

Conclusion

A series of d^{10} - d^{10} binuclear cradle complexes with μ -isocyanides (1-4), μ -aminocarbynes (5-9), and μ -nitrosyl (10) have been prepared and the electronic structures compared. A $Ni_2 \rightarrow \mu$ -CNR π^* excited state of complexes 1-4 provides the unique ability to activate CO_2 by an *associative* pathway.⁵ Due to the stability of the dinickel cradle core, a systematic study of the effects of placing different π -acceptor ligands in the bridgehead position was possible. The degree of π -acceptor ability of the bridging ligand results in profound changes in the degree of metal-metal bonding and the frontier orbitals. The series of μ -isocyanide, μ -aminocarbyne, and μ -nitrosyl compounds have also demonstrated

a remarkable difference in their photochemistry, owing to their subtle differences in electronic structure. The bridging isocyanide complexes show low-lying excited states that are described as MLCT; the aminocarbyne complexes show excited states that are described as LMCT; and the nitrosyl complex is best described as having an IL lowest energy excited state.

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Complexes of the Ligand 1,5,8,12-Tetraazadodecane (3,2,3-tet) with Manganese(III) and with a Valence-Trapped Manganese(III)/Manganese(IV) Hexanuclear Array. Crystal and Molecular Structures of [*trans*-Mn(3-IOBz)₂(3,2,3-tet)](ClO₄) and [Mn₆(3,2,3-tet)₄O₆(OAc)₃]₅·2H₂O·4C₄H₈O

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Mononuclear Mn(III) complexes containing two coordinated carboxylates and the tetraamine 1,5,8,12-tetraazadodecane (3,2,3-tet) have been synthesized by using substituted benzoates. The complexes *trans*-bis(3-iodobenzoato)(1,5,8,12-tetraazadodecane)-manganese(III) perchlorate (6) and *trans*-bis(4-nitrobenzoato)(1,5,8,12-tetraazadodecane)manganese(III) iodide (7) were prepared, and 6 was structurally characterized. Complex 6 crystallizes in the monoclinic space group $P2_1/c$, $Z = 4$, with $a = 22.973$ (9) Å, $b = 12.029$ (3) Å, $c = 10.833$ (5) Å, and $\beta = 102.38$ (3)°, and the structure has been refined to an R of 0.035. The geometry around the Mn(III) ion is an irregular octahedron with monodentate benzoato ligands bound in *trans* positions. With acetate and benzoate as the carboxylate groups, a number of hexanuclear species have been isolated. A hexanuclear complex [Mn₆(3,2,3-tet)₄(OAc)₃O₆]₅·2H₂O·4C₄H₈O (3) has been structurally characterized. It crystallizes in the monoclinic space group $C2/c$, $Z = 4$, with $a = 27.733$ (13) Å, $b = 13.663$ (7) Å, $c = 27.020$ (14) Å, and $\beta = 124.16$ (3)°, and the structure has been refined to an R of 0.055. The asymmetric unit contains three types of manganese ions, a Mn(IV) ion octahedrally coordinated to a 3,2,3-tet ligand and two μ_2 -oxo groups, a Mn(III) ion coordinated to a 3,2,3-tet ligand, a μ_3 -oxo group, and a μ_2 -acetato ligand, and a Mn(III) ion with six oxygen donor atoms, two μ_2 -oxo groups, two μ_3 -oxo groups, and two μ_2 -acetato groups. Preparation of related benzoate complexes is also described. ESR, infrared, and visible spectra of these complexes have been measured and are discussed.

Introduction

The chemistry of manganese in oxidation states III-V is relatively sparse but is under active investigation. Most of the complexes that have been characterized over the last few years are polynuclear with μ -oxo and/or μ -carboxylato groups linking two,¹⁻¹⁶ three,^{14g,17-19} or four^{14a,20-25} manganese ions. However, species with six,^{25,26} seven,²⁷ nine,²⁸ ten,²⁹ and twelve³⁰ manganese ions have also been reported. The discovery of these complexes suggests that Mn(III) and Mn(IV) have a rich and complex chemistry which is of considerable interest in developing models for the oxygen-evolving complex in photosynthesis,^{31,32} manganese-containing catalases,^{33,34} ribonucleotide reductases,³⁵ and superoxide dismutases.³⁶ The chemistry and biochemistry of these systems has been the subject of a number of recent reviews.³⁷

Mononuclear complexes of Mn in the III and IV oxidation states have received much less attention recently, but such complexes are known with amine, phosphine, and arsine oxide ligands,³⁸ macrocyclic triamines,³⁹ tetraamines,^{40,41} and pentaamines,⁴² amino carboxylates,⁴³ catecholates,⁴⁴ a variety of Schiff base ligands,⁴⁵⁻⁴⁸ and porphyrins.⁴⁹ A recent report has described a mononuclear Mn(V) complex.⁵⁰

We have prepared and are attempting to characterize mixed-ligand complexes of Mn(III) and Mn(IV) with linear polyamines, such as diethylenetriamine (1,4,7-triazaheptane), triethylene-tetramine (1,4,7,10-tetraazadecane), 2,3,2-tet (1,4,8,11-tetra-

zaundecane), and 3,2,3-tet (1,5,8,12-tetraazadodecane), and carboxylate anions, such as acetate and benzoate.^{19,27} In most

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cases polynuclear complexes have been isolated. The nature of the compound isolated is variable; it depends on the polyamine,

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Table I. Crystallographic Data for $[\text{Mn}(3,2,3\text{-tet})(\text{OBz})_2](\text{ClO}_4)$ (6) and $[\text{Mn}_6(3,2,3\text{-tet})_4(\text{OAc})_3\text{O}_6]_2 \cdot 2\text{H}_2\text{O} \cdot 4\text{C}_4\text{H}_8\text{O}$ (3)

