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Synthesis and Characterization of Bis(μ-oxo)dimanganese(III,III), -(III,IV), and -(IV,IV) Complexes with Ligands Related to *N,N'*-Bis(2-pyridylmethyl)-1,2-ethanediamine (Bispicen)

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The syntheses and characterization of a series of binuclear bis(μ-oxo)dimanganese(III,III), -(III,IV), and -(IV,IV) complexes of the general type $[(A)_4Mn(O)]_2^{2+/3+/4+}$, where the symbol A_4 represents the four nitrogen atoms from a tetradentate ligand, are described. The ligands $(A)_4$ used are *N,N'*-bis(2-pyridylmethyl)-*N,N'*-dimethyl-1,2-ethanediamine (bispicMe$_2$en) and *N,N'*-bis(2-pyridylmethyl)-*N,N'*-dimethyl-(–)$_D$-1,2-cyclohexanediamine (bispicMe$_2$(–)chxn). The syntheses and properties of the (III,III), (III,IV), and (IV,IV), complexes (where (III,III) represents dimanganese(III,III), etc.) of bispicMe$_2$en are described, as are those of the (III,IV) and (IV,IV) complexes of bispicMe$_2$(–)chxn. The (III,IV) complex $[(\text{bispicMe}_2\text{en})Mn(O)]_2(ClO_4)_3\cdot H_2O$ (**1**) crystallizes in the monoclinic space group $P2_1/c$ with 4 formula units in a cell of dimensions a = 19.839(4) Å, b = 12.468(3) Å, c = 19.878(3) Å, and β = 120.657(10)°. The structure refined to a final *R*-factor of 0.062 based on 2874 reflections. The isomer crystallized is the *cis*-α-species, in which the pyridine nitrogen atoms are *trans*. The Mn(1)–O bonds are approximately 0.06 Å longer than the Mn(2)–O bonds, and the geometry at Mn(1) is significantly axially elongated; hence, the manganese atoms can be distinguished as Mn(1) being Mn(III) and Mn(2) being Mn(IV). The Mn···Mn separation in the dimer is 2.678(2) Å. The (III,III) complex $[(\text{bispicMe}_2\text{en})Mn(O)]_2(ClO_4)_2\cdot 5H_2O$ (**3**) crystallizes in space group $Aba2$ of the orthorhombic system with four dinuclear formula units in a cell of dimensions a = 15.561(3) Å, b = 16.703(3) Å, and c = 16.430(3) Å. The structure has been refined to a final *R*-factor of 0.0564 based on 2548 observed independent reflections. The isomer is again the *cis*-α-species. There is a crystallographic 2-fold axis passing through the center of the dimer and relating one manganese(III) center to the other. As is expected for a d^4 Mn(III) ion, the geometry at manganese is axially elongated, the average Mn–N(axial) bond being approximately 0.12 Å longer than the average of the equatorial Mn–N bonds. The Mn···Mn separation in the dimers of 2.699(2) Å is comparable to that in related systems. The (III,IV) complex $[(\text{bispicMe}_2(-)\text{chxn})MnO_2Mn(\text{bispicMe}_2(-)\text{chxn})](ClO_4)_3$ (**4**) crystallizes in the orthorhombic space group $P2_12_12_1$ with four dinuclear formula units in a cell of dimensions a = 13.098(3) Å, b = 16.297(3) Å, and c = 23.273(4) Å. The structure has been refined to a final *R*-factor of 0.0620 based on 3057 observed independent reflections. The isomer is *cis*-α, with roughly isotropic geometry at Mn(2) and axial elongation at Mn(1). Thus atom Mn(1) is the *localized* d^4 Mn(III) site and Mn(2) is the *localized* d^3 Mn(IV) center. The Mn···Mn separation in the dimer is 2.693(2) Å. The complexes exhibit antiferromagnetic interactions, the (III,III) complex **3** having $2J = -201$ cm^{-1}, the (IV,IV) complexes **2** and **5** $2J$ values of –205 and –211 cm^{-1}, respectively, and the (III,IV) complexes **1** and **4** $2J$ values of –320 and –293 cm^{-1}, respectively.

Introduction

In a recent series of papers we[2–10] and others[11–19] have discussed the syntheses and characterization of a variety of bis(μ-oxo)dimanganese complexes. Our interest in these systems derives both from the established role of binuclear and/or polynuclear manganese complexes in biological redox processes and from their potential application as redox catalysts. In particular, we have isolated and characterized complexes in the three redox states, dimanganese(III,III), dimanganese(III,IV), and dimanganese(IV,IV) ((III,III), (III,IV), and (IV,IV)). From a catalytic viewpoint, the isolation of systems in which the (III,III) species

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is the stable form in aqueous medium in the absence of added oxidant or reductant may be of particular relevance, since the corresponding oxidized (IV,IV) species may be expected to be a very powerful oxidant. Indeed, we have demonstrated the ability of such (IV,IV) complexes to act as powerful oxidants toward organic compounds.[10]

It is our expectation that, in principle, a wide range of electrochemical properties can be obtained by suitable variation of the electronic and/or steric properties of the ligands. We initially demonstrated that the (III,III) form could be stabilized by either of these effects[9,10] and have had particular success by increasing the steric requirements of the ligand through suitable substitution.[10] We have also found, however, that substitution at sites relatively distant from the manganese binding site has virtually no effect in some cases. As example, we find that 6-methyl substitution on the pyridyl moieties of the tetradentate ligand *N,N'*-bis(2-pyridylmethyl)-1,2-ethanediamine (bispicen) to give 6-Mebispicen has a profound effect on the electrochemistry,[9,10] but methylation at the carbon atoms of the ethanediamine fragment has little impact. In the present paper, we have further studied the impact of substitution in the bispicen ligand on the electrochemical and other properties of these binuclear systems. We here report the syntheses, isolation, and characterization of bis(μ-oxo)dimanganese complexes of the ligands *N,N'*-bis(2-pyridylmethyl)-*N,N'*-dimethyl-1,2-ethanediamine (bispicMe$_2$en) and *N,N'*-bis(2-pyridylmethyl)-*N,N'*-dimethyl-(−)$_D$-1,2-cyclohexanediamine [bispicMe$_2$(−)chxn].

