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Crystal Structure and Magnetic Susceptibility of the Dinuclear Manganese(IV) Complex $Mn_2O_2(pic)_4 \cdot MeCN$ (picH = Picolinic Acid)

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Treatment of $[Mn_3O(OAc)_6(py)_3](ClO_4)$ in MeCN with Me_3SiCl followed by sodium picolinate, Na(pic), leads to slow crystallization of the known dimanganese(IV) complex $Mn_2O_2(pic)_4 \cdot MeCN$ (**1**·MeCN) in a form suitable for crystallography. This has allowed the structure of this complex to be finally obtained some 16 years after its original preparation. Complex **1**·MeCN crystallizes in tetragonal space group $P4/ncc$ with (at -154 °C) $a = b = 12.918$ (5) Å, $c = 15.726$ (5) Å, $Z = 4$, and $V = 2624.19$ Å^3. The structure was solved and refined by using 698 unique reflections with $F > 3.0\sigma(F)$ collected in the range $6° \leq 2\theta \leq 50°$. Final values of conventional indices R and R_w were both 4.11%. The structure consists of a $Mn_2(\mu\text{-}O)_2$ core with a Mn···Mn separation of 2.747 (2) Å. Peripheral ligation is provided by four bidentate pic$^-$ ligands disposed to give (imposed) D_2 symmetry and approximately octahedral metal geometry. Variable-temperature solid-state magnetic susceptibility data were collected in the range 10–320 K. The effective magnetic moment, μ_{eff}, gradually decreases from 3.09 μ_B/Mn_2 at 319 K to 1.10 μ_B at 10 K. The data were least-squares fit to the theoretical expression derived for an isotropic exchange interaction between two $S = {}^3/_2$ centers to give $J = -86.5$ cm^{-1} and $g = 1.83$. The magnitude of the antiferromagnetic exchange interaction is the smallest yet found in a $[Mn_2O_2]^{3+,4+}$ species, and a possible rationalization is presented.

Introduction

There is continuing intense interest in the synthesis and characterization of higher oxidation state manganese complexes with oxide (O^{2-}) bridges. This is primarily due to the identification of several Mn biomolecules that appear to contain di- or tetranuclear Mn units, including the water oxidation/oxygen evolution center within the photosynthetic apparatus of green plants and cyanobacteria,[2] the Mn catalases,[3] and possibly even the recently identified Mn ribonucleotide reductases.[4] The identification by the EXAFS technique of a short (~2.72 (3) Å) Mn···Mn separation[5] and the realization that such a separation results from the presence of two $\mu\text{-}O^{2-}$ bridges[6] have resulted in a growing pool of such species being prepared and studied.

Restricting further discussion to dinuclear species, the $Mn(\mu\text{-}O)_2Mn$ bridging unit has been structurally characterized to date only for $Mn^{III}Mn^{IV}$ and $Mn^{IV}Mn^{IV}$ complexes. Although several examples of the former are now known, examples of the latter are extremely few (vide infra). One potential member of this group has been known since 1973, however; the complex $[MnO(pic)_2]_n$ (picH = picolinic acid) displayed properties appropriate for a Mn^{IV} complex and magnetic susceptibility behavior characteristic of an $n > 1$ species.[7] The authors suggested the formulation $Mn_2O_2(pic)_4$ (**1**), but noted that a higher oligomer could not be ruled out. The very low solubility and platelike crystallinity of the material precluded a crystallographic investigation. The complex has since been prepared by other workers,[8] and all observed behavior has been consistent with the dinuclear formulation. During our own recent interest in Mn picolinate chemistry, we found this complex crystallizing slowly in a form suitable for crystallography and took advantage of this fact to finally obtain its crystal structure. We herein report the details of this investigation, together with the results of a detailed variable-temperature magnetic susceptibility investigation of a polycrystalline sample.

Experimental Section

Syntheses. The complex $[Mn_3O(OAc)_6(py)_3](ClO_4)$ was available from previous work.[9] Solid sodium picolinate Na(pic) was isolated as the dihydrate by treatment of picolinic acid with 1 equiv of NaOH in aqueous EtOH, followed by addition of Et_2O. The resulting white solid was filtered, washed copiously with $EtOH/Et_2O$ (1:1), and dried in vacuo (yield 76%). Me_3SiCl was used as received; MeCN was dried by distillation from CaH_2.