	6	3
chem formula	$\text{MnC}_{22}\text{H}_{30}\text{N}_4\text{Cl}_2\text{O}_8$	$\text{Mn}_6\text{C}_{54}\text{H}_{133}\text{N}_{16}\text{O}_{15}$
fw	694.7	2093.6
space group	$P2_1/c$	$C2/c$
<i>a</i> , Å	22.973 (9)	27.733 (13)
<i>b</i> , Å	12.029 (3)	13.663 (7)
<i>c</i> , Å	10.833 (5)	27.020 (14)
β , deg	102.38 (3)	124.16 (3)
<i>V</i> , Å ³	2924 (2)	8472 (7)
<i>Z</i>	4	4
μ , cm ⁻¹	16.02	5.36
λ , Å		0.71069
<i>T</i> , K		148
transm coeff	0.902–0.425	0.966–0.601
<i>R</i>	0.0348	0.0548
<i>R_w</i>	0.0375	0.0548

the carboxylate ion, and also on the nature of the counteranion. The solids isolated have proved difficult to characterize fully, as in many cases crystals suitable for X-ray structural determinations have not been obtained. In this paper we report the results of our investigations on the nature of the complexes formed by the tetraamine 3,2,3-tet.

Experimental Section

Safety Note. Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these should be handled with great caution.

Synthesis. $[\text{Mn}_6(3,2,3\text{-tet})_4(\text{OAc})_3\text{O}_6]_2 \cdot 4\text{H}_2\text{O}$ (1). The ligand 3,2,3-tet (0.5 g) in methanol (5 cm³) was added to a warm solution of Mn(OAc)₂ (0.7 g) in methanol (20 cm³). Solid NaClO₄ (1.05 g) was added, and the dark green solution was filtered hot. Upon cooling, a dark green solid formed, which was filtered out and dried in vacuo. The compound was recrystallized by vapor diffusion of methanol into a CH₃CN solution of the complex.

Anal. Calcd for C₃₈H₁₀₅N₁₆O₃₆Cl₂Mn₆: C, 24.41; H, 5.62; N, 11.99; Cl, 9.48; Mn, 17.64. Found: C, 24.30; H, 5.72; N, 11.50; Cl, 9.13; Mn, 18.97. Electronic spectrum (CH₃CN) [λ , nm (ϵ): 588 (1600), 521 (sh) (1960), 242 (37900)].

$[\text{Mn}_6(3,2,3\text{-tet})_4(\text{OAc})_3\text{O}_6]_2 \cdot 4\text{H}_2\text{O}$ (2). 3,2,3-tet (0.3 g) in methanol (5 cm³) was added to a warm solution of Mn(OAc)₃ (0.5 g) and NaOAc (0.3 g) in methanol (20 cm³). Potassium iodide (1.0 g) was added to the pale yellow solution, which was filtered hot. Upon cooling, the solution turned a green brown color and dark green needles formed on standing.

Anal. Calcd for C₃₈H₁₀₅N₁₆O₁₆I₂Mn₆: C, 22.74; H, 5.24; N, 11.17; I, 31.64; Mn, 16.44. Found: C, 22.59; H, 5.09; N, 10.87; I, 31.57; Mn, 16.08. Electronic spectrum (DMF) [λ , nm (ϵ): 590 (sh) (1400), 514 (sh) (1900), 242 (37900)].

$[\text{Mn}_6(3,2,3\text{-tet})_4(\text{OAc})_3\text{O}_6]_2 \cdot 2\text{H}_2\text{O} \cdot 4\text{C}_4\text{H}_8\text{O}$ (3). Crystals of 3 (the THF-solvated form of 2) suitable for X-ray examination were obtained by vapor diffusion of tetrahydrofuran (THF) into a dimethylformamide (DMF) solution of the complex. The X-ray analysis showed that these dark green crystals contained four molecules of THF and two molecules of water of crystallization.

$[\text{Mn}_6(3,2,3\text{-tet})_4(\text{OBz})_2\text{O}_6]_2 \cdot 7\text{H}_2\text{O}$ (4). 3,2,3-tet (0.5 g) in methanol (5 cm³) was added to a mixture of Mn(ClO₄)₂·6H₂O (0.73 g) and sodium benzoate (0.41 g) in hot methanol (30 cm³). The green solution was filtered hot. Upon cooling, a black powder precipitated, which was recrystallized by dissolving in a minimum volume of CH₃CN

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and diffusing in MeOH vapor. Black hexagonal crystals were obtained.

Anal. Calcd for $C_{60}H_{116}N_{16}Cl_4O_{40}Mn_6$: C, 33.16; H, 5.34; N, 10.31; Cl, 6.53; Mn, 15.18. Found: C, 33.51; H, 5.15; N, 10.44; Cl, 6.92; Mn, 15.05. Electronic spectrum (CH_3CN) [λ , nm (ϵ): 593 (1900), 523 (sh) (2400), 411 (sh) (4800), 283 (370 000), 229 (670 000).

[Mn₆(3,2,3-tet)₄(OBz)₃O₆]₂·H₂O·CH₃OH (5). The ligand 3,2,3-tet (0.5 g) in methanol (5 cm³) was added to a warm solution of MnBr₂ (0.62 g) and NaOBz (1.24 g) in methanol (30 cm³). Solid KI (1.43 g) was added, and the solution was filtered hot. Upon cooling, a solid formed, which was filtered out and dried in vacuo. The compound was recrystallized from a CH₃CN solution, yielding fragile red-black needles.

Anal. Calcd for $C_{54}H_{109}N_{16}O_{14}I_2Mn_6$: C, 29.87; H, 5.02; N, 10.32; I, 29.25; Mn, 15.20. Found: C, 29.66; H, 4.86; N, 10.26; I, 29.32; Mn, 15.65. Electronic spectrum (DMF) [λ , nm (ϵ): 587 (sh) (1490), 513 (sh) (2000), 270 (41 000).

trans-[Mn(3,2,3-tet)(IOBz)₂]ClO₄ (6). A solution of 3,2,3-tet (0.5 g) in methanol (5 cm³) was added dropwise to a warm solution of 3-iodobenzoic acid (1.42 g) and Mn(ClO₄)₂·6H₂O (0.73 g) in methanol (30 cm³). The color of the solution gradually changed from colorless to pale yellow green. After warming for a few minutes, the solution was cooled and allowed to stand overnight whereupon lime green hexagonal plates precipitated from a brown solution. The product was isolated and recrystallized from CH₃CN solution.