Experimental Section

Syntheses. Ligands. *N,N'-Bis(2-pyridylmethyl)-1,2-ethanediamine (bispicen).* This ligand was prepared by the methods described elsewhere.[20,21]

N,N'-Bis(2-pyridylmethyl)-N,N'-dimethyl-1,2-ethanediamine (bispicMe$_2$en). This ligand was prepared by direct methylation of bispicen using formic acid and formaldehyde by a standard method,[22] followed by purification as we have discussed elsewhere.[23] It can also be prepared as reported earlier.[24]

N,N'-Bis(2-pyridylmethyl)-(−)$_D$-1,2-cyclohexanediamine [bispic(−)chxn]. This ligand was prepared by the method described before.[20,21]

N,N'-Bis(2-pyridylmethyl)-N,N'-dimethyl-(−)$_D$-1,2-cyclohexanediamine, [bispicMe$_2$(−)chxn]. This ligand was prepared by direct methylation of bispic(−)chxn using formic acid and formaldehyde by a standard method.[22] From 14.2 g of bispic(−)chxn (48 mmol) was obtained 15 g of crude amine that was converted to the corresponding hydrochloride by the same method as described for bispicMe$_2$en.[23] Yield: 12.4 g (51%). Anal. Found: C, 47.55; N, 10.97; H, 6.57. Calcd for $C_{20}H_{28}N_4\cdot 4HCl\cdot 2H_2O$: C, 47.44; N, 11.07; H, 7.17. The compound was evidently very slightly contaminated with hydrochloric acid. The ligand can also be prepared as reported earlier.[25]

Complexes. *Warning! The following compounds were isolated as perchlorates and were treated as potential explosives.*

1. Bis(μ-oxo)bis[*N,N'*-bis(2-pyridylmethyl)-*N,N'*-dimethyl-1,2-ethanediamine]dimanganese(III,IV) Perchlorate, [(bispicMe$_2$en)MnO$_2$Mn(bispicMe$_2$en)](ClO$_4$)$_3$·H$_2$O. $MnCl_2\cdot 4H_2O$ (0.394 g, 2.00 mmol) was added to a solution of bispicMe$_2$en (0.568 g, 2.10 mmol) in hydrochloric acid (3 mL, 0.1 M). After the mixture was stirred for 15 min, the white precipitate was filtered out and washed with ethanol (96%). Yield: 0.751 g of presumed Mn(bispicMe$_2$en)Cl$_2$ (94%). This compound was suspended in water (4 mL). Ammonium peroxodisulfate (1.50 g, 6.58 mmol) was added. The precipitate dissolved quickly to give an olive-green solution. After being stirred for 30 min, the solution was filtered and cooled on ice. A solution of sodium perchlorate (10 mL, 1 M) was added dropwise which resulted in the precipitation of 0.336 g of an olive-green compound that was washed with a solution of sodium perchlorate (1 M) and of ethanol (96%). To the yellow mother liquor was added solutions of hydrogen peroxide (1 mL, 1 M), sodium hydroxide (a few drops, 2 M), and sodium perchlorate (1 mL, 1 M) to give an extra yield of 0.150 g. Total yield: 48%. The collected fractions were recrystallized from boiling water to give 0.375 g (37%). Washing was as above. Anal. Calcd for $[Mn(C_{16}H_{22}N_4)O]_2(ClO_4)_3\cdot H_2O$: Mn, 11.00; C, 38.47; N, 11.22; H, 4.64; Cl, 10.65. Found: Mn, 10.80; C, 38.11; N, 11.09; H, 4.60; Cl, 10.48. $(\epsilon, \lambda)_{max}$ (water): (458, 659), (480, 552), (1155, 430 sh), (1472, 380 sh).

2. Bis(μ-oxo)bis[*N,N'*-bis(2-pyridylmethyl)-*N,N'*-dimethyl-1,2-ethanediamine]dimanganese(IV,IV) Perchlorate, [(bispicMe$_2$en)MnO$_2$Mn(bispicMe$_2$en)](ClO$_4$)$_4$. The corresponding (III,IV) dimer (0.200 g, 0.198 mmol) was extracted on a filter with hydrochloric acid (7–10 mL, 1 M). The solution was cooled on ice, and a solution of sodium perchlorate (1 mL, 1 M) was added dropwise. After 60 min small, square, brown-black crystals were filtered out and washed with a solution of sodium perchlorate (1 M) and with ethanol (96%). Yield: 0.067 g (31%). In another experiment the yield was greater (48%), but the product was a powder. Anal. Calcd for $[Mn(C_{16}H_{22}N_4)O]_2(ClO_4)_4$: Mn, 10.17; C, 35.57; N, 10.37; H, 4.10; Cl, 13.13. Found: Mn, 10.16; C, 35.60; N, 10.35; H, 4.04; Cl, 13.02. $(\epsilon, \lambda)_{max}$ (water): (107, 792), (196, 700 sh), (595, 630), (957, 530 sh), (2057, 470 sh), (5147, 410 sh).

3. Bis(μ-oxo)bis[*N,N'*-bis(2-pyridylmethyl)-*N,N'*-dimethyl-1,2-ethanediamine]dimanganese(III,III) Perchlorate, [(bispicMe$_2$en)MnO$_2$Mn(bispicMe$_2$en)](ClO$_4$)$_2$·6.5H$_2$O. The corresponding (III,IV) dimer (0.110 g, 0.109 mmol) was dissolved in hot water (10 mL). Sodium thiosulfate (0.25 g, 1 mmol) was added. The red-brown solution was left in the dark until the next day, when a brown precipitate of MnO_2 was removed by filtration. The solution was again placed in the dark. After 5 days large, red-brown crystals could be isolated. They were washed with a solution of sodium perchlorate (1 M) and with ethanol (96%). Yield: 0.044 g (40%). Anal. Calcd: Mn, 11.00; C, 38.49; N, 11.22; H, 5.75; Cl, 7.10. Found: Mn, 11.04; C, 38.65; N, 11.25; H, 5.13; Cl, 7.48. $(\epsilon, \lambda)_{max}$ (water): (113, 760), (145, 575 sh), (323, 492), (294, 475), (503, 380 sh).

