

imine. It occurred to us that B might have been formed from A through removal of hydrogen atoms from the methinyl and a methyl carbon of the isopropyl group. Complex A was not converted to B in refluxing hexanes solution in the absence of imine. However, under slightly more vigorous conditions, namely, refluxing octane solution, A was converted to B in high (97%) yield. The ability of triosmium clusters to abstract hydrogen from alkyl groups has been observed on several previous occasions.¹²⁻¹⁴ The fate of the hydrogen atoms is not known. At present we can only assume that they were expelled from the cluster as H₂.

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Supplementary Material Available: Tables of structure factor amplitudes for both structures (47 pages). Ordering information is given on any current masthead page.

Notes

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Synthesis and Structure of a 12-Crown-4 Sandwich Complex of Manganese(II), Bis(1,4,7,10-tetraoxacyclododecane)manganese(II) Tribromide

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The coordination chemistry of crown ether ligands has drawn considerable interest. Natural macrocyclic antibiotics display unique selectivity for binding simple cationic metal ions, and much effort has been devoted to the design and preparation of synthetic chelating agents which demonstrate similar specificity.² While the primary focus of this research has concerned coordination complexes of alkali and alkaline metal ions, a large and growing compendium of transition-metal complexes exists.³ The crown ether oxygen donors show a much weaker affinity for transition-metal ions than for A group metal ions. Structural investigations carried out on presumed crown ether complexes of transition metals isolated from aqueous solution have shown a stronger tendency for hydrogen bond formation to coordinated aquo ligands than direct bonding to the metal. This has been found to be the result for [Co(H₂O)₆][CoCl₄·18-crown-6·(CH₃)₂CO]⁴, [Mn(H₂O)₆](ClO₄)₂·18-crown-6,⁵ and [Mn(NO₃)(H₂O)₅](NO₃)₃·18-crown-6·H₂O⁶ and should prove to be the case in similar complexes. In the absence of a better ligating agent, crown ether complexes of transition-metal ions can be isolated. In this note we report the preparation of the bis(12-crown-4)manganese(II) cation isolated as its tribromide salt and the results of a crystallographic molecular structure determination carried out on the compound.

Experimental Section

Synthesis of [Mn(C₈H₁₆O₄)₂](Br₃)₂. A solution containing 1.23 g (7 mmol) of 12-crown-4 and 1.72 g (8 mmol) of anhydrous MnBr₂ dissolved in 40 mL of dry methanol was refluxed for 4 h. After the solution was cooled in an ice bath, an excess (6 mL) of bromine was added. The yellow precipitate which immediately formed was filtered and washed with methanol and absolute ether. The crude yield was 84% on the basis of 12-crown-4. Crystals suitable for X-ray analysis were grown by recrystallization from dry methanol. They were observed to slowly decompose to a white powder during prolonged exposure to air.

Crystallography. A yellow-orange crystal of [Mn(C₈H₁₆O₄)₂](Br₃)₂ was mounted and coated with an amorphous resin to retard surface decomposition during data collection. Preliminary photographs indicated the monoclinic crystal system with extinctions of *hkl*, *h* + *k* = 2*n* + 1, consistent with the centric space group C2/*m* and acentric space groups C2 and *Cm*. The crystal was aligned on a Syntex P1 automated diffractometer equipped with a graphite crystal monochromator by using Mo K α radiation (λ = 0.71069 Å). The following cell constants were calculated from the refined settings of 22 independent high-angle reflections: *a* = 18.585 (2) Å, *b* = 8.513 (1) Å, *c* = 9.693 (1) Å, and β = 116.33 (1)°. An experimental density of 2.16 (3) g cm⁻³ agrees with a calculated value of 2.143 g cm⁻³ for two formula weights per unit cell.

Intensity data were collected at room temperature by using the $\theta/2\theta$ scan technique. A total of 1355 independent reflections with 2θ values less than 50° were measured. Of this number 707 were found to have $F_o^2 > 3\sigma(F_o^2)$ and were used in the refinement. Data were processed in the usual manner. Corrections were applied for Lorentz, polarization, and absorption effects. With μ = 97.8 cm⁻¹ transmission coefficients ranged from 0.18 to 0.26. The crystal was a parallelepiped of dimensions 0.17 × 0.23 × 0.51 mm with bounding planes of {001}, {110}, and {110}.