Anal. Calcd for $C_{22}H_{30}N_4I_2O_8ClMn$: C, 32.10; H, 3.65; N, 6.81; Cl, 4.31. Found: C, 32.78; H, 4.02; N, 6.64; Cl, 4.40. Electronic spectrum (DMF) [λ , nm (ϵ): 950 (17), 361 (1000), 273 (8950).

trans-[Mn(3,2,3-tet)(NO₂OBz)₂] (7). A solution of 3,2,3-tet (1.1 g) in methanol (10 cm³) was added dropwise to a hot solution of sodium 4-nitrobenzoate (5.6 g) and MnBr₂ (2.9 g) in methanol (50 cm³). Potassium iodide (3.0 g) was then added. Upon standing overnight, the solution yielded orange brown crystals.

Anal. Found: C, 38.13; H, 4.55; N, 12.47. Calcd for $C_{22}H_{30}N_6O_{12}ClMn$: C, 38.38; H, 4.39; N, 12.21. Electronic spectrum (DMF) [λ , nm (ϵ): 372 (sh) (1350), 274 (2900).

Crystallography. Information regarding the structure determinations is presented in Table I. Full details are included in the supplementary material. Crystals of both complexes suitable for X-ray studies were mounted on a glass fiber. The data sets were acquired on a Nicolet R3m diffractometer using Mo K α radiation. Cell dimensions were determined by least-squares refinement of 25 accurately centered reflections. Crystal stability was monitored by recording three check reflections every 100 reflections, and no significant variations were observed. Empirical absorption corrections were applied to both data sets.

For **6** direct methods revealed the position of the heavy atoms and the remaining non-hydrogen atoms were located by using difference Fourier maps. Hydrogen atoms were inserted in calculated positions by using a riding model with thermal parameters equal to 1.2U of their carrier atoms. Anisotropic thermal parameters were assigned to all non-hydrogen atoms.

For **3** the heavy atoms and most of the ligand atoms were located by direct methods. The remaining atoms of the amine and acetate ligands were located by a difference Fourier together with the oxygen of a molecule of water of crystallization. All of the atoms located at this stage were then refined anisotropically with the exception of the carbons of the acetate, which lie on the crystallographic mirror plane. Hydrogen atoms were added at calculated positions. At this stage the *R* value was 0.08. Inspection of the difference Fourier revealed the presence of two molecules of THF in the asymmetric unit. The oxygens of these molecules were located on the basis of their temperature factors and the bond lengths. Temperature factors of the atoms in the THF molecules are high; attempts to include these molecules at half-occupancy resulted in unsatisfactory bond lengths within the THF molecules. In subsequent refinement cycles therefore the THF molecules were refined isotropically at full occupancy. Hydrogen atoms of the THF molecules were included in their calculated positions. Further cycles of least-squares refinement gave an *R* value of 0.055. The final difference Fourier revealed that the two highest peaks (1.3 e \AA^{-3}) were within 1 \AA of I(2) and I(3), respectively, and the next highest peak was 0.7 \AA from the oxygen of the water of crystallization. Attempts to refine the structure in the alternative space group *Cc* resulted in a higher *R* factor with a larger number of parameters and with unsatisfactory geometries in the complex cation.

Final atomic coordinates for both **6** and **3** are given in Tables II and III. Tables containing the anisotropic thermal parameters, a complete set of bond distances and angles, and torsion angles around the tetramine ligands are available as supplementary material.

Other Measurements. Magnetic susceptibility measurements were made with the Faraday method. ESR spectra were recorded on a Varian E-Line Century series spectrometer as frozen glasses in DMF. Infrared spectra (Nujol mull and KBr disks) were recorded on a Perkin-Elmer 599B or a Biorad FTS40 Fourier transform spectrometer, and visible

Table II. Fractional Coordinates for the Non-Hydrogen Atoms of **6**

atom	x	y	z
Mn	0.2538 (1)	0.5580 (1)	0.3909 (1)
N(1)	0.2747 (2)	0.7246 (4)	0.4109 (4)
C(1)	0.3380 (3)	0.7551 (5)	0.4190 (5)
C(2)	0.3568 (3)	0.7260 (5)	0.2956 (6)
C(3)	0.3617 (3)	0.6012 (5)	0.2727 (6)
N(2)	0.3032 (3)	0.5422 (4)	0.2529 (4)
C(4)	0.3111 (3)	0.4200 (5)	0.2350 (5)
C(5)	0.2529 (3)	0.3642 (5)	0.2351 (5)
N(3)	0.2333 (2)	0.3938 (4)	0.3522 (4)
C(6)	0.1707 (3)	0.3582 (5)	0.3478 (6)*
C(7)	0.1512 (3)	0.3792 (5)	0.4702 (6)
C(8)	0.1455 (3)	0.5023 (5)	0.5013 (6)
N(4)	0.2059 (2)	0.5566 (4)	0.5289 (4)
O(11)	0.1754 (2)	0.6007 (3)	0.2510 (4)
C(10)	0.1697 (3)	0.6636 (4)	0.1557 (5)
O(12)	0.2100 (2)	0.7214 (3)	0.1286 (4)
C(11)	0.1079 (3)	0.6692 (4)	0.0720 (5)
C(12)	0.0589 (3)	0.6311 (4)	0.1178 (5)
C(13)	0.0021 (3)	0.6415 (4)	0.0465 (5)
I(1)	-0.0723 (1)	0.5960 (1)	0.1185 (1)
C(14)	-0.0069 (3)	0.6851 (5)	-0.0758 (6)
C(15)	0.0413 (3)	0.7175 (5)	-0.1238 (6)
C(16)	0.0994 (3)	0.7117 (5)	-0.0501 (6)
O(21)	0.3325 (2)	0.5233 (3)	0.5286 (4)
C(20)	0.3407 (3)	0.4390 (5)	0.6009 (5)
O(22)	0.3059 (2)	0.3587 (3)	0.5942 (4)
C(21)	0.3974 (3)	0.4380 (5)	0.7017 (5)
C(22)	0.4067 (3)	0.3533 (5)	0.7909 (5)
C(23)	0.4602 (3)	0.3445 (5)	0.8776 (5)
I(2)	0.4717 (1)	0.2146 (1)	0.1008 (1)
C(24)	0.5058 (3)	0.4210 (5)	0.8773 (5)
C(25)	0.4967 (3)	0.5065 (5)	0.7875 (5)
C(26)	0.4425 (3)	0.5140 (5)	0.7008 (5)
Cl(1)	0.2459 (1)	0.0352 (1)	0.3703 (1)
O(1)	0.2356 (2)	-0.0314 (4)	0.4746 (4)
O(2)	0.2790 (2)	-0.0294 (4)	0.2952 (4)
O(3)	0.2782 (3)	0.1335 (4)	0.4163 (4)
O(4)	0.1894 (2)	0.0655 (4)	0.2894 (4)

