for an increase in magnetic moment at higher temperatures, as would be expected for an antiferromagnetically coupled Mn(III)–semiquinone complex.

Electron Paramagnetic Resonance Spectra. At 77 K frozen solutions of $[Mn(Cat)_3]^{2-}$ in CH_3CN or CH_2Cl_2 exhibit an axial spectrum, with $g_{\parallel}$ = 2 and $g_{\perp}$ = 3.6.[34] Both lines are extremely broad, with line widths (ΔH_{pp}) of ~500 G. As a consequence of the extreme line breadth no ^{55}Mn hyperfine splitting was found. No EPR spectrum is observed for the $[Mn(Cat)_3]^{2-}$ ion at room temperature in CH_3CN or CH_2Cl_2.

The large g anisotropy of $[Mn(Cat)_3]^{2-}$ indicates that the Mn(IV) ion is in a field of axial rather than octahedral symmetry and that the zero-field splitting ($2D$) is large. The latter arises from the combined effect of an axial distortion and spin–orbit coupling (which mixes the $^4A_{2g}$ ground state with the $^4T_{2g}$ excited state). If $2D > h\nu$ ($h\nu$ = 0.31 cm^{-1} at X band), an axial spectrum is obtained, with effective g values $g_{\parallel} \approx 2$ and $g_{\perp} \approx 4$—just as observed for $[Mn(Cat)_3]^{2-}$.

We attribute the axial distortion and the resultant zero-field splitting of $[Mn(Cat)_3]^{2-}$ to the short bite distance of catechol.[35] Regular octahedral coordination of Mn(IV) at the observed Mn–O distance (1.91 (1) Å (average)) requires a ligand with 2.70-Å bite distance—hence Mn(IV) coordinated to catechol (bite distance 2.58 Å) *must suffer a trigonal compression.* The large zero-field splitting also provides an efficient relaxation mechanism, which accounts for the large line width and the failure to observe a room-temperature spectrum for $[Mn(Cat)_3]^{2-}$ (it also accounts for the previously reported[29] lack of a room-temperature spectrum for $[Cr^{III}(3,5\text{-}(t\text{-}Bu)_2Cat)_3]^{3-}$, which is isoelectronic with $[Mn(Cat)_3]^{2-}$).

Electron paramagnetic resonance spectra similar to that of $[Mn(Cat)_3]^{2-}$ have been seen previously for Mn(IV)-substituted heterpolymolybdates and -tungstates (g = 3.8)[36] and the tris(sorbitolato)manganese(IV)(2–) ion ($g_{\parallel}$ = 2, $g_{\perp}$ = 4)[37] as well as for other d^3 ions—e.g., for $[Cr(ox)_3]^{3+}$, $g_{\parallel} \approx 2$ and $g_{\perp} \approx 4$.[38] A beautiful example of the effect of extreme trigonal distortion on the EPR spectrum of a d^3 ion is provided by the work of Bradley, Gibson, and co-workers on tris(bis(trimethylsilyl)amido)chromium(III).[39] This complex is D_{3h} symmetry has $g_{\parallel}$ = 2, $g_{\perp} \approx 4$, and D = –1.85 cm^{-1}.

In short, the EPR specrum of $[Mn(Cat)_3]^{2-}$ is fully consistent with that expected for a d^3 ion and therefore strongly supports formulation of $[Mn(3,5\text{-}(t\text{-}Bu)_2Cat)_3]^{2-}$ as a Mn(IV)–catecholate complex.

Infrared Spectra. The infrared spectra of $K_2[Mn(3,5\text{-}(t\text{-}Bu)_2Cat)_3]\cdot 6CH_3CN$ and $(Et_3NH)_2[Mn(Cat)_3]$ are typical of metal–catecholate complexes and otherwise unremarkable. In contrast to $(Et_3NH)_2V(Cat)_3\cdot CH_3CN$,[6] for which no bands attributable to acetonitrile were observed, the C–N stretching vibration of the acetonitrile of crystallization of $K_2[Mn(3,5\text{-}(t\text{-}Bu)_2Cat)_3]\cdot 6CH_3CN$ appears at 2258 cm^{-1}. Bands in the 1440-cm^{-1} region have been suggested previously to be characteristic of semiquinone (as opposed to catechol) chelation.[40,41] Although $K_2[Mn(3,5\text{-}(t\text{-}Bu)_2Cat)_3]\cdot 6CH_3CN$ does not appear to contain a semiquinone ligand, it has a strong band at 1438 cm^{-1} (1468 cm^{-1} for $(Et_3NH)_2[Mn(Cat)_3]$). This result suggests that the infrared criterion be used with

