Synthesis and Characterization of the Mixed-valent Complex Ion Di-μ-oxobis(1,4,8,11-tetraazacyclotetradecane)dimanganese(III,IV), $[(cyclam)MnO]_2^{3+}$

PATRICIA A. GOODSON, DEREK J. HODGSON*

Department of Chemistry, University of Wyoming, Laramie, WY 82071 (U.S.A.)

and KIRSTEN MICHELSEN

Chemistry Laboratory I, Inorganic Chemistry, H. C. Ørsted Institute, Universitetsparken 5, DK-2100 Copenhagen Ø (Denmark)

(Received October 25, 1989)

Abstract

The synthesis and characterization of several salts of the mixed-valence binuclear cation $[(cyclam)MnO]_2^{3+}$, where cyclam is 1,4,8,11-tetraazacyclotetradecane, are reported.

The bromide salt, $[(cyclam)MnO]_2Br_3 \cdot 4H_2O$, crystallizes in the monoclinic space group $P2_1/n$ with two molecules in a cell of dimensions $a = 9.903(3)$, $b = 11.565(3)$, $c = 14.927(4)$ Å, $\beta = 107.87(2)°$ at −100 °C. Consequently, the two manganese centers are crystallographically equivalent. An analysis of the anisotropic displacement parameters (U_{ij}), coupled with evidence from other experiments, demonstrates a static disorder in the crystals between chemically inequivalent Mn(III) and Mn(IV) sites. The structure has been refined to a weighted R factor of 0.0378 based on 2368 independent intensities. The manganese–manganese separation in the dimer is 2.731(2) Å.

The dithionate salt crystallizes in the monoclinic space group $P2_1/a$ with four molecules in a cell of dimensions $a = 15.216(3)$, $b = 11.716(4)$, $c = 18.745(6)$ Å, $\beta = 92.49(2)°$ at −100 °C. The complex crystallizes with two independent centrosymmetric dimers in the cell, but again this is due to a static disorder in the crystals. Disorder about one of the dithionate ions fits a model in which some of the dithionate ion has been converted to thiosulfate. The Mn–Mn separations are 2.729(5) and 2.738(5) Å. The EPR spectrum of the complex at 4 K shows the sixteen line pattern commonly observed in di-μ-oxodimanganese(III,IV) complexes. The magnetic susceptibility of the complex demonstrates that the complex has a doublet ground state, exhibiting antiferromagnetic coupling with $2J = -237$ cm^{-1}.

Introduction

Interest in binuclear and polynuclear complexes of manganese in relatively high oxidation states stems largely from the involvement of such species in a wide variety of biological oxidative processes; the example most relevant to the present paper is the water oxidizing enzyme in photosystem II (PSII) [1]. The S_2 state in PSII exhibits an unusual sixteen-line EPR spectrum [2], and its X-ray absorption spectrum [3] is indicative of a short Mn···Mn separation of approximately 2.70 Å. These same physical properties are exhibited by the mixed-valent binuclear species $[(bpy)MnO_2Mn(bpy)]^{3+}$ (bpy = 2,2′-bipyridine) and by its 1,10-phenanthroline (phen) analogue [4–7], both of which have been structurally characterized by single crystal X-ray diffraction techniques [6, 7].

Our own interest in complexes of this general type stems more from their potential use as two-electron oxidation electrocatalysts; this interest is stimulated by the observations of Gref *et al.* [8] who have electrochemically oxidized alcohols and ethers in the presence of both the bpy and phen complexes, and by those of Ramaraj *et al.* [9] who have shown that the bpy complex oxidizes water in the presence of a chemical oxidant such as cerium(IV) ion. Consequently, we have initiated a comprehensive program designed to synthesize di-μ-oxodimanganese complexes with desired electrochemical properties, in the expectation of producing useful catalytic complexes. We have earlier reported on the synthesis and characterization of the *N,N′*-bis(2-pyridylmethyl)-1,2-diaminoethane (bispicen) and the tris(2-pyridylmethyl)amine (tmpa) analogues, and of complexes with related ligands [10, 11]; Suzuki *et al.* have subsequently reported the oxidized Mn(IV,IV) form of the tmpa complex [12]. Other workers have described the 2,2′,2″-triaminoethylamine (tren) [13], 1,4,7,10-tetraazacyclododecane (cyclen) [14], and

---

*Author to whom correspondence should be addressed.

0020-1693/90/$3.50

N,*N*-bis(2-pyridylmethyl)glycinato [15] complexes. While the present work was nearing completion, we learned that Calvin and coworkers had succeeded in isolating and characterizing the triflate salt of the 1,4,8,11-tetraazacyclotetradecane (cyclam) complex [14, 16, 17]. We report here the synthesis and properties of the bromide, nitrate and dithionate salts of the cyclam complex, $[(\text{cyclam})MnO_2Mn(\text{cyclam})]^{3+}$.

Experimental

Magnetic susceptibility measurements were performed by the Faraday method on equipment described elsewhere [18] in the temperature range 4–300 K. The molar susceptibilities were corrected for ligand diamagnetism using Pascal's constants.

EPR spectra were recorded at liquid helium temperature on a Bruker ESP 300 spectrometer operating at a frequency of 9.38 GHz. Samples were examined as frozen glasses in *N*-methylformamide solution.

Electronic spectra were obtained in aqueous solution and in *N*-methylformamide on a Perkin-Elmer Lambda 17 spectrometer.