spectra were recorded on a Shimadzu UV 160 or a Perkin-Elmer 330 spectrophotometer. Elemental analyses were performed by the micro-analytical service at Otago University.

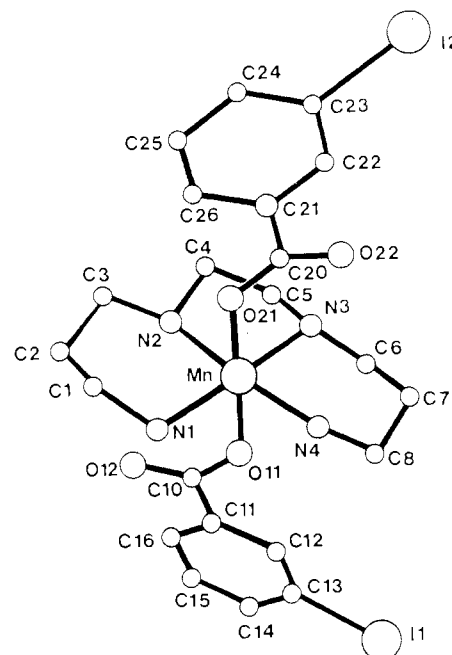
Results

The Experimental Section describes the preparation of four different hexanuclear complexes and two mononuclear complexes of the ligand 3,2,3-tet. These were produced either by the reaction in air of Mn(OAc)₃ with the 3,2,3-tet followed by the addition of a precipitating anion (ClO₄⁻, I⁻) or by the reaction of a solution of a Mn(II) salt, 3,2,3-tet, carboxylate, and the perchlorate anion (iodide is oxidized under these conditions). The final solutions in each case were a dark brown color. **3** has been produced by using both methods of preparation. From 3,2,3-tet and acetate, green black crystals of the hexanuclear species, [Mn₆(3,2,3-tet)₄(OAc)₃O₆]X₅ (X = I⁻, ClO₄⁻) were isolated. During attempts to obtain crystals suitable for X-ray investigations of this hexamer, complexes of Mn(III) and 3,2,3-tet with three other carboxylates, benzoate, 3-iodobenzoate, and 4-nitrobenzoate, were prepared. With benzoate we obtained what may be isostructural hexanuclear species [Mn₆(3,2,3-tet)₄(OBz)₄O₆](ClO₄)₄ (**4**) and [Mn₆(3,2,3-tet)₄(OBz)₃O₆]I₅ (**5**). However, some of the properties of the benzoate complexes differ from the properties of the acetate complexes. With the substituted benzoates quite different products were isolated. The hexanuclear species are dark green/black whereas the 3-iodobenzoate complex is lime green and the 4-nitrobenzoate species is a rusty orange solid. These complexes proved to be monomeric. Infrared, UV-vis, ESR, and magnetic measurements are introduced in the sections that follow.

Our experience with these and similar systems suggests that a range of polymeric species are present in solution and that the compound isolated from these labile systems is a consequence of its limited solubility under the particular experimental conditions chosen. The same phenomenon has been reported by Vincent et al.^{25c} in their study of the Mn/bpy system. Complexation of the