A stirred solution of $[Mn_3O(OAc)_6(py)_3](ClO_4)$ (0.87 g, 1.00 mmol) in MeCN (50 cm^3) was treated dropwise with Me_3SiCl (0.70 cm^3, 5.5 mmol) followed by addition of a solution of $Na(pic) \cdot 2H_2O$ (0.44 g, 2.88 mmol) in water (0.30 cm^3). After a few minutes, the resulting reaction mixture was filtered to remove some brown precipitate and the filtrate stored at 5 °C for 2 days. The resulting well-formed black needles of $Mn_2O_2(pic)_4 \cdot MeCN$ were collected by filtration, washed with MeCN (4 × 5 cm^3), and dried in vacuo. The yield was typically ~0.20 g (19% based on total available Mn). IR data (Nujol): ~3400 (br), 3090 (w), 3050 (w), 2275 (w), 1670 (s), 1605 (m), 1325 (s), 1275 (s), 1150 (m), 1040 (m), 845 (m), 765 (m), 705 (s), 675 (m), 640 (s), 455 (s), 405 (m) cm^{-1}. The material is only sparingly soluble in DMF and DMSO. The IR feature at ~3400 cm^{-1} assignable to H_2O molecules suggested the dried solid to be hygroscopic, and this was supported by the analytical data, which gave a reasonable fit for $Mn_2O_2(pic)_4 \cdot MeCN \cdot H_2O$. Anal. Calcd for $C_{26}H_{21}N_5O_{11}Mn_2$: C, 45.30; H, 3.07; N, 10.16; Mn, 15.94. Found: C, 45.1; H, 2.9; N, 10.7; Mn, 15.2. We have been unable to find a suitable recrystallization procedure due to the low solubility.

Table I. Crystallographic Data for Complex **1**

$C_{26}H_{19}N_5O_{10}Mn_2$	space group $P4/ncc$
$M_r = 671.35$	$T = -154$ °C
$a = b = 12.918$ (5) Å	$\lambda = 0.71069$ Å
$c = 15.726$ (5) Å	range $6° \leq 2\theta \leq 50°$
$Z = 4$	no. of obsd data 698
$V = 2624.19$ Å^3	$F > 3.0\sigma(F)$
$\rho_{calcd} = 1.699$ g cm^{-3}	$R = 4.11\%$
$\mu = 9.906$ cm^{-1}	$R_w = 4.11\%$

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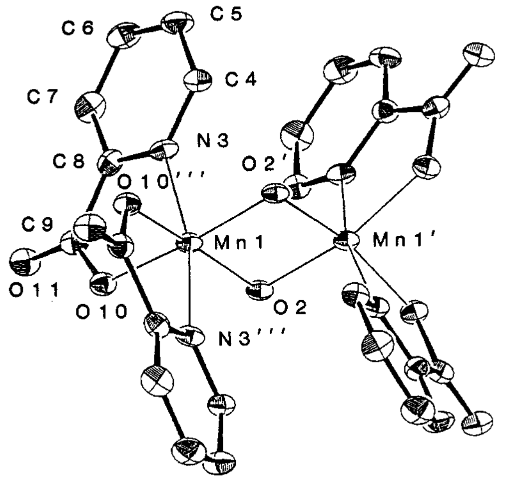

Figure 1. ORTEP representation of complex **1** at the 50% probability level. Unprimed and variously primed atoms are related by the rotation axes.

X-ray Crystallography and Structure Solution. Data were collected on a Picker four-circle diffractometer by using standard low-temperature facilities; details of the diffractometry, low-temperature facilities, and computational procedures employed by the Molecular Structure Center are available elsewhere.[10] Data collection parameters are summarized in Table I. A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima and systematic absences corresponding to the tetragonal space group *P4/ncc*. Attempts to solve the structure by direct methods were unsuccessful. Use of a Patterson map located the Mn atoms, and most of the remaining atoms were obtained from difference Fourier maps; however, the molecule would not refine properly, and it appeared that its position was incorrect. The center of the molecule was then relocated to a site of 222 symmetry, and refinement then proceeded satisfactorily. The asymmetric unit contains one-quarter of the molecule. All non-hydrogen atoms were refined with anisotropic thermal parameters by a full-matrix least-squares procedure. In the latter stages, hydrogen atoms were located and refined with isotropic thermal parameters. A MeCN solvate molecule was also located lying on a crystallographic 4-fold axis disordering its hydrogen atoms; thus, only the non-hydrogen atoms were included and refined. The final difference Fourier was essentially featureless, the largest peak being 0.6 e/Å^3 near the MeCN molecule. Final discrepancy indices are included in Table I.