Synthesis of the Complexes

The cyclam ligand was prepared by literature methods [19]. To a solution of 0.726 g cyclam (3.63 mmol) in 30 ml water was added a solution of 0.718 g (3.63 mmol) of $MnCl_2 \cdot 4H_2O$ in 5 ml H_2O. The solution became cloudy. After stirring for 5 min, approximately 0.35 g of 30% aq. H_2O_2 was added dropwise. The reaction mixture turned dark olive green. After 20 min, the solution was filtered, and to the filtrate was added a solution of 1.12 g (5.45 mmol) $Na_2S_2O_6$ in 15 ml H_2O. The precipitate which formed was filtered and washed with ethanol. Additional crystals were obtained upon cooling the filtrate. Yield: 0.51 g (34%). The compound analyzed satisfactorily for $[(\text{cyclam})MnO]_2(S_2O_6)_{3/2} \cdot 2H_2O$. *Anal.* Calc. for $Mn_2C_{20}H_{52}N_8O_{13}S_3$: C, 29.34; H, 6.40; N, 13.69; S, 11.75. Found: C, 30.23; H, 6.16; N, 13.95; S, 11.92%. (Analysis was performed by Atlantic Microlab Inc., Norcross, GA.) The subsequent X-ray diffraction study (*vide infra*) suggests that the dithionate anions have been partially oxidized to thiosulfate, and that the anion composition is better described as $(S_2O_6)_{1.37}(S_2O_3)_{0.13}$. The chemical analysis is consistent with this formulation as a monohydrate. Calc. for $Mn_2C_{20}H_{50}N_8O_{11.61}S_3$: C, 30.24; H, 6.34; N, 14.10; S, 12.10%.

The use of an external oxidant is not necessary for the formation of the III/IV dimer, however [17]. The bromide salt was prepared by the addition of $MnBr_2 \cdot 4H_2O$ (200 mg, 0.70 mmol) to a filtered solution of cyclam (150 mg, 0.75 mmol) in ethanol (4 ml, 99%). The gray–green precipitate was washed with ethanol. The crude product was extracted with water (3 ml) and an aqueous solution of LiBr (0.5 g in 0.5 ml) was added. The solution was allowed to stand on an ice bath, and well-formed green crystals separated out. Yield: 122 mg (41%). The compound analyzed satisfactorily for $[(\text{cyclam})MnO]_2Br_3 \cdot 4H_2O$. *Anal.* Calc. for $Mn_2C_{20}H_{56}Br_3N_8O_6$: Mn, 12.86; C, 28.12; H, 6.61; N, 13.12; Br, 28.06. Found: Mn, 12.71; C, 27.83; H, 6.55; N, 13.03; Br, 28.06%. (Analysis was performed by the microanalytical laboratory, H. C. Ørsted Institute.) Similarly, the nitrate salt was obtained by starting with $Mn(NO_3)_2 \cdot 4H_2O$, and the perchlorate salt was obtained from a solution of the bromide salt to which excess $NaClO_4$ was added.

Caution. Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small quantities of the perchlorate salt should be prepared and handled behind suitable protective shields.

X-ray Structure Determination

The structures of the bromide and dithionate salts were determined at −100 °C [173 K] on a Nicolet R3m/V diffractometer equipped with a molybdenum tube ($\lambda K\alpha_1 = 0.70926$ Å; $\lambda K\alpha_1 = 0.71354$ Å) and a graphite monochromator. Crystal data and experimental parameters are tabulated in Table 1. The data were corrected for Lorentz–polarization effects and for absorption. The structures were solved by Patterson and difference Fourier methods and refined by least-squares techniques; the programs used were from the SHELXTL system.

Bromide salt

The complex crystallizes in the centrosymmetric monoclinic space group $P2_1/n$ with two binuclear cations in the unit cell. All hydrogen atoms were located in a difference Fourier synthesis, and hydrogen atoms were refined isotropically while other atoms were refined anisotropically. The final values of the conventional *R* factors were $R = 0.0387$, $R_w = 0.0378$, based on 2368 independent data with $I > 3\sigma(I)$. The values of the agreement factors based on the entire data set are $R = 0.0584$, $R_w = 0.0485$. The final values of the atomic positional parameters, along with their estimated standard deviations, are presented in Table 2. See also 'Supplementary Material'.

Dithionate salt

The complex crystallizes in the centrosymmetric monoclinic space group $P2_1/a$ with four binuclear cations in the cell. Consequently, the six dithionate anions must occupy one general and one special position, the special position requiring that two of the dithionates in the cell have an inversion center in the middle of the S–S bond; this, of course, is not unexpected since the anion invariably exhibits approximate D_{3d} symmetry [20]. At a late stage of the refinement it was apparent that the special

TABLE 1. Crystallographic data for $[(\text{cyclam})\text{MnO}]_2^{3+}$

	Bromide	Dithionate
Formula	$Mn_2C_{20}H_{56}Br_3N_8O_6$	$Mn_2C_{20}H_{52}N_8O_{12.61}S_3$
a (Å)	9.903(3)	15.216(3)
b (Å)	11.565(3)	11.716(4)
c (Å)	14.927(4)	18.745(6)
β (°)	107.87(2)	92.49(2)
V (Å^3)	1627.1(8)	3339(2)
Z	2	4
Formula weight	854.31	812.51
Space group	$P2_1/n$	$P2_1/a$
T (°C)	−100	−100
λ (Å)	0.71073	0.71073
μ (mm^{-1})	4.44	0.98
R	0.0387	0.0657
R_w	0.0378	0.0790