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(32) The *tert*-butyl groups of 3,5-di-*tert*-butylcatechol do not perturb the twist angle sufficiently to vitiate comparison with complexes of catechol itself. Comparison of the isoelectronic complexes $[Mn(3,5\text{-}(t\text{-}Bu)_2Cat)_3]^{2-}$ and $[Cr(Cat)_3]^{3-}$ reveals nearly the same difference between observed and calculated twist angles (–1.5 and –1.0°, respectively). This observation encourages further comparison and suggests that the *tert*-butyl groups have only a minor effect on ϕ.

(33) Above 200 K greater deviation from the least-squares line was observed.

(34) The EPR spectrum of $[Mn(3,5\text{-}(t\text{-}Bu)_2Cat)_3]^{2-}$ has been the source of some confusion. This complex has been reported variously to exhibit an 11-line spectrum at 298 K with g = 2,[13] to have a two-line spectrum at 4 K with $g_{\parallel}$ = 2 and $g_{\perp}$ = 3.6,[14] and most recently to have no EPR spectrum at all (at 77 K).[31] We confirm the second report, having previously shown the first to be due to oxidation products of catechol,[15] but are unable to account for the third.

(35) While $(Et_3NH)_2[Mn(Cat)_3]$ has not been characterized structurally and by X-ray powder pattern is not isomorphous with $K_2[Mn(3,5\text{-}(t\text{-}Bu)_2Cat)_3]\cdot 6CH_3CN$, we presume that the axial symmetry observed in its EPR spectrum reflects trigonal site symmetry.

(36) Mishra, H. C.; Roy, S. K. *J. Indian Chem. Soc.* **1977**, *54*, 1105–6.

(37) Richens, D. T.; Sawyer, D. T. *J. Am. Chem. Soc.* **1979**, *101*, 3681–3.

(38) Singer, L. S. *J. Chem. Phys.* **1955**, *23*, 379–88.

(39) Bradley, D. C.; Copperthwaite, R. G.; Cotton, S. A.; Sales, K. D.; Gibson, J. F. *J. Chem. Soc., Dalton Trans.* **1973**, 191–4.

(40) Wicklund, P. A.; Beckmann, L. S.; Brown, D. G. *Inorg. Chem.* **1976**, *15*, 1996–7.

(41) Brown, D. G.; Hemphill, W. D. *Inorg. Chem.* **1979**, *18*, 2039–40.

caution in inferring whether a complex contains catecholate or semiquinone ligands.

Discussion

While the small bite distances of catechol causes trigonal compression and a highly anisotropic *g* factor for $[Mn(3,5\text{-}(t\text{-}Bu)_2Cat)_3]^{2-}$, for the larger Mn(III) ion it has a more profound effect: as a consequence of the small bite distance: Mn(III)–O bond length ratio, $[Mn^{III}(Cat)_3]^{3-}$ cannot even be *formed*. Reaction of $Mn(acac)_3$ with catechol in 1:2 ratio (in the presence of Et_3N) gives a green complex, $[Mn^{III}(Cat)_2(OH_2)_2]^-$.[42] The optical spectrum strongly resembles that of other bis(bidentate)diaquomanganese(III) ions (e.g. $[Mn^{III}(ox)_2(OH_2)_2]^-$ and $[Mn^{III}(mal)_2(OH_2)_2]^-$).[43] Addition of catechol even in 100-fold excess does not produce the tris complex, as evidenced by the lack of color change. (Similarly, electrochemical reduction of $[Mn(Cat)_3]^{2-}$ to $[Mn^{III}(Cat)_3]^{3-}$ is completely irreversible (see Experimental Section) apparently because reduction to Mn(III) is accompanied by rapid loss of a catechol.) Only at extremely high catechol concentration does the green bis complex become red, the color expected for the tris complex (cf. $[Mn^{III}(mal)_3]^{3-}$.[43] (This change can only be observed in nonaqueous solvents). Appearance of the red complex occurs only at such staggeringly high catechol concentrations (essentially a paste) that is might be due to coordination of two *monodentate* catechols rather than to chelation by one catechol. Monodentate coordination of catechol in a phenol-like fashion would of course require very high concentrations since the chelate effect would not be operative.