The crystal structure was solved by using both a sharpened Patterson map and direct methods. Initial refinement was carried out in space group C2/*m* with the half tribromide ion located on the mirror plane (special position *i*) and the manganese ion at a position of 2/*m* symmetry (special position *d*). These positions were consistent with the solutions obtained from the Patterson and refined to a conventional *R_F* of 0.122. The 2/*m* site symmetry imposed on the complex molecule in the centric space group requires substantial disorder of the crown ether ligands, and at this point the two acentric space groups were considered. In space group C2 the complex cation is required to have twofold symmetry with one independent tribromide anion. Space group *Cm* requires mirror symmetry for the complex molecule with two half tribromide anions also lying on the mirror plane. The conformational structure of the ethylene bridges of the 12-crown-4 ligand precludes a structure in which the ligands are bisected by the mirror plane without complete disorder of the carbon atoms. Also, the orientation of the complex molecule in C2 and *Cm* is different. In C2 the coordination geometry would be rotated approximately 22.5° from its orientation in *Cm*. Patterson vectors and the results obtained by

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Table I. Positional and Thermal Parameters for $[\text{Mn}(\text{C}_8\text{H}_{16}\text{O}_4)_2](\text{Br}_3)_2$

atom	x	y	z	B_{11}^a	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mn	0.5377 (7)	0	0.3921 (17)	2.22 (13)	2.60 (15)	1.89 (13)	0	0.95 (10)	0
Br1	0.1505 (2)	0	-0.0491 (3)	3.3 (3)	6.2 (5)	4.3 (4)	0	2.0 (3)	0
Br2	0.2369 (2)	0	-0.1887 (3)	3.2 (3)	3.5 (4)	2.8 (2)	0	1.0 (2)	0
Br3	0.3263 (2)	0	-0.3313 (3)	4.1 (3)	4.9 (4)	3.5 (3)	0	2.1 (3)	0
Br4	-0.0751 (2)	0	-0.1698 (3)	4.7 (4)	6.3 (5)	4.8 (4)	0	2.8 (3)	0
Br5	-0.1626 (2)	0	-0.0361 (3)	2.5 (3)	4.6 (4)	3.2 (3)	0	1.2 (3)	0
Br6	-0.2502 (2)	0	0.1090 (3)	3.6 (3)	8.3 (6)	4.2 (4)	0	1.8 (3)	0
O1	0.5843 (16)	0	0.6534 (33)	7.2 (15)	3.3 (13)	5.4 (13)	0	3.6 (11)	0
O2	0.4937 (10)	0.2250 (21)	0.4640 (22)	5.4 (8)	5.3 (10)	7.4 (10)	3.9 (9)	4.8 (8)	2.3 (10)
O3	0.4032 (13)	0	0.2742 (28)	1.9 (9)	6.4 (17)	4.6 (11)	0	1.6 (9)	0
O4	0.6503 (9)	0.1599 (22)	0.4534 (16)	3.2 (7)	4.9 (10)	2.9 (6)	1.6 (7)	0.7 (6)	-1.0 (6)
O5	0.5143 (18)	0.1492 (28)	0.1698 (49)	10.2 (17)	2.4 (12)	28 (4)	-0.7 (11)	12.8 (22)	-1.4 (16)
C1	0.5499 (37)	0.1352 (82)	0.7106 (53)	23 (6)	27 (7)	9 (3)	-14 (5)	12 (4)	-14 (3)
C2	0.5436 (22)	0.2274 (87)	0.5979 (28)	5 (2)	27 (6)	0 (1)	-6 (3)	-1 (1)	0 (2)
C3	0.4160 (19)	0.2420 (40)	0.4046 (54)	3 (1)	1 (2)	13 (3)	1 (1)	-1 (1)	-2 (2)
C4	0.3586 (25)	0.1197 (44)	0.2891 (63)	5 (2)	4 (2)	16 (4)	2 (1)	5 (2)	2 (2)
C5	0.7150 (21)	0.1000 (71)	0.5218 (52)	2 (2)	23 (8)	8 (2)	0 (2)	-1 (2)	3 (3)
C6	0.6403 (29)	0.2816 (42)	0.3500 (51)	18 (5)	1 (2)	10 (3)	4 (2)	8 (3)	3 (2)
C7	0.5753 (17)	0.2586 (39)	0.1897 (45)	4 (1)	7 (2)	7 (2)	-3 (1)	2 (1)	4 (2)
C8	0.4943 (26)	0.1069 (43)	0.0492 (32)	10 (2)	5 (2)	1 (1)	1 (1)	2 (1)	-3 (1)