Other Measurements. Variable-temperature magnetic susceptibility data were measured by using a series 800 VTS-50 SQUID susceptometer. The susceptometer was operated at a magnetic field strength of 10 kG. Diamagnetic corrections were estimated from Pascal's constants and subtracted from the experimental susceptibility data to obtain the molar paramagnetic susceptibilities of the compounds, which were then fit to the appropriate theoretical expressions by means of a least-squares-fitting computer program.[11] Infrared (Nujol mull) spectra were recorded on a Perkin-Elmer Model 283 spectrophotometer. Cyclic voltammograms were recorded on an IBM Model EC 225 voltammetric analyzer using a standard three-electrode assembly (glassy carbon working, Pt wire auxiliary, SCE reference) and 0.1 M $\mathrm{NBu^n_4ClO_4}$ as supporting electrolyte. The scan rate was 100 mV/s, and no *iR* compensation was employed.[12]

Results and Discussion

Synthesis and Structure. The present procedure to prepare complex **1**·MeCN has little to recommend it over two other procedures available in the literature.[7,8] The latter involve the oxidation of readily available Mn^{II} starting materials ($\mathrm{Mn(OAc)_2}$, $\mathrm{MnCO_3}$) with inexpensive reagents ($\mathrm{K_2S_2O_8}$, $\mathrm{KMnO_4}$), and the product is obtained in good yield and purity. The present procedure was discovered as part of our continuing investigation into the reactions of trinuclear $[\mathrm{Mn_3O}]^{7+}$-containing complexes with $\mathrm{Me_3SiCl}$. As we have also found previously for other reactions,[13] the reaction in the presence of picolinate leads to a disproportionation and the precipitation of a Mn^{IV}-containing product. The low yield of product (~19%) is primarily a consequence of this disproportionation,[14] since the maximum theoretical yield based on eq 1 is 50%. In addition, the crystallization filtrate is still darkly

$$4\mathrm{Mn^{III}} \rightarrow \mathrm{Mn^{IV}_2} + 2\mathrm{Mn^{II}} \qquad (1)$$

colored with additional Mn^{III} and/or Mn^{IV} products, but we have yet to identify these. The advantage of the present procedure is its slow crystallization of product and the well-formed nature of the resulting black crystals that have proven excellent diffractors of X-rays.

Table II. Fractional Coordinates (×10^4) and Thermal Parameters (×10)[a]

atom	*x*	*y*	*z*	B_{iso}
Mn(1)	7500*	2500*	31373 (1)	13
O(2)	6847 (2)	3153*	2500*	13
N(3)	6244 (3)	1603 (3)	3509 (3)	15
C(4)	5308 (4)	1763 (5)	3150 (4)	16
C(5)	4513 (5)	1076 (5)	3275 (4)	22
C(6)	4684 (5)	194 (6)	3739 (4)	23
C(7)	5649 (5)	33 (5)	4105 (4)	21
C(8)	6403 (4)	760 (4)	3990 (4)	16
C(9)	7470 (6)	720 (4)	4392 (3)	16
O(10)	8034 (3)	1523 (3)	4199 (2)	16
O(11)	7726 (3)	5 (3)	4838 (2)	20
C(12)	7500*	7500*	4729 (8)	30 (2)
C(13)	7500*	7500*	3811 (12)	54 (4)
N(14)	7500*	7500*	3064 (10)	63 (4)

[a] Parameters marked with an asterisk were not varied.