We consider the reluctance of Mn(III) to form a tris(catecholato) complex to be a consequence of both the Jahn–Teller distortion expected for Mn(III) and the short bite distance of catechol (2.58 Å). The present structural and EPR results show that the bite distance of catechol is short even for chelation to Mn(IV), which is smaller than Mn(III). The relative shortness of the catechol bite distance would be even more exaggerated in $[Mn^{III}(Cat)_3]^{3-}$, particularly if Jahn–Teller distorted. For concreteness assume the Mn(III) to be axially elongated: in this case formation of the tris complex would require two catechol ligands each to span a long axial and short equatorial site on an ion that even if octahedral would be too large for optimum coordination by catechol. At the same time, the axial Jahn–Teller elongation would imply equatorial *compression* of the coordination sphere, thereby *mitigating* the short catechol bite distance for the first two catechol ligands if they bind to equatorial positions. Accordingly, coordination of the first two catechol ligands (to yield a *trans*-bis(catecholato)manganese(III) species) should be particularly favorable, whereas coordination of a third catechol should be extremely *unfavorable*. As a consequence the ratio of the stepwise stability constants K_2/K_3 for addition of the second and third catechols, respectively, should be anomalously large for Mn(III).[44]

The above predictions are borne out qualitatively. While the requisite stability constant data for the Mn(III)–catechol system are unavailable, comparison with the well-studied Fe(III)–catechol system[45] is instructive (high-spin Mn(III) and Fe(III) have the same average ionic radius (0.785 Å)[46]). Both $[Fe^{III}(Cat)_2(OH_2)_2]^-$ and $[Mn^{III}(Cat)_2(OH_2)_2]^-$ are essentially fully formed (>99.9% in the case of Fe) at pH 10 when $[M(III)]_{tot}$ = 1 mM and $[cat]_{tot}$ = 2mM. At pH 10 and 3 mM $[cat]_{tot}$, >98% of the Fe(III) exists as $[Fe^{III}(cat)_3]^{3-}$. In striking contrast, even in *1 M* catechol (regardless of pH) there is *no* evidence whatsoever for the existence *in aqueous solution* of $[Mn^{III}(Cat)_3]^{3-}$. (Only in nonaqueous solution (vide supra) is there any evidence for this complex.) There is clearly a marked difference in K_2/K_3 for Fe(III) and Mn(III), despite their similarity in charge and average ionic radius. This difference apparently is attributable to Jahn–Teller distortion of Mn(III).

Another useful comparison is with a ligand of larger bite distance, such as acetylacetonate (acac) (2.8 Å[24] vs. 2.5–2.6 Å for catechol). While the bite distance of acac is sufficiently larger than that of catechol to permit facile formation of $Mn(acac)_3$,[47] coordination of the third acac to Mn(III) is much less favorable than to Fe(III) (log K_3 values are 3.86 and 7.4, respectively).[48]

The effect of Jahn–Teller destabilization of $[Mn^{III}(cat)_3]^{2-}$ has another ramification: it may contribute to the extreme unfavorability of forming $[Mn^{III}(Cat)_2(SQ)]^{2-}$. Equation 3 disfavors the Mn(III)–semiquinone complex relative to the Mn(IV)–catecholate complex (SQ = semiquinone).