TABLE 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^4$) for $[(\text{cyclam})\text{MnO}]_2\text{Br}_3\cdot 4H_2O$

	x	y	z	U_{eq}[a]
Br(1)	5212(1)	1459(1)	2187(1)	187(2)
Br(2)	0	0	5000	523(4)
Mn	−5(1)	832(1)	−650(1)	95(2)
O(1)	−741(3)	−605(3)	−613(2)	152(11)
N(1)	923(4)	2482(3)	−541(3)	138(14)
C(2)	78(6)	3268(5)	−151(4)	199(19)
C(3)	−1451(6)	3128(5)	−710(4)	204(19)
N(4)	−1844(5)	1907(4)	−637(3)	252(17)
C(5)	−3283(7)	1652(8)	−1299(5)	457(28)
C(6)	−3331(6)	1592(6)	−2310(4)	315(21)
C(7)	−2421(6)	654(5)	−2521(4)	227(18)
N(8)	−898(5)	908(4)	−2134(3)	155(15)
C(9)	−63(6)	113(5)	−2529(4)	250(21)
C(10)	1481(6)	389(5)	−2087(4)	218(19)
N(11)	1817(5)	254(4)	−1051(3)	213(16)
C(12)	3234(7)	670(6)	−536(6)	416(26)
C(13)	3379(7)	1961(6)	−474(5)	317(22)
C(14)	2452(5)	2533(5)	25(4)	201(18)
O(1W)	7783(6)	2231(4)	1263(4)	397(20)
O(2W)	3295(6)	445(4)	6149(3)	394(19)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

position was not occupied solely by dithionate anions since the original model could not account for one relatively large peak. An entirely similar phenomenon is observed in both the room temperature [11] and the low temperature [21] structures of the dithionate salt of the tmpa analogue, which led us to deduce that the observation is chemically meaningful. The only model which is consistent with all three sets of crystallographic data is one in which we assume that some of the dithionate has been oxidized to thiosulfate and oxygen. Electrochemical evidence for this transformation has been obtained by other workers [22]. In the present case, refinement of the occupancy factors of the two sulfur positions gives an occupancy of 0.13(1) for the thiosulfate ion, leading to 0.37(1) for the dithionate. Hence, the crystallographic data lead to a model with total anion occupancy of $(S_2O_6)_{1.37}(S_2O_3)_{0.13}$, rather than the expected $(S_2O_6)_{1.5}$. In the final model, hydrogen atoms were placed in calculated positions (C–H = 0.96 Å) and other atoms were refined anisotropically. The final values of the conventional R factors were 0.0657 and 0.0790, respectively, based on 1688 independent data with $I > 3\sigma(I)$. The positional parameters for this complex are listed in Table 3. See also 'Supplementary Material'.

Results and Discussion

Description of the Structures

Bromide salt

The structure consists of apparently centrosymmetric binuclear $[(\text{cyclam})\text{MnO}]_2^{3+}$ cations, bromide anions and water molecules. A view of the cation is given in Fig. 1. Principal distances and angles in the cation are listed in Tables 4 and 5, respectively.

The geometry about each manganese center is roughly octahedral, the ligating atoms being two *cis* oxo-bridges and four nitrogen atoms from the cyclam ligand. The *trans* angles at Mn fall in the range 158.6(2) to 174.1(2)°, with the greatest deviation from linearity occurring at the intraligand N(4)–Mn–N(11) angle defined by the two axial nitrogen atoms; similar observations have been made for other binuclear metal complexes involving macrocyclic ligands of this type [20]. The four chelating N–Mn–N angles fall in the range 80.2(2) to 85.4(2)°, with an average value of 82.7(26)°.

TABLE 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^4$) for [(cyclam)MnO]$_2$ dithionate