^a The form of the anisotropic thermal ellipsoid is $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$. The quantities given in the table are in units of Å^2 .

Table II. Selected Bond Distances and Angles within the Inner Coordination Sphere of the $\text{Mn}(\text{C}_8\text{H}_{16}\text{O}_4)_2^{2+}$ Cation

Distances (Å)			
Mn-O1	2.28 (2)	Mn-O4	2.34 (2)
Mn-O2	2.31 (2)	Mn-O5	2.37 (2)
Mn-O3	2.24 (2)		
Angles (Deg)			
O1-Mn-O2	71.1 (6)	O2-Mn-O2'	112.2 (10)
O1-Mn-O3	110.7 (10)	O3-Mn-O4	143.0 (5)
O1-Mn-O4	82.1 (7)	O3-Mn-O5	79.8 (8)
O1-Mn-O5	146.6 (8)	O4-Mn-O5	72.6 (8)
O2-Mn-O3	71.9 (6)	O4-Mn-O4'	71.1 (9)
O2-Mn-O4	80.6 (6)	O4-Mn-O5'	109.0 (8)
O2-Mn-O5	83.3 (8)	O5-Mn-O5'	64.8 (15)

direct methods calculations all showed that the shortest vectors within the Mn coordination sphere formed a square-antiprismatic coordination geometry about the metal. On the basis of the orientation of these vectors, the complex cation was judged to lie on the mirror plane in C_m with the plane bisecting both ligands. The difference Fourier calculated from the refinement carried out including the oxygen atoms failed to show two clear sets of carbon atoms for the two ligands. The disordered carbon atoms were treated by placing a single atom at the region of greatest electron density which was found midway between the two disordered sites. As the square antiprismatic geometry of the complex cation became clear, trial refinements were carried out in C_2 with the cation positioned about the twofold axis. The result was that oxygens refined away from the metal and certain carbon atoms refined into the metal, and it was apparent that the refinement was directly toward the solution in C_m . Space group C_m was therefore judged as correct and final cycles of refinement were carried out with the complex cation located on the mirror plane. The method of treating the disordered carbon atoms was not entirely satisfactory since the thermal parameters of atoms C1, C2, C6, and C8 were negative in final cycles of refinement. Nevertheless, this procedure accounted for most of the electron density in the region of the ethylene carbon atoms. The final Fourier showed peaks in this region which were 0.16 the height of an oxygen atom. At the conclusion of the refinement values for R_F and R_wF obtained by using calculational procedures and programs outlined previously⁷ were 0.039 and 0.046. The final estimated standard deviation of an observation of unit weight was 1.87. The positional and thermal parameters for the atoms of $[\text{Mn}(\text{C}_8\text{H}_{16}\text{O}_4)_2](\text{Br}_3)_2$ are given in Table I. A listing of the final observed and calculated structure factors is available as supplementary material.

Results and Discussion

The structural analysis of $\text{Mn}(\text{C}_8\text{H}_{16}\text{O}_4)_2(\text{Br}_3)_2$ shows that the complex cation consists of two 12-crown-4 ligands bonding

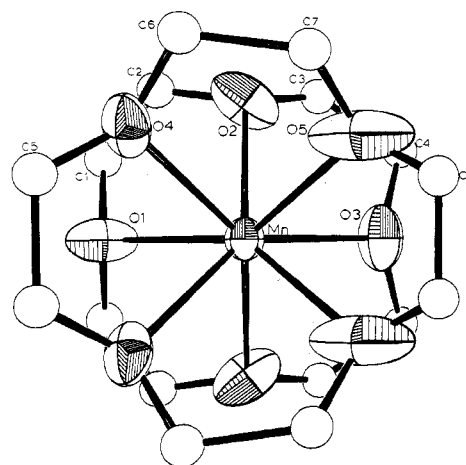


Figure 1. View of the $\text{Mn}(\text{C}_8\text{H}_{16}\text{O}_4)_2^{2+}$ cation down the pseudo-fourfold axis of the square antiprism. The carbon atoms are represented with small isotropic thermal ellipsoids for clarity. The Mn, O1, and O3 atoms lie on the crystallographic mirror plane.