$$\text{overall reaction:}\quad [Mn^{III}(Cat)_2(SQ)]^{2-} = [Mn^{IV}(Cat)_3]^{2-}$$

$$[Mn^{III}(Cat)_2(SQ)]^{2-} = [Mn^{III}(Cat)_2]^- + SQ^- \qquad (1)$$

$$SQ^- + e^- = Cat^{2-} \qquad (2)$$

$$[Mn^{III}(Cat)_2]^- + Cat^{2-} = [Mn^{III}(Cat)_3]^{3-} \qquad (3)$$

$$[Mn^{III}(Cat)_3]^{3-} = [Mn^{IV}(Cat)_3]^{2-} + e^- \qquad (4)$$

Conclusions

The present studies establish that $[Mn(3,5\text{-}(t\text{-}Bu)_2Cat)_3]^{2-}$ and $[Mn(Cat)_3]^{2-}$ are better formulated as Mn(IV)–catecholate complexes than Mn(III)–semiquinones; their existence underscores the remarkable ability of catechol to stabilize high oxidation states of metal ions. Analysis of the structure of $[Mn(3,5\text{-}(t\text{-}Bu)_2Cat)_3]^{2-}$ and other metal–catecholate complexes reveals the chemical significance of the short bite distance of catechol, a consideration hitherto unappreciated. In the present system this significance is clearly manifest: it effectively prevents formation of $[Mn^{III}(Cat)_3]^{3-}$ and somewhat disfavors the Mn(III)–semiquinone complex with respect to the Mn(IV)–catecholate. Since the bite distance is "short" relative to the M–O bond length, a short M–O bond length reduces the disparity between the bite distance offered by catechol and that necessary for octahedral coordination. Such short M–O bonds are found for high-oxidation-state ions, where the better "fit" expected may contribute significantly to the affinity of catechol for high-oxidation-state ions generally.

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(42) This tentative assignment is based on the manganese analysis and optical spectrum (see text) of the complex. The complex has 8.8% Mn (determined spectrophotometrically as MnO_4^-); 8.7% Mn is calculated for $(Et_3NH)[Mn^{III}(Cat)_2(OH_2)_2]$.

(43) Dingle, R. *Acta Chem. Scand.* **1966**, *20*, 33–44.

(44) A parallel argument for the axially compressed case leads to the same conclusion except that a *cis*-bis(catecholate) arrangement would be more favorable than a trans arrangement.

(45) Avdeef, A.; Sofen, S. R.; Bregante, T. L.; Raymond, K. N. *J. Am. Chem. Soc.* **1978**, *100*, 5362–70.

(46) Shannon, R. D. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1976**, *A32*, 751–67.

(47) Manganese(III) tris(tropolonate) exists, despite having a bite distance (2.55 Å)[25] comparable to that of catechol. While this observation tends to militate against the present discussion, the two forms in which manganese(III) tris(tropolonate) exists are both severely distorted from tetragonal symmetry. In the orthorhombically distorted form there are three different Mn–O bond lengths (1.94, 1.99, and 2.05 Å);[25] in the nominally tetragonally distorted form the elongated axis is bent by *17°* from linearity.[25] Evidently the interaction between Mn(III) and tropolonate is strong enough to induce sufficient distortion about the Mn to permit coordination, while that between Mn(III) and catechol is not.

(48) Martell, A. E.; Sillen, L. G. *Spec. Publ.-Chem. Soc.* **1964**, *No. 17*, 445.

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Registry No. $K_2[Mn(3,5\text{-}(t\text{-}Bu)_2Cat)_3]\cdot 6CH_3CN$, 83945-00-0; $(Et_3NH)_2[Mn(Cat)_3]$, 89164-55-6; $[Mn(Cat)_3]^{2-}$, 89144-62-7; $(Et_3NH)[Mn^{III}(Cat)_2(OH_2)_2]$, 89144-61-6; $Mn(acac)_3$, 14284-89-0; Mn, 7439-96-5.

Supplementary Material Available: Listings of atomic positional and thermal parameters, bond distances and angles, observed and calculated structure factors, and magnetic susceptibility data (15 pages). Ordering information is given on any current masthead page.