Table III. Selected Bond Distances (Å) and Angles (deg)

(a) Bonds			
Mn(1)···Mn(1)′	2.747 (2)	Mn(1)–O(2)	1.819 (3)
Mn(1)–N(3)	2.006 (4)	Mn(1)–O(10)	1.937 (4)
(b) Angles			
O(2)–Mn(1)–O(2)′	81.9 (2)	O(10)–Mn(1)–O(10)‴	95.9 (2)
O(2)–Mn(1)–O(10)	92.2 (2)	N(3)–Mn(1)–O(10)	80.8 (2)
O(2)–Mn(1)–N(3)	100.8 (2)	N(3)–Mn(1)–O(10)‴	91.0 (2)
O(2)′–Mn(1)–N(3)	88.5 (1)	N(3)–Mn(1)–N(3)‴	167.8 (3)
O(2)′–Mn(1)–O(10)	166.7 (1)	Mn(1)–O(2)–Mn(1)′	98.1 (2)

The structure of complex **1** is shown in Figure 1; fractional coordinates and selected structural parameters are listed in Tables II and III, respectively. The structure consists of two Mn^{IV} centers bridged by two μ-O^{2-} ions across a Mn···Mn separation of 2.747 (2) Å to yield a planar $\mathrm{Mn_2O_2}$ core. Approximately octahedral coordination at each Mn is completed by four peripheral picolinate groups whose carboxylate oxygens occupy the positions trans to the bridging oxides. The disposition of the picolinate groups results in D_2 symmetry for the complex, all of whose elements are crystallographically imposed with the asymmetric unit consequently containing one-quarter of the molecule.

In an attempt to ascertain whether the material obtained by Walton and co-workers did indeed correspond to that from the present work, a sample was prepared by their original method.[7] An IR comparison shows the two spectra to be essentially superimposable, except for the bands from the solvate molecules in the sample from the present work. In addition, the solubility characteristics of the two materials are identical, being only sparingly soluble in DMF and DMSO.

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(14) Mn^{II} byproducts (tan or pink solids) are also obtained in the $\mathrm{Me_3SiCl}$ reactions, supporting disproportionation as the source of Mn^{IV}; in this particular reaction, we have not pursued the identity of the Mn^{II} product.

Table IV. Comparative Data for Mn_2O_2-Containing Complexes

complex[a]	Mn···Mn, Å	Mn–O_b, Å	Mn–O–Mn, deg	J, cm^{-1} [b]
1	2.747 (2)[c]	1.819 (3)	98.1 (2)	–87
$[Mn_2O_2(OH)_2(TACN)_2]^{2+}$	2.625 (2)[d]	1.818–1.834	91.9 (2)	na
$[Mn_2O_2(phen)_4]^{4+}$	2.748 (2)[e]	1.797–1.805	99.5 (2)	–144
$[Mn_2O_2(bpy)_4]^{3+}$	2.716 (na)[f]	1.784–1.856	na	–150
$[Mn_2O_2(phen)_4]^{3+}$	2.700 (1)[e]	1.808–1.820	96.0 (1)	–134
$[Mn_2O_2(bispicen)_2]^{3+}$	2.659 (2)[g]	1.793–1.833	na	na
$[Mn_2O_2(tren)_2]^{3+}$	2.679 (1)[h]	1.773–1.852	95.4 (2)	–146
$[Mn_2O_2(N_3O\text{-}py)_2]^{+}$	2.656 (2)[i]	1.784–1.822	94.0 (3)	–151
$[Mn_2O_2(tpa)_2]^{3+}$	2.643 (1)[j]	1.771–1.839	na	na
$[Mn_2O_2(OAc)(TACN)_2]^{2+}$	2.588 (2)[k]	1.808–1.817	91.1 (1)	–220
$Mn_2O_2(OAc)Cl_2(bpy)_2$	2.667 (2)[l]	1.793–1.843	94.4 (2)	–114
$[Mn_2O_3(TMACN)_2]^{2+}$	2.296 (2)[d]	1.817–1.833	78.0, 78.2	–390

[a] The first three and the last entries are Mn^{IV}_2; the rest are $Mn^{III}Mn^{IV}$. Abbreviations: TACN = 1,4,7-triazacyclononane; TMACN = 1,4,7-trimethyl-1,4,7-triazacyclononane; phen = 1,10-phenanthroline; bpy = 2,2′-bipyridine; bispicen = *N,N′*-bis(2-pyridylmethyl)ethane-1,2-diamine; tren = tris(2-aminoethyl)amine; N_3O-py = *N,N*-bis(2-pyridylmethyl)glycinate; tpa = tris(2-pyridylmethyl)amine; na = not available. [b] Based on the spin Hamiltonian $\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2$. [c] This work. [d] Reference 15. [e] Reference 16; 100 K data are quoted. [f] Reference 17. [g] Reference 18. [h] Reference 19. [i] Reference 20. [j] Reference 21. [k] Reference 22. [l] Reference 13a.