4. Bis(μ-oxo)bis[*N,N'*-bis(2-pyridylmethyl)-*N,N'*-dimethyl-(−)$_D$-1,2-cyclohexanediamine]dimanganese(III,IV) Perchlorate, [(bispicMe$_2$(−)chxn)MnO$_2$Mn(bispicMe$_2$(−)chxn)](ClO$_4$)$_3$·3H$_2$O. $MnCl_2\cdot 4H_2O$ (0.197 g, 1.00 mmol) was added to a solution of bispicMe$_2$(−)chxn·4HCl·2H$_2$O (0.506 g, 1.00 mmol) in a solution of sodium carbonate (3 mL, 1 M). A white precipitate separated immediately. After the mixture was stirred for 15 min, hydrogen peroxide (4 mL, 1 M) was added dropwise. The precipitate dissolved quickly to give an olive-green solution. A few drops of the sodium carbonate solution were added. After stirring and oxidation for 60 min, the solution was filtered and cooled on ice. A solution of sodium perchlorate (20 mL, 1 M) was added dropwise, which resulted in the precipitation of 0.268 g (47%) of an olive-green compound, which was washed with a solution of sodium perchlorate (1 M) and of ethanol (96%). The red-brown mother liquor was left over night to give an extra yield, 0.101 g (18%). The compound was recrystallized from boiling water to give 0.230 g of large, dark, black-green crystals by direct cooling of the solution and 0.075 g of smaller crystals by the addition of a solution of sodium perchlorate to the filtrate from the recrystallization. Total yield: 53%. Washing was as above. Anal. Calcd for $[Mn(C_{20}H_{28}N_4)O]_2(ClO_4)_3\cdot 3H_2O$: Mn, 9.61; C, 42.03; N, 9.80; H, 5.47; Cl, 9.30. Found: Mn, 9.70; C, 42.44; N, 9.80; H, 5.32; Cl, 9.56. $(\lambda, \epsilon)_{max}$ (acetonitrile): (658, 481), (552, 540), (430 sh, 1332).

5. Bis(μ-oxo)bis[*N,N'*-bis(2-pyridylmethyl)-*N,N'*-dimethyl-(−)$_D$-1,2-cyclohexanediamine]dimanganese(IV,IV) Perchlorate, [(bispicMe$_2$(−)chxn)MnO$_2$Mn(bispicMe$_2$(−)chxn)](ClO$_4$)$_4$. The corresponding (III,IV) dimer (0.075 g, 0.066 mmol) was extracted with hydrochloric acid (1 M) on a filter. The solution was cooled on ice, and a solution of sodium perchlorate (1 mL, 1 M) was added dropwise. After 60 min small, brown crystals were filtered out and washed with a solution of sodium perchlorate (1 M) and with ethanol (96%). Yield: 0.028 g (36%). Anal. Calcd for $[Mn(C_{20}H_{28}N_4)O]_2(ClO_4)_4$: Mn, 9.24; C, 40.42; N, 9.43; H, 4.75; Cl, 11.93. Found: Mn, 9.30; C, 40.66; N, 9.41; H, 4.77; Cl, 12.09. $(\lambda, \epsilon)_{max}$ (acetonitrile): (792, 112), (700 sh, 200), (634, 500), (530 sh, 987).

Analyses. The metal analyses were performed on a Perkin-Elmer 403 atomic absorption spectrometer. The microanalytical laboratory of the H. C. Ørsted Institute carried out the carbon, nitrogen, hydrogen, and halogen analyses by standard methods.

Spectroscopy. Electronic spectra were recorded on a Cary Model 118 spectrophotometer. The compounds were dissolved in water (**1**–**3**) or acetonitrile (**4** and **5**) as appropriate to their solubilities. Circular dichroism spectra were recorded on a Roussel-Jouan Dichrographe III. The compounds were dissolved in acetonitrile. The extrema are given

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Table 1. Crystallographic Data for the Complexes **1**, **3**, and **4**

	1	**3**	**4**		**1**	**3**	**4**
formula	$C_{32}H_{46}Cl_3Mn_2N_8O_{15}$	$C_{32}H_{54}Cl_2Mn_2N_8O_{15}$	$C_{40}H_{58}Cl_3Mn_2N_8O_{15}$	fw	983.0	971.6	1107.2
a, Å	19.839(4)	15.561(3)	13.098(3)	space group	$P2_1/c$	$Aba2$	$P2_12_12_1$
b, Å	12.468(3)	16.703(3)	16.297(3)	T, °C	22	22	22
c, Å	19.878(3)	16.430(3)	23.273(4)	μ, mm^{-1}	0.833	0.791	0.742
β, deg	120.657(10)	90	90	NO[a]	4267	2548	5723
V, Å^3	4230(1)	4270.4(14)	4967.8(17)	NO [$I > 3\sigma(I)$]	2874	1683	3057
Z	4	4	4	R[b]	0.0618	0.0564	0.0620
R_w[c]	0.0833	0.0565	0.0785				