Table III. Fractional Coordinates for the Non-Hydrogen Atoms of **3**

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
I(1)	0.2500	0.2500	0.0000
I(2)	0.3566 (1)	0.6431 (1)	0.4136 (1)
I(3)	0.1345 (1)	0.5202 (1)	0.1281 (1)
Mn(1)	0.5281 (1)	0.3116 (2)	0.3742 (1)
Mn(2)	0.4392 (1)	0.3813 (1)	0.2280 (1)
Mn(3)	0.3244 (1)	0.4152 (2)	0.1848 (1)
O(1)	0.5148 (3)	0.3681 (6)	0.3053 (3)
O(2)	0.3910 (3)	0.3987 (6)	0.2561 (3)
O(3)	0.3664 (3)	0.3960 (6)	0.1542 (3)
O(11)	0.4677 (3)	0.1949 (7)	0.3251 (3)
O(12)	0.4268 (3)	0.2182 (7)	0.2271 (3)
O(22)	0.4534 (4)	0.5456 (7)	0.2349 (3)
N(11)	0.5936 (4)	0.2169 (7)	0.3884 (4)
N(12)	0.5302 (4)	0.2501 (9)	0.4462 (4)
N(13)	0.4709 (4)	0.4087 (8)	0.3778 (4)
N(14)	0.6027 (4)	0.4185 (8)	0.4327 (4)
N(31)	0.2464 (4)	0.4333 (9)	0.0993 (4)
N(32)	0.3346 (4)	0.5638 (8)	0.1894 (4)
N(33)	0.2828 (4)	0.4433 (9)	0.2284 (4)
N(34)	0.3035 (4)	0.2695 (9)	0.1787 (4)
C(11)	0.5989 (5)	0.1153 (10)	0.4112 (5)
C(12)	0.6003 (6)	0.1161 (11)	0.4685 (6)
C(13)	0.5431 (5)	0.1461 (11)	0.4597 (6)
C(14)	0.4725 (6)	0.2720 (12)	0.4355 (6)
C(15)	0.4628 (6)	0.3793 (11)	0.4256 (5)
C(16)	0.4778 (6)	0.5161 (11)	0.3775 (6)
C(17)	0.5378 (5)	0.5540 (12)	0.4267 (6)
C(18)	0.5865 (5)	0.5238 (11)	0.4207 (5)
C(31)	0.2489 (6)	0.5029 (10)	0.0573 (5)
C(32)	0.2625 (5)	0.6073 (11)	0.0806 (5)
C(33)	0.3246 (6)	0.6177 (11)	0.1365 (6)
C(34)	0.3041 (6)	0.6086 (12)	0.2148 (6)
C(35)	0.3053 (5)	0.5393 (12)	0.2579 (5)
C(36)	0.2907 (6)	0.3731 (12)	0.2732 (6)
C(37)	0.2711 (6)	0.2724 (12)	0.2474 (6)
C(38)	0.3098 (6)	0.2216 (11)	0.2314 (6)
C(1)	0.4446 (5)	0.1632 (10)	0.2721 (5)
C(2)	0.4356 (6)	0.0562 (11)	0.2628 (6)
C(3)	0.5000	0.5902 (14)	0.2500
C(4)	0.5000	0.7023 (25)	0.2500
O(4)	0.1091 (7)	0.2802 (12)	0.1763 (7)
C(51)	0.1894 (9)	0.4012 (16)	0.3281 (9)
C(52)	0.2072 (9)	0.4835 (17)	0.3689 (9)
C(53)	0.2510 (9)	0.4411 (17)	0.4290 (9)
C(54)	0.2812 (9)	0.3692 (16)	0.4128 (9)
O(55)	0.2365 (6)	0.3318 (11)	0.3567 (6)
C(61)	0.8775 (11)	0.3264 (20)	0.0525 (11)
C(62)	0.9027 (10)	0.3176 (20)	0.0164 (10)
C(63)	0.9682 (10)	0.3504 (19)	0.0621 (10)
C(64)	0.9742 (10)	0.3536 (19)	0.1214 (10)
O(65)	0.9174 (13)	0.3427 (21)	0.1120 (13)

**Figure 1.** Structure of the cation of **6**, showing the atom-labeling scheme.**Table IV.** Bond Distances (Å) and Angles (deg) around Mn Atoms in **6** and **3**

6			
Distances			
Mn-N(1)	2.062 (5)	Mn-N(2)	2.070 (6)
Mn-N(3)	2.053 (5)	Mn-N(4)	2.038 (6)
Mn-O(11)	2.153 (4)	Mn-O(21)	2.123 (4)
Angles			
N(1)-Mn-N(2)	90.8 (2)	N(1)-Mn-N(3)	174.3 (2)
N(2)-Mn-N(3)	84.4 (2)	N(1)-Mn-N(4)	94.6 (2)
N(2)-Mn-N(4)	174.2 (2)	N(3)-Mn-N(4)	90.3 (2)
N(1)-Mn-O(11)	89.0 (2)	N(2)-Mn-O(11)	91.1 (2)
N(3)-Mn-O(11)	88.0 (2)	N(4)-Mn-O(11)	90.9 (2)
N(1)-Mn-O(21)	88.5 (2)	N(2)-Mn-O(21)	88.5 (2)
N(3)-Mn-O(21)	94.5 (2)	N(4)-Mn-O(21)	89.7 (2)
O(11)-Mn-O(21)	177.4 (2)		
3			
Distances			
Mn(1)-Mn(2)	3.413 (2)	Mn(2)-Mn(3)	2.746 (2)
Mn(2)-Mn(2)'	2.881 (3)	Mn(1)-Mn(3)	5.257 (4)
Mn(1)-O(1)	1.852 (7)	Mn(3)-O(2)	1.785 (7)
Mn(1)-O(11)	2.146 (9)	Mn(3)-O(3)	1.786 (8)
Mn(1)-N(11)	2.082 (10)	Mn(3)-N(31)	2.112 (9)
Mn(1)-N(12)	2.086 (10)	Mn(3)-N(32)	2.044 (12)
Mn(1)-N(13)	2.112 (10)	Mn(3)-N(33)	2.101 (10)
Mn(1)-N(14)	2.290 (10)	Mn(3)-N(34)	2.048 (13)
Mn(2)-O(1)	1.968 (7)	Mn(2)-O(2)	1.888 (7)
Mn(2)-O(3)	1.890 (7)	Mn(2)-O(12)	2.251 (9)
Mn(2)-O(22)	2.271 (10)	Mn(2)-O(1)'	1.939 (7)
Angles			
O(1)-Mn(1)-O(11)	92.4 (3)	O(2)-Mn(3)-O(3)	86.2 (3)
O(1)-Mn(1)-N(12)	171.8 (4)	O(3)-Mn(3)-N(33)	174.0 (4)
O(11)-Mn(1)-N(14)	171.7 (4)	O(2)-Mn(3)-N(31)	178.8 (4)
N(11)-Mn(1)-N(12)	90.8 (4)	N(31)-Mn(3)-N(32)	88.3 (4)
N(11)-Mn(1)-N(13)	169.2 (4)	N(32)-Mn(3)-N(34)	172.2 (4)
N(12)-Mn(1)-N(13)	80.8 (4)	N(32)-Mn(3)-N(33)	83.4 (4)
N(13)-Mn(1)-N(14)	88.8 (4)	N(33)-Mn(3)-N(34)	90.2 (4)
Mn(3)-Mn(2)-Mn(2)'	170.0 (4)	O(1)-Mn(2)-O(2)	99.1 (3)
O(1)-Mn(2)-O(3)	179.0 (4)	O(1)-Mn(2)-O(12)	89.3 (3)
O(1)-Mn(2)-O(22)	88.3 (3)	O(2)-Mn(2)-O(3)	80.5 (3)
O(2)-Mn(2)-O(12)	89.7 (3)	O(2)-Mn(2)-O(22)	88.3 (3)
O(3)-Mn(2)-O(12)	91.6 (3)	O(3)-Mn(2)-O(22)	90.9 (3)
O(12)-Mn(2)-O(22)	176.5 (3)		