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Synthesis and Crystal Structure of Bis(μ-hydroxo)bis[oxo(1,4,7-triazacyclononane)vanadium(IV)] Dibromide, a μ-Hydroxo-Bridged Cation with Antiferromagnetically Coupled V(IV) Centers

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The reaction of $VO(SO_4)\cdot 5H_2O$ with 1,4,7-triazacyclononane ([9]aneN_3, $C_6H_{15}N_3$) in H_2O yields dinuclear μ-hydroxo-bridged complexes of vanadium(IV). Blue $[V_2O_2(\mu\text{-}OH)(\mu\text{-}SO_4)([9]aneN_3)_2]ClO_4\cdot 2H_2O$ and gray salts (bromide, iodide, perchlorate) containing the cation $[V_2O_2(\mu\text{-}OH)_2([9]aneN_3)_2]^{2+}$ have been isolated. $[V_2O_2(\mu\text{-}OH)_2([9]aneN_3)_2]Br_2$ crystallizes in the monoclinic space group $P2_1/c$ (C_{2h}^5, No. 14) with $a = 7.236$ (1) Å, $b = 14.003$ (2) Å, $c = 10.405$ (2) Å, $\beta = 97.37$ (2)°, $V = 1045.8$ (3) Å^3, and $d_{calcd} = 1.861$ g/cm^3 for $Z = 2$ and molecular weight 586.1. Least-squares refinement of the structure based on 1199 observations led to final discrepancy indices of $R_1 = 0.043$ and $R_2 = 0.037$. The structure consists of discrete dinuclear cations with crystallographically imposed C_i symmetry. The geometry around each vanadium is distorted octahedral: a terminal oxo group, V–O2 = 1.603 (5) Å, two hydroxo bridges, V–O1 = 1.956 (5) Å and V–O1′ = 1.969 (5) Å, and the tridentate cyclic amine. There are two distinct V–N bond lengths of 2.303 (6) Å for the nitrogen trans to the terminal oxo group and 2.151 (5) and 2.159 (5) Å for the nitrogens trans to the hydroxo bridges. Magnetic susceptibility measurements indicate strong antiferromagnetic coupling of the two vanadium(IV) centers (d^1–d^1 configuration; $J = -177$ cm^{-1}).

Introduction

The structural chemistry of dinuclear complexes of vanadium(IV) has received surprisingly little attention in the past. Only a rather limited number of dinuclear complexes have been synthesized and characterized by X-ray diffraction methods.[2-4] In particular, although a dinuclear complex containing μ-fluoro bridges, $[N(CH_3)_4]_2[V_2O_2(OH)_2(\mu\text{-}F)_2F_4]$, with a V⋯V distance of 3.292 (1) Å has been reported,[4] no such complex appears to have been synthesized containing structurally very similar μ-hydroxo bridges. The neutral complex $V_2O_2Cl_4(\mu\text{-}Hmph)_3\cdot CH_2Cl_2$ (Hmph = 2-hydroxy-6-methylpyridine) has a V⋯V distance of 3.175 (1) Å[2]. No magnetic measurements on such dinuclear d^1–d^1 species of vanadium(IV) have been reported although interesting antiferromagnetic coupling should be expected.[5] An additional point of interest is the possibility of direct metal–metal bonding, which has been observed for dinuclear vanadium(II) and vanadium(III) compounds.[6,7]

In this paper we describe the synthesis and X-ray crystallographic and magnetic characterization of the first bis(μ-hydroxo)-bridged complex of vanadium(IV).

Experimental Section

The ligand 1,4,7-triazacyclononane was prepared according to procedures described in the literature.[8] The magnetic susceptibilities of powdered samples were measured by the Faraday method (Sartorius microbalance, Bruker B-E10C8 research magnet, and Bruker B-VT 1000 automatic temperature control) between 93 and 300 K.

Preparation of $[V_2O_2(\mu\text{-}OH)_2([9]aneN_3)_2]Br_2$. To 1,4,7-triazacyclononane ($C_6H_{15}N_3$ = [9]aneN_3) (1.3 g) dissolved in 40 mL of water was added $VOSO_4\cdot 5H_2O$ (2.5 g). The temperature was raised to 60 °C for 15 min. To the filtered solution was added NaBr (15 g), and the pH of the solution was adjusted to 4 with 0.1 M NaOH. A blue-violet precipitate formed, which was filtered off and was recrystallized from an aqueous solution with NaBr. Gray crystals were obtained (1.2 g). X-ray-quality single crystals were grown from such solutions at 0 °C. Anal. Calcd for $V_2C_{12}H_{32}N_6O_4Br_2$: C, 24.59; H, 5.5; N, 14.34; Br, 27.27; V, 17.38. Found: C, 24.4; H, 5.2; N, 13.7; Br, 27.3; V, 17.4. Iodide and perchlorate salts were obtained analogously.