[a] NO = number of observed reflections. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Coefficients (Å^2) for $[(bispicMe_2en)Mn(O)]_2(ClO_4)_3 \cdot H_2O$, **1**

atom	x	y	z	U(eq)[a]	atom	x	y	z	U(eq)[a]
Mn(1)	0.74230(10)	0.12732(11)	0.25888(8)	0.031(1)	C(35)	0.8798(7)	0.4354(8)	0.3508(6)	0.042(7)
Mn(2)	0.73377(9)	0.33906(10)	0.23290(8)	0.029(1)	C(36)	0.9560(8)	0.4648(9)	0.3906(7)	0.056(8)
O(1)	0.7420(4)	0.2204(4)	0.1865(3)	0.032(4)	C(37)	1.0078(9)	0.4223(11)	0.3709(8)	0.069(10)
O(2)	0.7343(4)	0.2520(5)	0.3051(3)	0.034(4)	C(38)	0.9789(9)	0.3505(9)	0.3089(8)	0.063(10)
N(1)	0.6153(6)	0.0913(6)	0.1833(5)	0.039(6)	C(39)	0.9002(7)	0.3261(8)	0.2687(6)	0.046(7)
C(2)	0.5686(9)	0.1043(8)	0.1053(6)	0.051(8)	N(40)	0.8507(6)	0.3672(6)	0.2891(5)	0.040(5)
C(3)	0.4906(9)	0.0810(9)	0.0660(6)	0.061(8)	H2O	0.1261(10)	0.1888(11)	0.2800(9)	0.173(14)
C(4)	0.4586(8)	0.0445(10)	0.1087(9)	0.072(10)	Cl(1)[b]	0.2262	0.2225	–0.0041	0.058
C(5)	0.5047(8)	0.0310(8)	0.1892(9)	0.060(9)	O(3)	0.1936	0.2198	0.0449	0.086
C(6)	0.5829(6)	0.0555(8)	0.2245(6)	0.044(7)	O(4)	0.1677	0.1956	–0.0815	0.137
C(7)	0.6370(8)	0.0462(8)	0.3089(7)	0.055(8)	O(5)	0.2886	0.1477	0.0235	0.115
N(8)	0.7199(6)	0.0220(6)	0.3284(5)	0.045(6)	O(6)	0.2549	0.3270	–0.0031	0.136
C(9)	0.7742(9)	0.0332(10)	0.4134(7)	0.067(10)	Cl(1′)	0.2263	0.2197	0.0076	0.056
C(10)	0.7219(8)	–0.0896(8)	0.3012(7)	0.056(8)	O(3′)	0.1766	0.2389	0.0381	0.102
C(11)	0.7840(8)	–0.1003(7)	0.2816(7)	0.056(8)	O(4′)	0.2058	0.2897	–0.0562	0.126
N(12)	0.7765(6)	–0.0164(6)	0.2241(5)	0.043(6)	O(5′)	0.2177	0.1119	–0.0182	0.114
C(13)	0.7197(10)	–0.0547(10)	0.1424(7)	0.076(11)	O(6′)	0.3053	0.2383	0.0667	0.122
C(14)	0.8500(8)	0.0035(9)	0.2287(7)	0.060(8)	Cl(2)	0.5122	–0.2773	0.1492	0.057
C(15)	0.9080(7)	0.0556(8)	0.3068(7)	0.048(8)	O(7)	0.5030	–0.3877	0.1294	0.074
C(16)	0.9872(9)	0.0472(10)	0.3426(9)	0.066(10)	O(8)	0.4436	–0.2388	0.1464	0.098
C(17)	1.0342(8)	0.1002(12)	0.4137(9)	0.081(10)	O(9)	0.5249	–0.2192	0.0954	0.098
C(18)	0.9983(9)	0.1578(11)	0.4466(8)	0.067(9)	O(10)	0.5773	–0.2637	0.2258	0.106
C(19)	0.9165(8)	0.1650(8)	0.4052(7)	0.054(9)	Cl(2′)	0.5096	–0.2720	0.1335	0.058
N(20)	0.8722(6)	0.1165(7)	0.3365(5)	0.042(6)	O(7′)	0.5031	–0.3853	0.1304	0.073
N(21)	0.6133(5)	0.3441(5)	0.1703(4)	0.037(5)	O(8′)	0.5048	–0.2333	0.1980	0.093
C(22)	0.5644(6)	0.3174(7)	0.1967(6)	0.039(6)	O(9′)	0.4480	–0.2275	0.0634	0.102
C(23)	0.4842(6)	0.3185(7)	0.1494(6)	0.044(7)	O(10′)	0.5826	–0.2419	0.1424	0.109
C(24)	0.4520(6)	0.3461(8)	0.0720(6)	0.049(7)	Cl(3)	0.0627	–0.2729	0.4016	0.078
C(25)	0.5004(7)	0.3727(7)	0.0450(6)	0.043(7)	O(11)	–0.0160	–0.2427	0.3738	0.201
C(26)	0.5803(6)	0.3713(7)	0.0936(5)	0.035(6)	O(12)	0.0892	–0.3404	0.4678	0.131
C(27)	0.6406(8)	0.3981(8)	0.0711(6)	0.047(7)	O(13)	0.1104	–0.1799	0.4229	0.165
N(28)	0.7101(6)	0.4444(6)	0.1387(5)	0.041(6)	O(14)	0.0674	–0.3288	0.3420	0.132
C(29)	0.7733(9)	0.4555(9)	0.1193(7)	0.057(9)	Cl(3′)	0.0893	–0.2893	0.4093	0.081
C(30)	0.6920(9)	0.5520(8)	0.1599(7)	0.057(8)	O(11′)	0.1674	–0.3223	0.4363	0.234
C(31)	0.7468(8)	0.5742(8)	0.2458(6)	0.050(8)	O(12′)	0.0854	–0.1757	0.4071	0.162
N(32)	0.7419(6)	0.4847(6)	0.2928(5)	0.039(6)	O(13′)	0.0651	–0.3284	0.4607	0.123
C(33)	0.6793(8)	0.5026(9)	0.3118(7)	0.062(9)	O(14′)	0.0393	–0.3307	0.3332	0.126
C(34)	0.8190(9)	0.4757(8)	0.3678(6)	0.059(9)					

[a] $U(eq) = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*a_ia_j$. [b] Occupation factors for perchlorate ions: Cl(1), 0.532(9); Cl(1′), 0.468(9); Cl(2), 0.645(8); Cl(2′), 0.355(8); Cl(3), 0.589(11); Cl(3′), 0.411(11).

as $(\lambda, \Delta\epsilon)_{ex} = [\lambda\ (\epsilon_l - \epsilon_r)]_{ex}$. $[Coen_3]Cl_3 \cdot {}^1/_2NaCl \cdot 3H_2O$ was used as a standard with $(\lambda, \Delta\epsilon)_{ex}$ = (489, 192). EPR spectra were recorded at liquid-helium temperature on a Bruker ESP 300 spectrometer operating at a frequency of 9.38 GHz (X-band) with magnetic field modulation of 100 kHz, modulation amplitude of 7 G, and microwave power of 10 mW. Samples were examined as frozen glasses in *N*-methylformamide solution.