Complex **1** represents the third structurally characterized example of a $[Mn_2O_2]^{4+}$ complex; in contrast, several structurally characterized examples of $[Mn_2O_2]^{3+}$ complexes are now known. Since most of these were reported only recently, we felt it timely to collect these in Table IV, together with selected structural parameters for convenient comparison. We have also included the remarkable complex $[Mn_2O_3(TMACN)_2](PF_6)_2$, possessing a $[Mn^{IV}_2(\mu\text{-}O)_3]^{2+}$ core. Some general conclusions are readily evident from Table IV: (i) Mn···Mn separations are in the fairly narrow range of 2.588–2.748 Å, and there is no correlation between Mn···Mn separation and oxidation level ($Mn^{III}Mn^{IV}$ vs Mn^{IV}_2). Only when a third O^{2-} bridge is present does the Mn···Mn separation alter appreciably, to 2.296 Å. In addition, we have already pointed out elsewhere[6] that if only *one* O^{2-} bridge is present Mn···Mn separations are invariably >3 Å. (ii) Variations in Mn–O (bridging) distances are again small, with the greater *range* of distances seen in the $Mn^{III}Mn^{IV}$ complexes being due to their trapped-valence nature and the noticeably smaller Mn^{IV}–O versus Mn^{III}–O distances. (iii) The bridging Mn–O–Mn angles are all in the fairly narrow range 91.1–99.5°, with a significantly more acute angle (of ~78°) only being seen when the third O^{2-} decreases the Mn···Mn separation.

It has been noted above that EXAFS data on the water oxidation enzyme indicate the presence of a Mn···Mn separation of 2.72 (3) Å. We recently concluded that this separation was consistent only with a $(\mu\text{-}O^{2-})_2$ bridge,[6] on the basis of the handful of available synthetic complexes with this core; this conclusion is still valid even with the significantly greater number of Mn_2O_2 complexes now available and listed in Table IV.

Magnetic Susceptibility Studies. With the structure of complex **1**·MeCN unequivocally established, we undertook an investigation of its magnetic susceptibility properties. Variable-temperature, solid-state susceptibility measurements were made on powdered samples in the temperature range 10–320 K. The effective magnetic moment per dinuclear complex, μ_{eff}/Mn_2, gradually decreases from 3.09 μ_B at 319 K to a value of 1.27 μ_B at 50 K, below which it decreases more gradually to 1.10 μ_B at 10 K (Figure 2). The 319 K value corresponds to 2.18 μ_B/Mn^{IV}, considerably less than the value expected for a magnetically isolated Mn^{IV} (d^3) ion (3.87 μ_B).

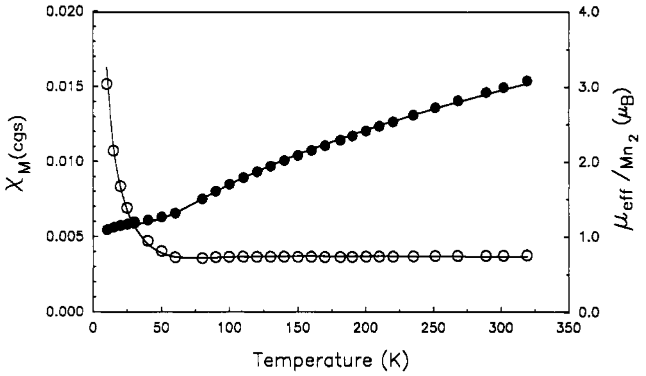

Figure 2. Plots of the molar paramagnetic susceptibility, χ_M (○), and effective magnetic moment per dinuclear complex, μ_{eff}/Mn_2 (●), versus temperature for a polycrystalline sample of complex **1**·MeCN. The solid lines result from a least-squares fit of the susceptibility data to eq 2. See the text for fitting parameters.