	x	y	z	U_{eq}[a]
Mn(1)	524(2)	803(2)	330(1)	225(9)
O(1)	−564(7)	705(11)	−113(6)	380(47)
N(1)	1829(8)	798(13)	793(8)	358(55)
C(2)	2443(11)	785(16)	205(9)	344(48)
C(3)	2166(11)	1688(16)	−310(10)	397(51)
N(4)	1269(8)	1473(12)	−557(8)	369(57)
C(5)	893(14)	2377(17)	−1021(11)	510(59)
C(6)	669(12)	3425(16)	−582(10)	405(52)
C(7)	−50(13)	3209(15)	−65(10)	368(48)
N(8)	290(8)	2548(11)	561(7)	250(49)
C(9)	−360(11)	2535(15)	1137(8)	271(44)
C(10)	7(11)	1760(14)	1724(9)	289(46)
N(11)	104(9)	636(11)	1443(8)	338(54)
C(12)	612(14)	−159(19)	1968(12)	653(67)
C(13)	1560(11)	76(18)	1998(10)	483(53)
C(14)	2031(13)	−103(18)	1337(10)	525(57)
Mn(2)	4685(2)	−73(2)	5671(1)	235(9)
O(2)	5685(6)	396(9)	5240(6)	268(40)
N(21)	3496(8)	−695(12)	6080(7)	306(53)
C(22)	3527(11)	−1968(15)	6038(9)	325(49)
C(23)	4401(11)	−2327(16)	6375(9)	356(49)
N(24)	5099(8)	−1838(13)	5963(8)	349(57)
C(25)	5981(13)	−2008(17)	6321(11)	527(59)
C(26)	6207(12)	−1259(16)	6959(10)	409(53)
C(27)	6146(11)	−10(16)	6835(9)	379(47)
N(28)	5252(9)	390(11)	6682(8)	336(54)
C(29)	5164(12)	1639(16)	6741(10)	401(51)
C(210)	4252(12)	2010(16)	6524(10)	421(55)
N(211)	4073(9)	1629(13)	5789(8)	358(57)
C(212)	3148(14)	1761(19)	5534(12)	655(68)
C(213)	2520(13)	976(16)	5873(11)	506(57)
C(214)	2679(10)	−307(13)	5685(9)	278(47)
S(1)	2536(3)	−1026(4)	−1844(3)	307(17)
O(3)	2806(8)	−2126(10)	−1596(7)	484(52)
O(4)	2342(9)	−971(12)	−2598(7)	565(56)
O(5)	1872(7)	−503(10)	−1429(7)	447(48)
S(2)	3671(3)	−5(5)	−1646(3)	357(17)
O(6)	3422(8)	1137(11)	−1835(7)	560(58)
O(7)	4302(8)	−507(13)	−2101(7)	602(58)
O(8)	3886(8)	−171(11)	−900(6)	455(50)
S(3)	5128(4)	5503(5)	4547(3)	381(25)
O(9)	4659(9)	4921(12)	3962(7)	434(54)
O(10)	4762(8)	6637(10)	4729(8)	327(53)
O(11)	6086(8)	5438(12)	4484(8)	443(58)
S(4)	5262(31)	4336(60)	4675(31)	857(321)
O(1W)	3913(9)	5952(14)	2754(8)	779(67)
O(2W)	7724(11)	7257(16)	2457(11)	1147(92)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

The Mn–Mn separation of 2.731(2) Å is compared with the values for other di-μ-oxodimanganese complexes in Table 6. While a direct comparison between these complexes is clouded by the fact that some results are from room temperature structural studies while others are low temperature data, the essential conclusion is that for (III,IV) systems the Mn(III)–Mn(IV) separation is evidently in the range 2.64 to 2.74 Å. It is noteworthy in this connection that the Mn(IV)–Mn(IV) separations in the analogous Mn(IV/IV) complexes are 2.672(1) to 2.748(2) Å, [7, 10b, 11b] which is at the upper end of the range for III/IV complexes but is not significantly longer. The Mn–O–Mn bond angle of 97.2(1)° is similar to

TABLE 4. Bond lengths (Å) in $[(\mathrm{cyclam})\mathrm{MnO}]_2^{3+}$

Atoms	Bromide	Dithionate(1)	Dithionate(2)
Mn–O(1)	1.822(3)	1.824(11)	1.838(10)
Mn–O(1a)	1.820(3)	1.815(13)	1.815(11)
Mn–N(1)	2.103(4)	2.132(13)	2.123(13)
Mn–N(4)	2.211(5)	2.197(14)	2.224(15)
Mn–N(8)	2.119(4)	2.123(13)	2.119(14)
Mn–N(11)	2.172(5)	2.217(15)	2.215(15)
Mn–Mn(a)	2.731(2)	2.729(5)	2.738(5)
N(1)–C(2)	1.471(8)	1.476(22)	1.493(22)
C(2)–C(3)	1.497(7)	1.480(25)	1.508(24)
C(3)–N(4)	1.477(7)	1.445(21)	1.457(22)
N(4)–C(5)	1.493(7)	1.471(24)	1.487(23)
C(5)–C(6)	1.496(10)	1.525(27)	1.512(27)
C(6)–C(7)	1.504(9)	1.514(27)	1.485(26)
C(7)–N(8)	1.470(7)	1.482(22)	1.455(21)
N(8)–C(9)	1.475(8)	1.495(21)	1.474(23)
C(9)–C(10)	1.502(8)	1.514(23)	1.494(25)
C(10)–N(11)	1.487(7)	1.428(21)	1.462(23)
N(11)–C(12)	1.459(8)	1.538(26)	1.475(24)
C(12)–C(13)	1.500(10)	1.468(27)	1.488(29)
C(13)–C(14)	1.502(10)	1.473(27)	1.566(25)
C(14)–N(1)	1.492(6)	1.491(24)	1.490(20)

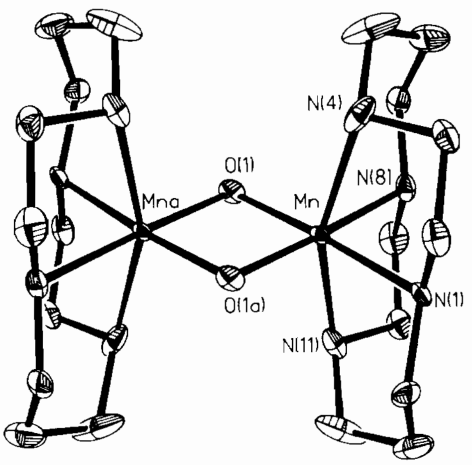

Fig. 1. View of the $[(\mathrm{cyclam})\mathrm{MnO}]_2^{3+}$ cation in the crystal of the bromide salt; the two independent cations in the dithionate salt are essentially similar to this. Atoms Mn(a) and O(1a) are related to Mn and O(1), respectively, by inversion through the center of the dimer.

the values of 97.1 and 97.7° in the triflate salt [17]; these results are slightly larger than other reported values, which range from 94.0 to 96.6°.