Magnetochemistry. Magnetic susceptibilities of powdered samples were measured by the Faraday method in the temperature range 4–300 K at a field strength of 1.3 T. The magnetic field was calibrated with $Hg[Co(NCS)_4]$. A detailed description of the instrumentation has been published elsewhere.[26] The molar susceptibilities were corrected for ligand diamagnetism using Pascal's constants.

X-ray Structure Determination. The structures were determined at room temperature using Mo radiation [$\lambda(K\alpha_1)$ = 0.709 26 Å; $\lambda(K\alpha_2)$ = 0.713 54 Å] and a graphite monochromator. Data were corrected for background, Lorentz, and polarization effects and for absorption. The structure of the (III,IV) complex **1** was determined using a Huber diffractometer. The structures of the (III,III) complex **3** and the (III,IV) complex **4** were determined on a Nicolet R3m/V diffractometer. The structures were solved by direct methods and refined by least-squares techniques; the programs used for the solution of **1** were from SHELX86;[27a] those for **3** and **4** were from SHELXTL.[27b] Crystal data and experimental parameters for **1**, **3**, and **4** are presented in Table 1.

Bis(μ-oxo)bis[*N*,*N*′-bis(2-pyridylmethyl)-*N*,*N*′-dimethyl-1,2-ethanediamine]dimanganese(III,IV) Perchlorate, $[(bispicMe_2en)MnO_2Mn(bispicMe_2en)](ClO_4)_3 \cdot H_2O$. (1). The complex crystallizes in the monoclinic space group $P2_1/c$ with four dinuclear formula units in the cell. The crystals are twinned on (100); orientation matrices were determined for the two twins (twin 1 and twin 2 giving reflections R1 and R2) and the positions of the peaks calculated. There are four possibilities: (a) R2 is outside the scan and R1 is accepted. (b) R1 is exactly overlapped by a symmetry related R2, *e.g.* *hk*0 and –*hk*0; here F was divided by $\sqrt{2}$. Other reflections were plotted on a graphics screen. (c) If R1 and R2 were distinct, R2 was edited out. (d) If this was not possible, the reflection was rejected. The structure was refined by the least-squares minimization of $\sum w(|F_o| - |F_c|)^2$, a separate scale factor being refined for reflections of type b. It was clear that the perchlorate ions were disordered and these

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(26) Pedersen, E. *Acta Chem. Scand.* **1972**, *26*, 333–342.

(27) (a) Sheldrick, G. M. SHELX86. Program for the Solution of Crystal Structures. University of Göttingen, Germany. (b) Sheldrick, G. M. *SHELXTL-PLUS Crystallographic System*, version 2; Nicolet XRD Corp.: Madison, WI, 1987.

Table 3. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for [(bispicMe$_2$en)Mn(O)]$_2$(ClO$_4$)$_2$·5H$_2$O, 3

	x	*y*	*z*	*U*(eq)[a]
Mn(1)	429(1)	702(1)	8746	34(1)
O(1)	706(3)	−373(2)	8738(5)	40(1)
N(1)	174(4)	1933(4)	9063(4)	43(2)
N(2)	1708(4)	1174(3)	8506(4)	43(2)
N(3)	656(6)	819(5)	10133(5)	48(3)
N(4)	469(5)	919(5)	7383(5)	47(3)
C(1)	1037(5)	2353(5)	9114(6)	52(2)
C(2)	1599(6)	2066(5)	8446(5)	59(2)
C(11)	−225(5)	1959(5)	9879(5)	53(2)
C(12)	−419(6)	2352(5)	8492(5)	62(3)
C(21)	2378(6)	983(5)	9105(6)	65(2)
C(22)	1987(6)	833(6)	7692(6)	67(3)
C(31)	1057(5)	289(5)	10619(5)	49(2)
C(32)	1060(6)	394(6)	11447(6)	60(2)
C(33)	620(7)	1031(7)	11789(7)	67(3)
C(34)	241(5)	1559(5)	11296(5)	56(2)
C(35)	239(5)	1425(5)	10465(5)	44(2)
C(41)	1263(6)	894(5)	7092(5)	47(2)
C(42)	1423(7)	900(6)	6256(6)	70(3)
C(43)	779(7)	934(6)	5733(7)	64(3)
C(44)	−57(7)	992(6)	6021(6)	64(2)
C(45)	−175(6)	994(5)	6853(6)	53(2)
Cl(1)	2519(2)	3101(1)	11236(3)	73(1)
O(2)	2620(12)	2670(13)	10526(9)	258(11)
O(3)	1958(7)	2731(8)	11714(10)	181(7)
O(4)	3352(6)	3072(7)	11541(7)	145(5)
O(5)	2304(9)	3846(6)	11042(12)	235(11)
O(1W)	2239(4)	3880(4)	4008(6)	102(4)
O(2W)	1341(6)	9158(5)	3065(6)	114(4)
O(3W)	221(12)	5413(10)	8803(15)	126(8)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

were constrained to be exact tetrahedra; all Cl–O distances were assumed equal, but the Cl–O distance was allowed to vary. The thermal parameters of the perchlorate ions were described by **T** and **L** tensors and a center of reaction.[28] Hydrogen atoms were kept fixed at calculated positions except for those on the water molecule which were omitted. The solution refined to R = 0.0618 and R_w = 0.0833 based on 2874 independent reflections. Positional parameters are listed in Table 2.