Preparation of $[VO(NCS)_2([9]aneN_3)]$. To 1,4,7-triazacyclononane (1.3 g) dissolved in 40 mL of water was added $VOSO_4\cdot 5H_2O$ (2.5 g). A precipitate formed immediately, which dissolved slowly upon heating the solution to 60 °C, during which time the pH of the solution dropped from ~9 to 3. To the filtered solution was added NaSCN (15 g). When the solution was cooled (10 °C), blue-violet crystals precipitated, which were filtered off, washed with ethanol and ether, and air-dried. The material was recrystallized from acetone; yield 2.1 g. Anal. Calcd for $VO(SCN)_2$ $(C_6H_{15}N_3)$: C, 30.77; H, 4.84; N, 22.43; S, 20.53. Found: C, 30.7; H, 4.9; N, 22.4; S, 20.3.

Preparation of $[V_2O_2(\mu\text{-}OH)(\mu\text{-}SO_4)([9]aneN_3)_2](ClO_4)\cdot 2H_2O$. To a solution of 1,4,7-triazacyclononane (0.65 g) in 10 mL of water was added a solution of $VOSO_4\cdot 5H_2O$ (1.2 g) in 10 mL of H_2O. The solution was heated to 60 °C until the formed precipitate was redissolved and the pH of the solution had dropped to 4–3. To the filtered solution was added solid $NaClO_4$ (10 g). When the mixture was cooled, a blue microcrystalline product was obtained. Attempts to recrystallize this material from aqueous solutions afforded the sulfate-free $[V_2O_2(\mu\text{-}OH)_2([9]aneN_3)_2](ClO_4)_2\cdot H_2O$. Anal. Calcd for $[V_2O_2(\mu\text{-}OH)(\mu\text{-}SO_4)(C_6H_{15}N_3)_2]ClO_4\cdot 2H_2O$: C, 22.49; H, 5.51; N, 13.11; V, 15.90; ClO_4, 15.52; SO_4, 14.99. Found: C, 22.1; H, 5.1; N, 12.8; V, 15.9; ClO_4, 16.1; SO_4, 14.5. An iodide salt, $[V_2O_2(\mu\text{-}OH)(\mu\text{-}SO_4)([9]aneN_3)_2]I$, has been prepared with use of NaI instead of $NaClO_4$.

X-ray Structural Determination of $[V_2O_2(\mu\text{-}OH)_2([9]aneN_3)_2]Br_2$. A gray prismatic crystal of $[V_2O_2(\mu\text{-}OH)_2([9]aneN_3)_2]Br_2$ was attached to the end of a glass fiber and mounted on a Syntex R3 four-circle diffractometer. Preliminary examinations showed that the crystal belonged to the monoclinic system, space group $P2_1/c$. The

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(1) (a) Ruhr-Universität Bochum. (b) Universität Heidelberg.
(2) Cotton, F. A.; Lewis, G. E.; Mott, G. N. *Inorg. Chem.* **1983**, *22*, 378.
(3) Walterson, K. *Cryst. Struct. Commun.* **1978**, *7*, 507.
(4) Bukovec, P.; Miličev, S.; Demšăr, A.; Golič, L. *J. Chem. Soc., Dalton Trans.* **1981**, 1802.
(5) Hodgson, D. J. *Prog. Inorg. Chem.* **1975**, *19*, 173.
(6) Cotton, F. A.; Millar, M. *J. Am. Chem. Soc.* **1977**, *99*, 7886.
(7) Cotton, F. A.; Lewis, G. E.; Mott, G. N. *Inorg. Chem.* **1983**, *22*, 560.
(8) (a) Atkins, T. J.; Richman, J. E.; Oettle, W. F. *Org. Synth.* **1978**, *58*, 86. (b) Wieghardt, K.; Schmidt, W.; Nuber, B.; Weiss, J. *Chem. Ber.* **1979**, *112*, 2220.

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