TABLE 5. Principal bond angles in $[(\mathrm{cyclam})\mathrm{MnO}]_2^{3+}$

Atoms	Bromide	Dithionate(1)	Dithionate(2)
Mn–O–Mn(a)	97.2(1)	97.1(6)	97.1(5)
O(1)–Mn–O(1a)	82.8(1)	82.9(6)	82.9(5)
O(1)–Mn–N(1)	174.1(2)	175.1(6)	174.6(5)
O(1)–Mn–N(4)	100.0(2)	99.5(5)	98.9(5)
O(1)–Mn–N(8)	91.6(2)	89.8(5)	90.2(5)
O(1)–Mn–N(11)	95.9(2)	97.5(5)	97.7(5)
O(1a)–Mn–N(1)	91.3(2)	92.8(5)	91.9(5)
O(1a)–Mn–N(4)	98.4(2)	98.9(5)	96.4(5)
O(1a)–Mn–N(8)	174.1(2)	172.3(5)	173.1(5)
O(1a)–Mn–N(11)	97.7(2)	98.0(5)	99.6(5)
N(1)–Mn–N(4)	80.2(2)	78.9(5)	80.2(5)
N(1)–Mn–N(8)	94.3(2)	94.6(5)	94.9(5)
N(1)–Mn–N(11)	85.4(2)	85.3(5)	84.6(5)
N(4)–Mn–N(8)	84.5(2)	84.7(5)	85.3(5)
N(4)–Mn–N(11)	158.6(2)	157.3(5)	158.2(6)
N(8)–Mn–N(11)	80.8(2)	80.5(5)	80.6(5)
Mn–N(1)–C(2)	107.6(3)	107.7(10)	107.2(10)
Mn–N(1)–C(14)	115.0(3)	116.2(11)	115.0(10)
C(2)–N(1)–C(14)	110.6(4)	112.7(13)	107.8(12)
N(1)–C(2)–C(3)	108.3(4)	108.0(14)	106.6(13)
C(2)–C(3)–N(4)	107.9(4)	108.8(15)	108.6(14)
Mn–N(4)–C(3)	107.5(4)	109.3(11)	106.9(16)
Mn–N(4)–C(5)	120.3(4)	120.4(11)	118.4(11)
C(3)–N(4)–C(5)	111.1(5)	113.7(14)	111.9(14)
N(4)–C(5)–C(6)	113.9(6)	110.5(15)	116.7(16)
C(5)–C(6)–C(7)	114.1(5)	113.3(15)	116.0(15)
C(6)–C(7)–N(8)	112.5(4)	110.9(15)	113.6(14)
Mn–N(8)–C(7)	116.8(4)	113.4(10)	115.8(11)
Mn–N(8)–C(9)	106.6(3)	105.0(9)	106.6(10)

(continued)

TABLE 5. *(continued)*

Atoms	Bromide	Dithionate(1)	Dithionate(2)
C(7)–N(8)–C(9)	110.6(4)	111.0(13)	113.1(13)
N(8)–C(9)–C(10)	108.2(4)	107.2(13)	110.8(14)
C(9)–C(10)–N(11)	107.8(5)	109.0(13)	107.4(15)
Mn–N(11)–C(10)	108.3(3)	107.7(10)	107.9(11)
Mn–N(11)–C(12)	120.0(4)	119.9(11)	117.5(12)
C(10)–N(11)–C(12)	112.6(5)	112.4(14)	114.1(15)
N(11)–C(12)–C(13)	114.8(5)	112.1(17)	114.8(17)
C(12)–C(13)–C(14)	114.1(6)	117.0(16)	112.9(16)
N(1)–C(14)–C(13)	111.7(4)	112.4(16)	108.4(13)

TABLE 6. Mn(III)–Mn(IV) separations in $[(L)MnO]_2^{3+}$

L	Mn–Mn (Å)	*T* (°C)	Reference
tmpa	2.643(1)	RT	11a
N_3O-py	2.656(2)	RT	15
bispicen	2.659(2)	RT	10a
tren	2.679(1)	RT	13
$(phen)_2$	2.700(1)	−173	7
	2.695(9)	−73	7
$(bpy)_2$	2.716(2)	RT	6
cyclam	2.741(1)[a]	RT	17
	2.731(2)[b]	−100	this work
	2.729(5), 2.738(5)[c]	−100	this work

[a] Triflate salt. [b] Bromide salt. [c] Dithionate salt; in this complex there are two independent dimers (see text).

The presence of the crystallographic inversion center in the middle of the dimer causes the two manganese centers to be crystallographically equivalent. While this could indicate that the two manganese centers are chemically equivalent, and that the complex is delocalized, it could also be due to a static disorder resulting from the crystallographic superposition of an equal number of Mn(III)–Mn(IV) and Mn(IV)–Mn(III) cations, or from a dynamic disorder due to rapid (on the crystallographic time scale) electron transfer between the two manganese centers. The combination of the present experiments and the earlier experiments allows us to distinguish between these three alternatives.