amine without concomitant oxidation of the coordinated ligand was suggested by the infrared spectrum of all of the products and has been confirmed by X-ray structural studies of the hexanuclear complex **3** and the 3-iodobenzoate derivative **6**.

Discussion

Structural Studies. Despite many attempts we were unable to obtain crystals of **1**, **4**, or **5** that are suitable for X-ray studies. Well-formed crystals of **4** were obtained, but they proved to be poor diffractors of X-rays. Crystals of **3** that were suitable for structural studies were obtained by vapor diffusion of THF into a DMF solution of **2**. Crystals of the iodobenzoate derivative **6** suitable for structural studies were obtained without difficulty. The structure of **7** was not investigated as it is expected to be very similar to that of **6**.

Description of the Structure of 6. The crystal structure of the salt [Mn(3,2,3-tet)(IOBz)₂](ClO₄) (**6**) consists of the complex cation, a view of which is shown in Figure 1, and a perchlorate anion. No unusual features are shown by the perchlorate anion or the 3-iodobenzoate moiety. The geometry around the Mn(III) ion is close to octahedral with the 3-iodobenzoates bound as monodentate ligands in trans axial positions. Selected bond distances and angles are given in Table IV. The amine nitrogens

and the Mn(III) ion form a plane, where the maximum deviation of these atoms from the plane is 0.035 Å. The six-membered chelate rings of the ligand adopt chair conformations, and the

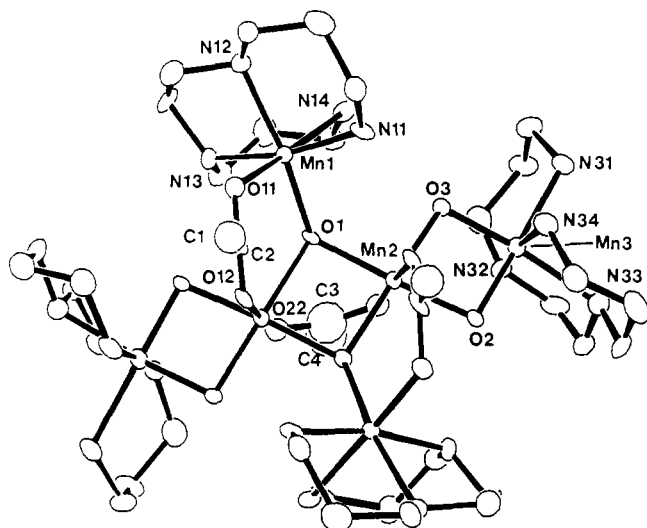


Figure 2. Structure of the cation of 3, showing the atom-labeling scheme.

five-membered chelate ring adopts a skew conformation. Bonding within the ligand and its coordination to the metal is similar to the bonding and coordination in the complexes of 3,2,3-tet with Co(III).⁵¹ The bonding to the metal ion by the tetraamine ligand is very similar to that in the structure of the [Mn(teta)Cl₂]⁺ cation (teta is *meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) described by Hambley et al.⁴¹

Description of the Structure of 3. The average metal oxidation state of 3 is +3.33, which is consistent with two Mn(IV) and four Mn(III) centers. The asymmetric unit as revealed by the structural study contains half the cation, as a crystallographic 2-fold axis bisects the cation and one of the iodide ions. Distances and angles pertaining to the inner coordination sphere of the manganese ions are presented in Table IV. Full details are given in the supplementary material. The atomic numbering system used is shown in Figure 2, which presents a view of the complex cation.

The core of the cation is an approximately linear arrangement of four manganese ions Mn(2), Mn(3), and the symmetry-related Mn(2') and Mn(3') (the Mn(3)–Mn(2)–Mn(2') angle is 170°). Mn(2) is linked to Mn(1) (and the symmetry-related Mn(1')) by a μ_3 -oxo group and μ_2 -acetato groups. The coordination sphere of the Mn(1) atom is completed by a 3,2,3-tet ligand. Mn(3) is joined to Mn(2) via two μ_2 -oxo groups. The coordination sphere of Mn(3) is also completed by four nitrogens of a 3,2,3-tet ligand. The remaining coordination requirement of the Mn(2) atom is satisfied by a bridging μ_2 -acetato group, which links Mn(2) and Mn(2'). The carbon atoms of this bridging acetato group lie on the 2-fold axis. The arrangement of the manganese atoms in this structure is different from that of the previously reported structures of hexanuclear manganese species, which is described as two tetrahedra of Mn atoms that share an edge.²⁶