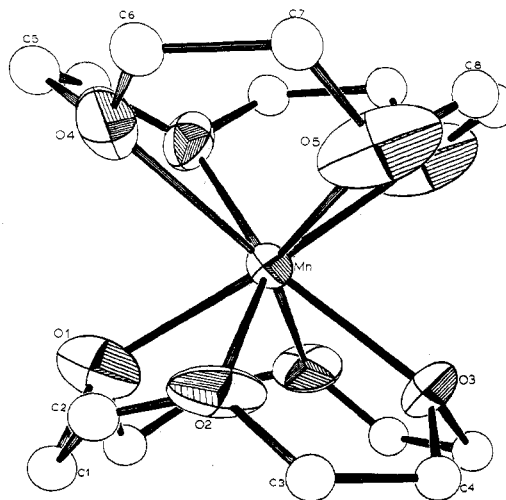


Figure 2. A perspective view of the $\text{Mn}(\text{C}_8\text{H}_{16}\text{O}_4)_2^{2+}$ cation.

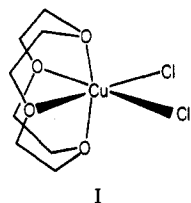
in "sandwich" fashion to a Mn(II) ion. The metal ion is located on a crystallographic mirror plane which requires that the O4 fragments of the two crown ether ligands be coplanar.

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The ligands are staggered about the metal forming a regular square-antiprismatic coordination geometry. Views of the complex cation are shown in Figures 1 and 2. Selected bond distances and angles are given in Table II. The 12-crown-4 ligand has been found previously to form similar coordination polyhedra with Na^+ and Ca^{2+} . The $[\text{Na}(\text{C}_8\text{H}_{16}\text{O}_4)_2]\text{X}\cdot 5\text{H}_2\text{O}$, $\text{X} = \text{Cl}, \text{OH}$, species have been examined structurally and shown to have square-antiprismatic coordination geometries.^{8,9} In one case the metal ion was oriented along a twofold axis. For this reason space group $C2$ was given careful consideration in the present refinement. The calcium complex $[\text{Ca}(\text{C}_8\text{H}_{16}\text{O}_4)(\text{H}_2\text{O})_4]\text{Cl}_2\cdot 4\text{H}_2\text{O}$ has also been found to have a square-antiprismatic coordination geometry, consisting of one crown ether ligand and four aquo ligands.¹⁰

Unfortunately, the large standard deviations associated with the carbon and oxygen atom positions eliminate a detailed discussion of the specific features of the coordination geometry of $\text{Mn}(\text{C}_8\text{H}_{16}\text{O}_4)_2^{2+}$. The magnitude of these errors results from the combined effects of carbon atom disorder and the large contributions to the diffraction effect made by the heavy atoms. Nevertheless, the average Mn-O length of the structure shows clearly that the crown ether ligands are very weakly bound to the metal. This value of 2.31 Å is greater than 0.1 Å longer than Mn-O lengths in $\text{Mn}(\text{H}_2\text{O})_6^{2+}$ which average to 2.18 Å.¹¹

One other 12-crown-4 complex of a transition-metal ion has been characterized structurally. The $\text{Cu}(\text{C}_8\text{H}_{16}\text{O}_4)\text{Cl}_2$ molecule has been shown to have a distorted octahedral coordination geometry with cis chloro ligands (I).¹² In this structure



the flexibility and the steric constraints of the crown ether ligand are reflected in the trans O-Cu-O angle of 135.2 (1)°. The cis O-Cu-O angle is 84.2 (1)°. It is interesting to note in this structure the difference in Cu-O lengths at the two coordination positions. Values at the positions trans to the chloro ligands reflect relatively strong bonding (2.12 Å) compared with the trans Cu-O values (2.37 Å) and the values which we find for $\text{Mn}(\text{C}_8\text{H}_{16}\text{O}_4)_2^{2+}$. While crown ether coordination in $\text{Mn}(\text{C}_8\text{H}_{16}\text{O}_4)_2^{2+}$ is relatively weak, this need not be the case in all transition-metal complexes.