Bürgi and coworkers noted an analogous crystallographic symmetry in the phen complex, where the dimer has apparent C_2 symmetry leading to crystallographically equivalent manganese centers [7], and their excellent and detailed analysis need not be repeated here. The essential point is that since Mn(III) is a d^4 ion it is expected to undergo a Jahn–Teller distortion leading to lengthened axial Mn–N bonds, while Mn(IV) is a d^3 ion and is expected to be roughly spherical. Hence, in a disordered structure we would expect to see an averaging of the nitrogen positions, leading to large apparent thermal motion of the axial nitrogen atoms along the Mn–N bond direction. This effect is clearly evident in Fig. 1, where the apparent elongation of the ellipsoids for N(4) and N(11) relative to those of N(1) and N(8) is obvious, and from an inspection of Table S3 (see 'Supplementary Material') which shows this apparent anisotropy in quantitative terms. Hence, as was the case for the phen complex [7], the crystallographic experiment leads to the conclusion that the two sites are chemically inequivalent, and that we are dealing with either a static or a dynamic disorder.

The distinction between these two forms of disorder cannot be made on the basis of a single crystallographic experiment, but in the present case we may appeal to other crystallographic data. While the bromide and dithionate (*vide infra*) salts of the cyclam complex exhibit this disorder, the triflate complex gives a perfectly localized structure [17] like those found in other complexes. Hence, we may be certain that electron transfer between the two manganese centers is not rapid in the cyclam complex, since the rate of intramolecular electron transfer would be virtually independent of the anion. Consequently, in the present case we may conclude that the bromide and dithionate cyclam salts exhibit a static disorder in the crystals due to superposition of the Mn(III) and Mn(IV) ends of the cation.

There is extensive hydrogen bonding in the crystals, with all potential donors participating. Ligand nitrogen atoms N(1) and N(8) form N–H··· Br hydrogen bonds to Br(1), while N(4) and N(11) participate in N–H···O hydrogen bonds to water molecule O1W. The water molecules also donate hydrogen bonds to the bromide ions, and form one O1W–H2W1···OW2 hydrogen bond. For details of the hydrogen bonding see 'Supplementary Material'.

Dithionate salt

With four dimers in the cell, no crystallographic symmetry need be imposed on the cations. In fact, however, the complex crystallizes with two independent cations each having an inversion center in the middle; this behavior, while uncommon, has been observed in other binuclear complexes [23]. The structures of the two independent cations are essentially similar, however, and both are similar to that of the bromide. Because the crystals obtained were small and of relatively low quality, we were unable to observe as many data as in the bromide salt, and consequently the metrical parameters for the dithionate are less precise than those for the bromide.

The structures of the two independent cations are very like that in Fig. 1, and the bond lengths and angles are compared with those of the bromide in Tables 4 and 5, respectively. The Mn–Mn separations are 2.729(5) and 2.738(5) Å, neither of which is significantly different from the bromide value of 2.731(2) Å. The crystallographic inversion center is again due to static disorder in the crystals, the cation being comprised of localized Mn(III) and Mn(IV) centers which are superimposed on each other in the solid state.

The structure of the ordered dithionate anion is consistent with that found in other structures [20]. Thus, the ion exhibits approximate D_{3d} geometry. The S(1)–S(2) bond length is 2.120(7) Å and the S–O bonds are in the range 1.425(13) to 1.438(13) Å [average 1.433(5) Å]; the O–S–S angles are from 103.0(6) to 106.2(5)° [average, 104.4(12)°] while the O–S–O angles are from 113.1(8) to 114.5(8)° [average, 113.9(6)°]. These values are entirely consistent with those observed elsewhere [20].

Electronic Spectra

The visible electronic spectrum of the bromide salt is shown in Fig. 2. The spectrum is similar to those of related complexes, and consists of a very intense band in the UV whose maximum is not shown in Fig. 2 but which occurs at less than 300 nm, with two distinct peaks in the visible at 550 and 644 nm. The intense band is a charge transfer, presumably L → M, band. The peak at 550 nm has been identified as a d–d transition centered on Mn(III). It is noteworthy that this peak has a weak, but discernible, high energy shoulder at about 540 nm which causes the peak to appear asymmetric; this peak may be due to a d–d transition centered on Mn(IV) [17, 24].

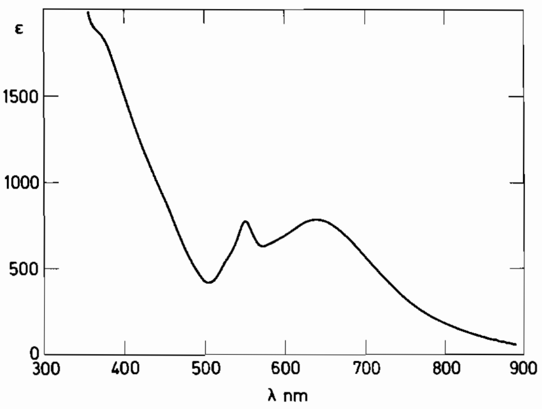

Fig.2. The visible electronic spectrum of the bromide salt of [(cyclam)MnO]$_2^{3+}$ in *N*-methylformamide. The spectrum in water is very similar.