An alternative view of the structure of the cation is that it consists of a "butterfly" core similar to that observed in [Mn₄O₂(OAc)₇(bpy)₂]⁺^{25c} with Mn(2) and Mn(2') occupying the "hinge" sites and Mn(3) and Mn(3') occupying the "wing-tip" sites. The body of the butterfly is elongated by the addition of the Mn(1) and Mn(1') atoms, which are linked to the hinge atoms by the μ_2 -oxo groups. As in the previously observed butterfly structure, there is an acetato group bridging the two hinge atoms. In 3, however, there is only one carboxylato group in addition to the μ_3 -oxo group linking the wing tips to the hinge atoms whereas in [Mn₄O₂(OAc)₇(bpy)₂]⁺ there are three carboxylato groups linking these atoms. In 3 the Mn(2)–Mn(2') distance is 2.881 (3) Å whereas in [Mn₄O₂(OAc)₇(bpy)₂]⁺ the corresponding distance is 2.848 (5) Å. In 3 the distance from the wing tip to the hinge manganese atoms, when these are linked via a μ_2 -acetato

group, is 3.413 (2) Å, similar to the corresponding distance 3.385 (5) Å in [Mn₄O₂(OAc)₇(bpy)₂]⁺. The other wing tip to hinge distance in 3 is significantly longer (3.490 Å) than this distance or the distance between the atoms in [Mn₄O₂(OAc)₇(bpy)₂]⁺ (3.299 Å) linked via two μ_2 -acetato ligands.

Inspection of the bond angles and distances in Table IV reveals that the complex ion is valence trapped, with Mn(3) in the IV oxidation state and Mn(1) and Mn(2) in the III oxidation state. The Mn(3)–N and Mn(3)–O bond distances are shorter than the Mn(1)–N and Mn(2)–O bonds, and the Mn(3) coordination sphere does not display the marked Jahn–Teller distortion expected for a high-spin d⁴ ion and which is evident in the Mn(1) geometry. The Mn(3)– μ_2 -O bond lengths are within the range observed for other Mn(IV)– μ_2 -O bonds. The Mn(2)– μ_2 -O bonds are slightly longer than those usually observed for bonds to Mn(III), but the compounds that are used in the comparison have a mixed oxygen/nitrogen coordination sphere. The only known Mn(III) complex with all oxygen donor atoms has a five-coordinate coordination sphere,²³ and so direct comparisons are probably not very meaningful; however, the Mn–O bonds in 3 are longer than those in the five-coordinate species (Mn–O average = 1.99 Å).

Most of the bond types linking the manganese ions in 3 have been observed previously. Mn(IV) and Mn(III) atoms linked by two μ_2 -oxo groups have been observed in a number of dimeric complexes;^{5,8–10} Mn(III) atoms linked via two μ_3 -oxo groups and a μ_2 -acetato group have been observed in [Mn₄O₂(OAc)₇(bpy)₂]⁺.^{25c} The novel feature of the bonding in 3 is the trinuclear Mn₃O unit linked by a μ_3 -oxo and one μ_2 -acetato ligand.

3,2,3-tet may coordinate to pseudooctahedral metal ions in three different ways. The two coordination sites not occupied by the 3,2,3-tet ligand may be trans to each other, trans to the two secondary amines, or trans to a primary and a secondary amine. In 6 the benzoato ligands are trans to each other. In 3 the two ligands are folded and the oxygen atoms bound to Mn(1) and Mn(3) are trans to primary and secondary amines. Comparison of the torsion angles within the three different ligands in 3 and 6 reveals very little difference (<±5°) with the exception of the angles where the ligand bends out of the plane of the three coplanar nitrogens in 3 compared to 6. This suggests that the ligand accommodates the different coordination requirements of the two Mn(III) ions and the Mn(IV) ion by adjusting the bond lengths to the metal but that the ligand is relatively rigid.

Infrared Spectra. All complexes show common features in their infrared spectra. All except 6 and 7 have broad OH stretches in the 3450–3650-cm⁻¹ region, and all have N–H bands in the 3300–3000-cm⁻¹ region, C=O vibrations between 1600 and 1350 cm⁻¹ and intense Mn–O bands between 720 and 600 cm⁻¹. The lowest energy C=O vibration, which is observed in the range 1385–1420 cm⁻¹ in the polynuclear complexes, occurs at lower frequencies 1365–1390 cm⁻¹ in the mononuclear complexes consistent with the change from bridging to monodentate coordination.⁵² A broad band comprising at least two peaks at ca. 550 and 530 cm⁻¹ is observed in the polynuclear complexes; it is absent from the spectra of the mononuclear complexes. This is consistent with the assignment of this band to a symmetric Mn–O–Mn vibration.¹

Ultraviolet–Visible Spectra. Details of the electronic spectra of the complexes are presented in the Experimental Section. The spectra of the hexanuclear complexes are similar. Each exhibits two bands of relatively low intensity in the visible region and a very intense charge-transfer band in the ultraviolet region. Compound 4 exhibits a more complex spectrum, but the basic pattern is similar. The spectra of the monomeric complexes 6 and 7 are similar to the spectra reported for the [Mn(teta)Cl₂]⁺ complex;⁴¹ there is broad weak d–d absorption band at ~895 nm and much stronger absorptions (assigned to charge-transfer transitions) below 400 nm. A single weak d–d transition is expected for a high-spin d⁴ complex, and magnetic susceptibility measurements, to be discussed below, indicate that the complexes

(51) Payne, N. C. *Inorg. Chem.* 1972, 11, 1376–81. Payne, N. C. *Inorg. Chem.* 1973, 12, 1151–1156.

(52) Nakamoto, K. *Infrared Spectra of Inorganic and Coordination Compounds*, 2nd ed.; Wiley-Interscience: New York, 1970.