Bis(μ-oxo)bis[*N,N'*-bis(2-pyridylmethyl)-*N,N'*-dimethyl-1,2-ethanediamine]dimanganese(III,III) Perchlorate, [(bispicMe$_2$en)MnO$_2$Mn(bispicMe$_2$en)](ClO$_4$)$_2$·5H$_2$O. (3). Three separate data sets from three different crystals were collected and solved in an attempt to obtain better precision in the structure, and indeed the third was significantly better than the others. Consequently, the data presented here refer solely to this third data set; there are no chemically meaningful differences between the three sets of results. The complex crystallizes in the orthorhombic space group *Aba*2 with four dinuclear formula units in the cell. All hydrogen atoms except those associated with the water groups were placed in calculated positions (C–H = 0.96 Å). All non-hydrogen atoms were refined anisotropically. The final values of the conventional *R* factors were R = 0.0564 and R_w = 0.0565, based on 2548 independent reflections with $I > 3\sigma(I)$. Positional parameters are listed in Table 3.

Bis(μ-oxo)bis[*N,N'*-bis(2-pyridylmethyl)-*N,N'*-dimethyl-(−)$_D$-1,2-cyclohexanediamine]dimanganese(III,IV) Perchlorate, [(bispicMe$_2$(−)chxn)MnO$_2$Mn(bispicMe$_2$(−)chxn)](ClO$_4$)$_3$·H$_2$O. (4). The complex crystallizes in the noncentrosymmetric orthorhombic space group $P2_12_12_1$ with four dinuclear formula units in the unit cell. The water molecule is disordered into two positions, each of which is half-occupied. All hydrogen atoms except those associated with the water groups were placed in calculated positions (C–H = 0.96 Å). All non-hydrogen atoms were refined anisotropically. The final values of the conventional *R* factors were R = 0.0620 and R_w = 0.0785, based on 3057 independent reflections with $I > 3\sigma(I)$. Positional parameters are listed in Table 4.

Results and Discussion

Table 4. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for [(bispicMe$_2$(−)chxn)Mn(O)]$_2$(ClO$_4$)$_3$·H$_2$O, 4

	x	*y*	*z*	*U*(eq)[a]
Mn(1)	559(1)	10056(1)	9003(1)	34(1)
Mn(2)	2321(1)	9991(1)	8409(1)	36(1)
O(1)	996(5)	10104(5)	8243(3)	38(2)
O(2)	1944(5)	9960(5)	9153(3)	39(2)
N(1A)	384(8)	11431(6)	9034(5)	43(4)
N(8A)	72(8)	10311(5)	9857(4)	39(3)
N(1B)	323(9)	8696(6)	9086(5)	48(4)
N(8B)	−1040(7)	9884(6)	8850(4)	38(3)
N(1C)	2597(7)	11239(6)	8464(5)	38(3)
N(8C)	2857(7)	10262(6)	7574(4)	41(3)
N(1D)	2252(8)	8761(6)	8260(5)	41(4)
N(8D)	3868(7)	9651(6)	8550(4)	44(4)
C(2A)	277(10)	11936(8)	8594(7)	59(5)
C(3A)	174(13)	12768(10)	8684(9)	76(7)
C(4A)	195(15)	13067(10)	9228(11)	93(9)
C(5A)	303(10)	12556(8)	9679(7)	63(6)
C(6A)	419(9)	11723(8)	9573(6)	48(5)
C(7A)	594(10)	11100(7)	10032(5)	47(4)
C(9A)	−1074(9)	10402(7)	9841(5)	38(4)
C(10A)	−1568(10)	10364(8)	10430(6)	60(5)
C(11A)	−2715(11)	10528(10)	10391(7)	79(6)
C(12A)	414(11)	9663(8)	10281(5)	57(5)
C(2B)	938(14)	8160(9)	9333(6)	72(7)
C(3B)	729(15)	7307(10)	9318(9)	84(8)
C(4B)	−103(20)	7043(10)	9039(10)	105(10)
C(5B)	−736(14)	7612(8)	8777(8)	79(7)
C(6B)	−507(11)	8432(7)	8810(6)	50(5)
C(7B)	−1164(10)	9100(8)	8537(6)	52(5)
C(9B)	−1560(9)	9807(7)	9426(5)	47(5)
C(10B)	−2722(9)	9911(9)	9418(5)	53(4)
C(11B)	−3182(11)	9856(10)	10013(6)	72(6)
C(12B)	−1508(11)	10541(8)	8472(6)	58(5)
C(2C)	2707(10)	11654(8)	8961(6)	53(5)
C(3C)	2798(11)	12483(8)	8967(7)	57(5)
C(4C)	2791(15)	12920(10)	8484(10)	100(9)
C(5C)	2705(12)	12477(8)	7931(6)	65(6)
C(6C)	2601(10)	11633(7)	7971(6)	50(5)
C(7C)	2443(10)	11112(7)	7453(5)	46(4)
C(9C)	4035(10)	10304(8)	7600(6)	53(5)
C(10C)	4532(11)	10272(9)	7015(6)	70(6)
C(11C)	5694(12)	10314(9)	7074(7)	74(7)
C(12C)	2481(10)	9708(8)	7117(5)	55(5)
C(2D)	1538(10)	8376(7)	7949(6)	51(5)
C(3D)	1574(12)	7525(8)	7875(7)	65(6)
C(4D)	2348(14)	7089(9)	8084(7)	73(7)
C(5D)	3105(11)	7471(8)	8384(7)	61(6)
C(6D)	3065(10)	8314(8)	8480(6)	52(5)
C(7D)	3808(11)	8816(7)	8808(7)	64(6)
C(9D)	4392(9)	9620(7)	7992(5)	43(4)
C(10D)	5570(10)	9639(8)	8025(6)	60(5)
C(11D)	6053(12)	9601(11)	7424(8)	87(8)
C(12D)	4392(9)	10209(8)	8968(6)	56(5)
Cl(1)	−4426(3)	9917(2)	11839(1)	52(1)
O(3)	−3385(8)	9876(9)	11783(6)	122(6)
O(4)	−4874(9)	9982(7)	11304(4)	93(4)
O(5)	−4650(13)	10626(6)	12170(6)	114(6)
O(6)	−4817(9)	9196(6)	12127(4)	78(4)
Cl(2)	6412(4)	7352(2)	9015(2)	73(2)
O(7)	6807(24)	7931(12)	9374(9)	288(18)
O(8)	5377(11)	7194(10)	9158(8)	150(8)
O(9)	6576(14)	7655(9)	8468(6)	147(8)
O(10)	6972(9)	6624(7)	9052(6)	117(6)
Cl(3)	−4017(5)	12441(3)	8462(3)	117(2)
O(11)	−4554(15)	12087(13)	8037(7)	300
O(12)	−3064(9)	12593(14)	8280(10)	300
O(13)	−3998(19)	11944(12)	8920(7)	300
O(14)	−4461(16)	13158(9)	8610(10)	300
O(1W)	3346(32)	10096(27)	532(17)	219(17)
O(2W)	−2247(33)	12533(23)	9567(17)	180(14)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Description of the Structures. Bis(μ-oxo)bis[*N,N'*-bis(2-pyridylmethyl)-*N,N'*-dimethyl-1,2-ethanediamine]dimanganese(III,IV) Perchlorate, [(bispicMe$_2$en)MnO$_2$Mn(bispicMe$_2$en)](ClO$_4$)$_3$·H$_2$O. (1). The structure consists of dinuclear [(bispicMe$_2$en)MnO]$_2^{3+}$ cations, perchlorate anions, and water molecules. Principal bond distances and angles are listed in Table 5.