The peak near 644 nm exhibits a broad shoulder near 800 nm. The peak is in the same energy region as has been observed for monomeric Mn(IV) complexes with oxygen ligands [25], and may be assigned as an oxygen–Mn(IV) charge transfer transition. In a mixed-valent complex, we might expect to observe an intervalence charge transfer band. In the bpy complex, a broad low energy feature centered near 800 nm in the near IR has been attributed to intervalence charge transfer [24]. The spectrum in Fig. 2 also exhibits this broadening, and hence this observed absorption in the near IR of the cyclam complex may also be due to the Mn(III)–Mn(IV) intervalence interaction.

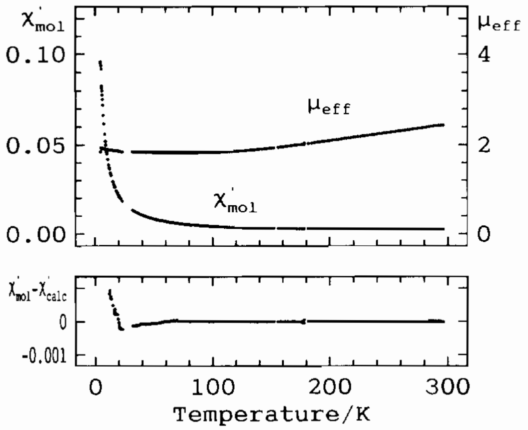

Fig. 3. The temperature dependence of the magnetic susceptibility (left scale) and effective magnetic moment (right scale) of the bromide salt of [(cyclam)MnO]$_2^{3+}$.

Magnetic Susceptibility

The temperature dependence of the magnetic susceptibility of the complex is entirely consistent with its other properties. In the case of the bromide salt, as is shown in Fig. 3, the effective magnetic moment decreases gradually from a value of 2.4 μ_B at room temperature to 1.8 μ_B at 4.4 K. This result is consistent with the behavior predicted for a Mn(III)/Mn(IV) complex with a doublet ground state ($S = 1/2$).

The susceptibility data were analyzed by fitting them to the expression

$$\chi'_{\text{mol}} = -\frac{N}{H}\,\frac{\sum\limits_i \frac{\delta E_i}{\delta H}\exp(-E_i/kT)}{\sum\limits_i \exp(-E_i/kT)} + K + \frac{C}{T}$$

where the E_i are the energies of the twenty components of the ground state manifold. The fitting was accomplished using the simple Van Vleck Hamiltonian

$$\mathcal{H} = -2J\vec{S}_1\cdot\vec{S}_2 + g\mu_B MS'$$

where $S' = S_1 + S_2$ and the only exchange variable is J. The energies of the quartet, sextet and octet states, relative to the doublet ground state, are -3, -8 and -15 J, respectively, in this model. The fitting leads to a value of $2J = -237 \pm 3$ cm^{-1}, which gives energies of 355.5, 948, and 1777.5 cm^{-1} for the quartet, sextet and octet states, respectively.

The value of $|2J| = 237$ cm^{-1} ($|J| = 118.5$ cm^{-1}) determined here for the bromide salt of the cyclam complex is smaller (in magnitude) than J values in the range -134 to -221 cm^{-1} ($2J = -268$ to -442 cm^{-1}) reported in other III/IV complexes of this type [4, 7, 10b, 11b, 13, 14, 16]. In other related series of binuclear complexes, a correlation between the structure of the bridging $(MO)_2$ unit and the magnetic properties of the dimer has been observed [26, 27]. In the present case, it is noteworthy that the bridging Mn–O–Mn angle, ϕ, in the cyclam complex is larger than those in the other complexes reported (*vide supra*) while $|J|$ is smaller; hence, it may be that further magnetochemical study of related complexes will reveal a relationship between J and ϕ analogous to those observed for di-μ-hydroxodicopper(II) [26] and di-μ-hydroxodichromium(III) [27] complexes.

Electron Paramagnetic Resonance Spectroscopy

The EPR spectrum of the bromide salt of the cyclam complex obtained at 3.8 K in *N*-methylformamide is shown in Fig. 4. The spectrum at 80 K is essentially the same as that at 3.8 K and exhibits the (by now) expected sixteen-line pattern centered near $g = 2$. The EPR spectrum was interpreted by means of the hyperfine term [10b]

$$A_1\vec{S}_1\cdot\vec{I}_1 + A_2\vec{S}_2\cdot\vec{I}_2$$

in the spin Hamiltonian with $S_1 = 2$, $S_2 = 3/2$ and equal hyperfine constants $A_1 = A_2$.

The observed spectrum comes exclusively from the doublet ($S = 1/2$) ground state. The spacing between adjacent lines is equal to A, the hyperfine coupling constant, the pattern being centered around $(2g_1 - g_2)$. Hence, the present spectrum gives a value of $A = 80 \pm 1$ G. The spectrum reported here is similar to those reported for the related species [4, 10b, 11b, 13, 14, 16].

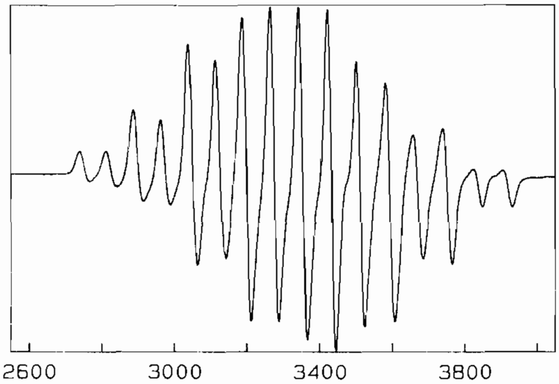

Fig. 4. The X-band EPR spectrum of the bromide salt of $[(\text{cyclam})\text{MnO}]_2^{3+}$ in *N*-methylformamide at 4 K. The spectrum at 80 K is substantially similar to this spectrum.