A theoretical expression describing the molar magnetic susceptibility (χ_M/Mn_2) versus temperature dependence was derived by employing the isotropic spin Hamiltonian $\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2$ and the van Vleck equation.[23] For complex **1**, $S_1 = S_2 = {}^3/_2$ and the derived expression is given in eq 2, where $x = J/kT$, μ_B is the Bohr magneton, and the other symbols have their usual meaning. The experimental data were fit to this expression by using a least-squares-fitting computer program.[11] A satisfactory fit was obtained with $J = -86.5$ cm^{-1}, $g = 1.83$, TIP = 400 × 10^{-6} cgsu, and PAR = 0.5%, where TIP is the temperature-independent paramagnetism and PAR is the percentage of a paramagnetic impurity assumed to be a mononuclear Mn^{IV} species.

$$\chi_M = \frac{Ng^2\mu_B^2}{kT}\left[\frac{2\exp(2x) + 10\exp(6x) + 28\exp(12x)}{1 + 3\exp(2x) + 5\exp(6x) + 7\exp(12x)}\right] \qquad (2)$$

The magnitude and sign of the magnetic exchange interaction J determined for complex **1** can be compared to those determined for other $[Mn_2O_2]^{3+,4+}$ species. Where available, these values have been included for the complexes in Table IV. In all cases the exchange interactions in such complexes are antiferromagnetic (negative J values) and in the range $|J|$ = 87–220 cm^{-1}. The value for complex **1** is thus the smallest to be observed to date. Since there is nothing in its structural parameters that would rationalize this difference, it is tempting to assign the latter to the increased O-based peripheral ligation relative to the other complexes in Table IV, which are predominantly N-ligated. A significant number of better π-bonding oxygen ligands would be expected to increase

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the energy of the metal d_π ("t_{2g}") orbitals, which are π^* with respect to metal–ligand bonding. Relative to complete N-ligation, this would increase the energy mismatch between these d orbitals and the bridging oxide p_π orbitals that mediate the π-superexchange mechanism, and hence decrease the magnitude of the antiferromagnetic exchange interaction. However, additional examples are required before such arguments can be entertained further.

An increase to 3 in the number of bridging oxides increases the magnitude of the antiferromagnetic exchange interaction to $-390\ \text{cm}^{-1}$, whereas a decrease to a single oxide bridge decreases the magnitude of this interaction, in some cases becoming weakly ferromagnetic (positive *J*). Thus, the growing pool of mono-, bis-, and now tris(oxide)-bridged systems continues to support the belief that the number of oxide bridges (and its resulting influence on the Mn···Mn separation and Mn–O–Mn bridging angles) represents the single most important parameter influencing the magnitude of the magnetic exchange interactions in discrete oxide-bridged Mn complexes.

Electrochemistry. The electrochemical properties of complex **1** in DMF solution were investigated by the cyclic voltammetric technique. Two processes were observed, a reversible one-electron reduction at +0.66 V vs SCE ($i_c/i_a = 1.02$; $\Delta E_p = 110$ mV) and an irreversible reduction at $E_{p,c} = -0.47$ V. These observations define the three-component electron-transfer series of eq 3. These

$$\text{Mn}^{IV}\text{Mn}^{IV} \xrightleftharpoons{+0.66\text{ V}} \text{Mn}^{III}\text{Mn}^{IV} \xrightarrow{-0.47\text{ V}} \text{Mn}^{III}\text{Mn}^{III} \quad (3)$$

values compare reasonably well with those found for $(\text{NMe}_4)[\text{Mn}_2\text{O}_2(\text{pic})_4]$ in MeCN;[8] this compound is the one-electron-reduced version ($\text{Mn}^{III}\text{Mn}^{IV}$) of complex **1**, and it displays a reversible one-electron oxidation to **1** at +0.53 V vs SCE and an irreversible reduction at −0.42 V.

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Registry No. 1·MeCN, 122797-77-7; $[\text{Mn}_3\text{O}(\text{OAc})_6(\text{py})_3](\text{ClO}_4)$, 52705-71-2.

Supplementary Material Available: Complete listings of data collection and refinement parameters, crystal data, atomic coordinates, anisotropic thermal parameters, bond lengths and angles, and observed and calculated magnetic susceptibility data (6 pages); a list of observed and calculated structure factors (2 pages). Ordering information is given on any current masthead page. A complete MSC structure report (No. 87168) is available on request from the Indiana University Chemistry Library.