The geometry about the manganese atoms is roughly octahedral, with ligation by the pyridine and amine nitrogen atoms

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(28) Pawley, G. S. *Adv. Struct. Res. Diffr. Methods* **1971**, *4*, 1–64.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for **1**

Bond Lengths

Mn(1)–Mn(2)	2.679(2)	Mn(1)–O(1)	1.846(5)
Mn(1)–O(2)	1.853(6)	Mn(1)–N(8)	2.112(8)
Mn(1)–N(12)	2.151(8)	Mn(1)–N(1)	2.223(9)
Mn(1)–N(20)	2.233(10)	Mn(2)–O(2)	1.795(6)
Mn(2)–O(1)	1.794(5)	Mn(2)–N(40)	2.027(10)
Mn(2)–N(21)	2.057(9)	Mn(2)–N(32)	2.131(8)
Mn(2)–N(28)	2.134(7)		

Bond Angles

Mn(1)–O(1)–Mn(2)	94.7(2)	Mn(1)–O(2)–Mn(2)	94.5(2)
O(1)–Mn(1)–O(2)	83.8(2)	O(1)–Mn(1)–N(8)	169.4(4)
O(1)–Mn(1)–N(12)	98.6(3)	O(1)–Mn(1)–N(1)	92.7(3)
O(1)–Mn(1)–N(20)	96.9(3)	O(2)–Mn(1)–N(8)	95.6(3)
O(2)–Mn(1)–N(12)	168.2(3)	O(2)–Mn(1)–N(1)	98.6(3)
O(2)–Mn(1)–N(20)	93.9(3)	N(8)–Mn(1)–N(12)	84.1(3)
N(8)–Mn(1)–N(1)	76.9(4)	N(8)–Mn(1)–N(20)	93.7(4)
N(12)–Mn(1)–N(1)	92.8(3)	N(12)–Mn(1)–N(20)	74.3(3)
N(1)–Mn(1)–N(20)	164.9(3)	O(2)–Mn(2)–O(1)	87.0(3)
O(2)–Mn(2)–N(40)	97.2(3)	O(2)–Mn(2)–N(21)	91.9(3)
O(2)–Mn(2)–N(32)	95.8(3)	O(2)–Mn(2)–N(28)	169.2(3)
O(1)–Mn(2)–N(40)	92.8(3)	O(1)–Mn(2)–N(21)	95.5(3)
O(1)–Mn(2)–N(32)	171.3(4)	O(1)–Mn(2)–N(28)	95.4(3)
N(40)–Mn(2)–N(21)	168.0(3)	N(40)–Mn(2)–N(32)	78.8(3)
N(40)–Mn(2)–N(28)	93.2(3)	N(21)–Mn(2)–N(32)	92.6(3)
N(21)–Mn(2)–N(28)	77.4(3)	N(32)–Mn(2)–N(28)	83.4(3)

of the ligand and the two *cis* oxygen atoms of the bridging oxo ligands. The two manganese atoms are bridged by the oxo ligands to form a dimeric $Mn_2(\mu\text{-}O)_2$ unit. The amine nitrogen atoms are trans to the oxo ligands, both halves of the dimer having the *cis*-α-configurations. The chiralities of the manganese centers are either both Δ or both Λ. This configuration allows the planes defined by the pyridine rings to be nearly parallel, whereas the meso form would have two short contacts between the pyridine units across the Mn_2O_2 framework (the α-hydrogen atoms on the adjacent pyridine rings would collide).

The bond distances at Mn(1) are typical for manganese(III), the axial Mn(1)–N bonds of 2.223(9) and 2.233(9) Å [average 2.228(6) Å] being longer than the equatorial Mn(1)–N distances of 2.112(8) and 2.151(8) Å [average 2.131(6) Å]; the axial Mn(2)–N distances are 2.057(9) and 2.027(10) Å [average 2.042(7) Å] while the equatorial distances are 2.131(8) and 2.134(7) Å [average 2.133(6) Å]. Similarly, the Mn(1)–O distances of 1.846(5) and 1.853(6) Å [average 1.850(4) Å] are, as expected, longer than the Mn(2)–O distances of 1.795(6) and 1.794(5) Å [average 1.795(4) Å]. Thus the manganese(III) and manganese(IV) atoms are readily distinguished. The Mn···Mn distance is 2.679(2) Å, and the Mn–O–Mn angles are 94.7(2) and 94.6(2)° [average 94.6(1)°].