Supplementary Material

Tables S1 and S2 (hydrogen atom positional parameters), Tables S3 and S4 (anisotropic thermal parameters), Table S5 (hydrogen bonding in the bromide salt), Tables S6 and S7 (observed and calculated structure amplitudes) are available from author D.J.H. on request.

Acknowledgements

This work was supported by the Petroleum Research Fund, administered by the American Chemical Society, through grant No. 19457-AC3 (to D.J.H.), by the National Science Foundation through grant No. CHE-8912675 (to D.J.H.), and by the Scientific Affairs Division, North Atlantic Treaty Organization (NATO) through grant No. 85/0790. We are very grateful to Ms Karen Margarenthe Nielsen, Ms Solveig Kallesøe and Dr. Jørgen Glerup for experimental assistance.

References

1 G. C. Dismukes, *Photochem. Photobiol., 43* (1986) 99–115.
2 G. C. Dismukes and Y. Siderer, *Proc. Natl. Acad. Sci. U.S.A., 78* (1981) 274–278.
3 J. A. Kirby, A. S. Robertson, J. P. Smith, A. C. Thompson, S. R. Cooper and M. P. Klein, *J. Am. Chem. Soc., 103* (1981) 5529–5537.
4 S. R. Cooper, G. C. Dismukes, M. P. Klein and M. Calvin, *J. Am. Chem. Soc., 100* (1978) 7248–7252.
5 R. S. Nyholm and A. Turco, *Chem. Ind. (London)*, (1960) 74–75.
6 P. M. Plaksin, R. C. Stoufer, M. Mathew and G. J. Palenik, *J. Am. Chem. Soc., 94* (1972) 2121–2122.
7 M. Stebler, A. Ludi and H.-B. Bürgi, *Inorg. Chem., 25* (1986) 4743–4750.
8 A. Gref, G. Balavoine, H. Rivière and C. P. Andrieux, *Nouv. J. Chim., 8* (1984) 615–618.
9 R. Ramaraj, A. Kira and M. Kaneko, *Angew. Chem., Int. Ed. Engl., 25* (1986) 825–827.
10 (a) M. A. Collins, D. J. Hodgson, K. Michelsen and E. Pedersen, *J. Chem. Soc., Chem. Commun.*, (1987) 1659–1660; (b) P. A. Goodson, J. Glerup, D. J. Hodgson,

K. Michelsen and E. Pedersen, *Inorg. Chem., 29* (1990) 503–508.

11 (a) D. K. Towle, C. A. Botsford and D. J. Hodgson, *Inorg. Chim. Acta, 141* (1988) 167–168; (b) A. R. Oki, J. Glerup and D. J. Hodgson, *Inorg. Chem.*, in press.

12 M. Suzuki, S. Tokura, M. Suhara and A. Uehara, *Chem. Lett.*, (1988) 477–480.

13 K. S. Hagen, W. H. Armstrong and H. Hope, *Inorg. Chem., 27* (1988) 969–971.

14 K. J. Brewer, A. Liegeois, J. W. Otvos, M. Calvin and L. O. Spreer, *J. Chem. Soc., Chem. Commun.*, (1988) 1219–1220.

15 M. Suzuki, H. Senda, Y. Kobayashi, H. Oshio and A. Uehara, *Chem. Lett.*, (1988) 1763–1766.

16 L. O. Spreer, personnal communication.

17 K. J. Brewer, M. Calvin, R. S. Lumpkin, J. W. Otvos and L. O. Spreer, *Inorg. Chem., 28* (1989) 4446–4451.

18 J. Josephsen and E. Pedersen, *Inorg. Chem., 16* (1977) 2534–2538; E. Pedersen, *Acta Chem. Scand., 26* (1972) 333–342.

19 *Inorg. Synth., 16* (1976) 220–225.

20 D. J. Hodgson, E. Pedersen, H. Toftlund and C. Weiss, *Inorg. Chim. Acta, 120* (1986) 177–184, and refs. therein.

21 D. J. Hodgson and M. H. Lynn, unpublished observations; M. H. Lynn, *Thesis,* University of Wyoming, 1989.

22 A. Tasaka, A. Itani, S. Katayama and M. Yamashita, *Denki Kagaku Oyobi Kogyo Butsuri Kagaku, 49* (1981) 578–583.

23 R. P. Scaringe, W. E. Hatfield and D. J. Hodgson, *Inorg. Chim. Acta, 22* (1977) 175–183.

24 S. R. Cooper and M. Calvin, *J. Am. Chem. Soc., 99* (1977) 6623–6630.

25 H. Okawa, M. Nakamura and S. Kida, *Bull. Chem. Soc. Jpn., 55* (1982) 466–470.

26 V. H. Crawford, H. W. Richardson, J. R. Wasson, D. J. Hodgson and W. E. Hatfield, *Inorg. Chem., 15* (1976) 2107–2110.

27 J. Glerup, D. J. Hodgson and E. Pedersen, *Acta Chem. Scand., Ser. A, 37* (1983) 161–164.