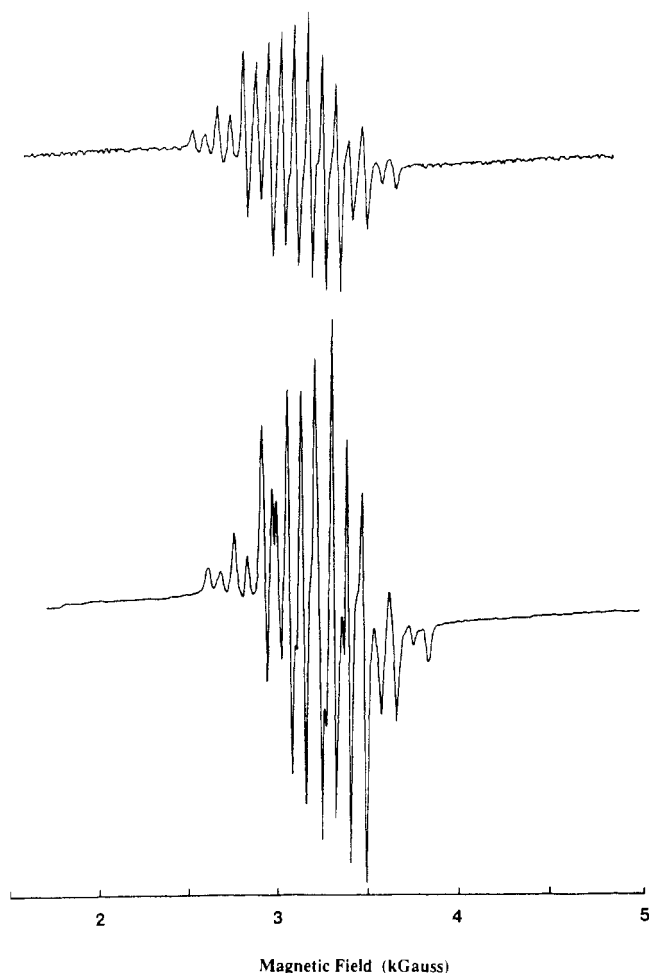


Figure 3. Frozen-solution ESR spectra for compounds **4** (top) and **5** (bottom) in DMF. Conditions: for **4** and **5**, temperature $-160\text{ }^{\circ}\text{C}$; for **4**, microwave power 0.98 mW, modulation amplitude 12.5 G, gain 1×10^3 , frequency 8.99 G Hz; for **5**, power 17 mW, modulation amplitude 12.6 G, gain 2.5×10^3 , frequency 8.99 G Hz.

are high spin. Hambley et al.⁴¹ analyzed the spectrum of the $[\text{Mn}(\text{tetra})\text{Cl}_2^+]$ complex ion in terms of a low-spin d^4 complex, but this analysis must be incorrect as the tetra complex is also high spin.⁴⁰

ESR Spectra. Complexes **1** and **3** were ESR silent in frozen DMF solutions. The spectra of **4** and **5** are shown in Figure 3. The spectrum of **4** consists of a single resonance at $g = 2.02$, which is composed of 16 hyperfine lines separated by 84 G. The spectrum of **5** shows two resonances, an intense 18-line hyperfine pattern centered at $g = 2.02$ and a small broad resonance at half-field $g = 3.95$. The different patterns at $g = 2$ in these two spectra probably result from the overlap of a 16-line pattern due to Mn(III)/Mn(IV) coupling and a six-line pattern due to Mn(IV). Different degrees of overlap of the two features result in variations in the number of observed hyperfine lines. A small amount of dissociation of the hexanuclear complex may give rise to the

half-field resonance in the spectrum of **5**, or it may be due to a Mn(IV) impurity.

Both **6** and **7** gave ESR spectra, which is unusual, as in general Mn(III) complexes are ESR silent due to very fast relaxation times.⁵³ Both spectra had two resonances, a six-line hyperfine pattern centered at $g = 2$, separated by ca. 100 G, and a broad peak at $g = 9.17$. These ESR spectra suggest that disproportionation of the Mn(III) complex into Mn(II) and Mn(IV) complexes has occurred under the conditions of these experiments. The $g = 2$ signal can be assigned to Mn(II), and the $g = 9.17$ signal, to Mn(IV). The spectrum is almost certainly due to monomeric Mn species, as the DMF solution was the same color as the solid sample before and after the ESR experiments and showed no tendency toward the formation of a brown/black color, which would indicate polynuclear complexes.

Magnetic Measurements. The magnetic moments of the complexes at room temperature were 8.03, 7.77, 8.23, 7.69, 4.65, and $4.79\ \mu_{\text{B}}$ for **1**, **2**, **4**, **5**, **6**, and **7**, respectively. The values for **6** and **7** are smaller than the spin-only value for a high-spin d^4 ion but are comparable to the values determined for other monomeric Mn(III) complexes.⁴¹ The values for **1**–**5** indicate that spin coupling occurs in these complexes, but a detailed temperature study is necessary before any useful information regarding the magnetic interactions is obtained.

Finally, a comment on the structure of the benzoate complexes **4** and **5** is called for. Compound **5** has the same formula (with the substitution of benzoate for acetate) as **3**, and we believe that the structure is probably very similar despite the fact that **5** gives an ESR spectrum and **3** is ESR silent under the same experimental conditions. We are supported in this belief by a structural analysis of a $[\text{Mn}_6(2,3,2\text{-tet})_4\text{O}_6(\text{OBz})_3]\text{I}_5$ complex that is currently in progress.²⁷ The ESR spectrum of the $[\text{Mn}_6(2,3,2\text{-tet})_4\text{O}_6(\text{OBz})_3]\text{I}_5$ complex and that of **5** are very similar, and while the structural analysis is not yet complete, a structure similar to that of **3** is indicated. The exact nature of the perchlorate salt **4** is not clear. The simplest explanation is that **4** contains the same cation as **5** and that there are four perchlorates and one ionic benzoate balancing the charge. If this were the case, then the infrared spectrum of **4** should be more complex than that of **5** due to the presence of ionic and coordinated benzoate anions. This is not observed however so that this simple explanation is probably not correct.

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Supplementary Material Available: Tables listing complete details of the crystallographic data, thermal parameters for **3** and **6**, full details of the bonding in **3** and **6**, and torsion angles in **3** and **6** (12 pages); tables of observed and calculated structure factors (49 pages). Ordering information is given on any current masthead page.

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