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Crown Thioether Chemistry. The Silver(I) Complexes of Trithia-9-crown-3, Trithia-12-crown-3, and Hexathia-18-crown-6

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The coordination chemistry of the three crown thioethers 1,4,7-trithiacyclononane (9S3), 1,5,9-trithiacyclododecane (12S3), and 1,4,7,10,13,16-hexathiacyclooctadecane (18S6) with Ag(I) has been investigated by structural and electrochemical methods. The bis complex $[\text{Ag}(9\text{S}3)_2](\text{CF}_3\text{SO}_3)$ contains a six-coordinate Ag(I) ion with Ag–S distances ranging from 2.696 (2) to 2.753 (1) Å. Chemical or electrochemical oxidation yields $[\text{Ag}(9\text{S}3)_2]^{2+}$, which has been studied by optical and EPR methods. The halide adducts [Ag(9S3)Cl] and [Ag(18S6)Br] both contain a tetrahedral AgS_3X core. In the former case, 9S3 coordinates in a tridentate fashion to yield a discrete, monomeric complex. In the latter, 18S6 provides two thioethers to one Ag(I) and a third to another to yield a polymeric chain. In $[\text{Ag}(12\text{S}3)](\text{CF}_3\text{SO}_3)\cdot\text{MeCN}$, each Ag(I) ion coordinates to three thioether groups (one from each of three independent 12S3 molecules) as well as a CF_3SO_3^- counterion to yield distorted-tetrahedral geometry. In turn, the three ligand S atoms coordinate to different Ag(I) ions to generate a network structure. These results highlight the profound influence of ligand conformation on the structure and solution chemistry of their complexes. Crystal data: $[\text{Ag}(9\text{S}3)_2](\text{CF}_3\text{SO}_3)$, orthorhombic system, space group *Pnam*, $a = 7.884$ (2) Å, $b = 12.396$ (5) Å, $c = 23.546$ (7) Å, $Z = 4$; [Ag(9S3)Cl], monoclinic system, space group $I2/a$, $a = 14.144$ (2) Å, $b = 6.684$ (1) Å, $c = 22.277$ (2) Å, $\beta = 91.653$ (9)°, $Z = 8$; [Ag(18S6)Br], triclinic system, space group $P\bar{1}$, $a = 10.359$ (1) Å, $b = 10.420(1)$ Å, $c = 11.311(2)$ Å, $\alpha = 115.72$ (1)°, $\beta = 115.56$ (1)°, $\gamma = 82.62$ (1)°, $Z = 2$; $[\text{Ag}(12\text{S}3)](\text{CF}_3\text{SO}_3)\cdot\text{MeCN}$, orthorhombic system, space group $P2_12_12_1$, $a = 8.601(1)$ Å, $b = 14.224$ (3) Å, $c = 16.098$ (2) Å, $Z = 4$.

Introduction

Despite the strong affinity of thioether sulfur for silver,[1] little information is available concerning the crown thioether complexes of Ag(I).[2-4] We report here the reactions of Ag(I) with the tridentate crown thioethers 1,4,7-trithiacyclononane (9S3) and 1,5,9-trithiacyclododecane (12S3) and the hexadentate crown thioether 1,4,7,10,13,16-hexathiacyclooctadecane (18S6) (Figure 1). These complexes attract interest since crown thioethers can induce unusual electronic and redox behavior (e.g., stabilization of low-spin Co(II), monomeric Rh(II), Pd(III), and Pt(III));[5,6] apparently the unique conformational properties of 9S3[7] impart high stability and novel structures to its complexes.

The stark contrast between the structural and electrochemical properties of the 9S3 complexes on one hand and those of 12S3 and 18S6 on the other underscores the critical role played by conformation in crown thioether chemistry.

Experimental Section

Physical Measurements. ^{1}H NMR spectra were recorded with a Bruker WH 300 spectrometer calibrated against residual solvent protons. Infrared spectra were recorded with a Perkin-Elmer 1710 FT spectrometer. EPR spectra were obtained with a Bruker ESP 300 spectrometer with the samples contained in quartz capillaries. UV–visible spectra were obtained with a Perkin-Elmer 552 spectrophotometer, with the sample temperature controlled through use of a jacketed cell. Elemental analyses

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