Structural features of the tribromide anions are quite regular with an average Br-Br length of 2.544 (7) Å and a linear bond angle of 179.2 (1)°.

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Registry No. $[\text{Mn}(\text{C}_8\text{H}_{16}\text{O}_4)_2](\text{Br}_3)_2$, 73017-46-6.

Supplementary Material Available: A listing of structure factor amplitudes (3 pages). Ordering information is given on any current masthead page.

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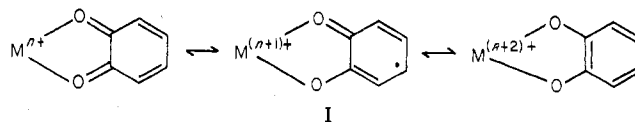
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Structural Features of $\text{Ir}(\text{NO})(\text{PPh}_3)(\text{O}_2\text{C}_6\text{Br}_4)$, a Complex Molecule Containing both Quinone and Nitrosyl Ligands

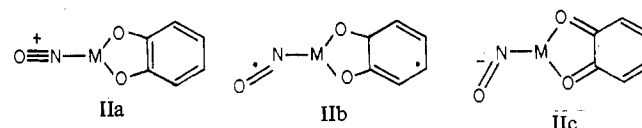
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The ability of the nitrosyl ligand to bond with transition metals as either a one- or three-electron donor has been well established.² We have recently discussed the tautomeric forms of the *o*-quinone chelate ring which enable ligands of this type to alter charge at the metal center via intramolecular transfer of one or two electrons between the metal ion and the quinone π^* level (I).³ Both ligands have demonstrated the property



of modulating charge at the metal center, and we have sought to exploit this feature catalytically by investigating a series of iridium complexes containing nitrosyl and quinone ligands.⁴ In addition to regulating charge at the metal center the two types of ligands are capable of influencing their own modes of coordination intramolecularly. One can envision a series with members related by the transfer of electrons between the quinone and nitrosyl π^* levels (II). Through the series the



formal charge of the metal remains constant. Structural studies have played a central role in the characterization of both quinone and nitrosyl complexes. The structure of $\text{Ir}(\text{NO})(\text{PPh}_3)(\text{O}_2\text{C}_6\text{Br}_4)$ has been determined crystallographically to characterize fully the modes of quinone and nitrosyl coordination in the $\text{Ir}(\text{NO})(\text{PPh}_3)_2(\text{Cat})$ complexes.

Experimental Section

A sample of $\text{Ir}(\text{NO})(\text{PPh}_3)(\text{O}_2\text{C}_6\text{Br}_4)$, prepared by methods outlined previously,⁴ was recrystallized from dichloromethane. Large prismatic crystals of the complex obtained by this procedure were found to contain one solvent molecule with the complex. Preliminary photographs indicated only triclinic symmetry, and space group $P\bar{1}$ was assumed. A crystal of dimensions 0.104 × 0.175 × 0.274 mm was mounted and aligned on a Syntex $P\bar{1}$ automated diffractometer. Lattice constants of $a = 8.846$ (1) Å, $b = 15.848$ (2) Å, $c = 10.307$ (2) Å, $\alpha = 87.68$ (2)°, $\beta = 93.12$ (2)°, $\gamma = 106.68$ (2)°, and $V = 1381.5$ Å³ were obtained from a least-squares refinement of the centered settings of 15 high-angle reflections. A calculated density of 2.145 g cm⁻³ agrees with an experimental value of 2.15 g cm⁻³ for two formula units of composition $\text{Ir}(\text{NO})(\text{P}(\text{C}_6\text{H}_5)_3)(\text{O}_2\text{C}_6\text{Br}_4)\cdot\text{CH}_2\text{Cl}_2$ per unit cell. Intensity data were collected within the angular range 3° ≤ 2θ ≤ 50° by the θ-2θ scan technique using Mo Kα radiation.

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