The perchlorate ions in the structure are highly disordered, and in the refinement they were constrained to be regular tetrahedra. All Cl–O distances were assumed to be the same and refined to a value of 1.418(4) Å.

Bis(μ-oxo)bis[*N,N'*-bis(2-pyridylmethyl)-*N,N'*-dimethyl-1,2-ethanediamine]dimanganese(III,III) Perchlorate, [(bispicMe$_2$en)-MnO$_2$Mn(bispicMe$_2$en)](ClO$_4$)$_2$·5H$_2$O. (3). The structure consists of dinuclear $[(bispicMe_2en)MnO]_2^{2+}$ cations, perchlorate anions, and water molecules. A view of the cation is shown in Figure 1. Principal bond distances and angles are listed in Table 6.

As can be seen in Figure 1, the isomer is the *cis*-α-species in which the pyridine nitrogen atoms N(3) and N(4) are *trans*. In the present case, there is a crystallographic 2-fold axis passing through the center of the dimer and relating one manganese(III) center (the top half in Figure 1) to the other. As is expected for a d^4 Mn(III) ion, the geometry at manganese is axially elongated, the Mn–N(3) and Mn–N(4) bond lengths of 2.314(9) and 2.270(9) Å (average 2.292 Å) being approximately 0.12 Å longer than those of 2.159(6) and 2.177(6) Å (average 2.168 Å) for the equatorial bonds Mn–N(1) and Mn–N(2), respectively. These values may be compared with those observed in other bis(μ-oxo)dimanganese(III) complexes we have examined[9,10] and also those at the localized Mn(III) site in the related bis(μ-oxo)dimanganese(III,IV) complexes examined by us[2–8] and by others.[11b,12b,13–16] The Mn···Mn separation in the dimer of 2.699(2) Å is again comparable to that in related systems, as are the Mn–O bond lengths of 1.846(4) and 1.851(4) [average 1.849(4) Å] and the bridging Mn–O–Mn angles of 93.8(2)°.[9,10]

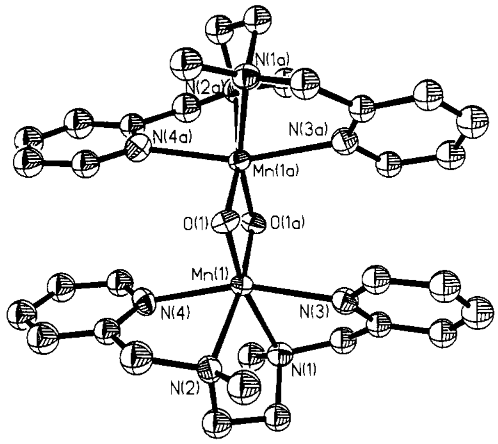

Figure 1. View of the dinuclear bis(μ-oxo)bis[*N,N'*-bis(2-pyridylmethyl)-*N,N'*-dimethyl-1,2-ethanediamine]dimanganese(III,III) cation, $[(bispicMe_2en)MnO_2Mn(bispicMe_2en)]^{2+}$ (**3**). The crystallographic 2-fold axis passes from left to right in the picture and relates the top half of the dimer to the bottom half.

Table 6. Selected Bond Lengths (Å) and Angles (deg) for **3**

Bond Lengths

Mn(1)–O(1)	1.846(4)	Mn(1)–N(1)	2.159(6)
Mn(1)–N(2)	2.177(6)	Mn(1)–N(3)	2.314(9)
Mn(1)–N(4)	2.270(9)	Mn(1)–Mn(1A)	2.699(2)
Mn(1)–O(1A)	1.851(4)		

Bond Angles

O(1)–Mn(1)–N(1)	166.2(3)	O(1)–Mn(1)–N(2)	97.9(2)
N(1)–Mn(1)–N(2)	82.3(2)	O(1)–Mn(1)–N(3)	93.1(3)
N(1)–Mn(1)–N(3)	73.1(3)	N(2)–Mn(1)–N(3)	90.5(3)
O(1)–Mn(1)–N(4)	98.1(3)	N(1)–Mn(1)–N(4)	95.2(3)
N(2)–Mn(1)–N(4)	74.9(3)	N(3)–Mn(1)–N(4)	162.6(3)
O(1)–Mn(1)–O(1A)	86.2(2)	N(1)–Mn(1)–O(1A)	96.3(2)
N(2)–Mn(1)–O(1A)	168.3(3)	N(3)–Mn(1)–O(1A)	100.3(3)
N(4)–Mn(1)–O(1A)	93.8(3)	Mn(1)–O(1)–Mn(1A)	93.8(2)

The perchlorate ions in the structure are reasonably ordered at this temperature, although there is the usual high apparent librational motion associated with the oxygen atoms which may be indicative of some disorder. The Cl–O bond lengths are in the range 1.327(12)–1.390(10) Å, with an average value of 1.36(3) Å; the O–Cl–O bond angles are in the broad range 100.4–114.3°, with an average of 109.3(48)°; while lacking in precision, all of these metrical parameters are consistent with earlier observations of this anion.[23,29]

Bis(μ-oxo)bis[*N,N'*-bis(2-pyridylmethyl)-*N,N'*-dimethyl-(−)$_D$-1,2-cyclohexanediamine]dimanganese(III,IV) Perchlorate, [(bispicMe$_2$(−)chxn)MnO$_2$Mn(bispicMe$_2$(−)chxn)](ClO$_4$)$_3$·H$_2$O. (4). The structure consists of dinuclear $[(bispicMe_2(-)chxn)MnO]_2^{3+}$ cations and perchlorate anions. A view of the cation is shown in Figure 2. Principal bond distances and angles are listed in Table 7.

The geometry about the manganese centers is again roughly octahedral, and as can be seen in Figure 2, the isomer is again the *cis*-α-species. Necessarily, since one metal ion is Mn(III) while the other is Mn(IV), the two metal centers are *chemically* inequivalent, and as would be expected but is not always observed,[5,6,8,12b] they are also *crystallographically* inequivalent in the present case. The geometry at Mn(2) is roughly isotropic, with the axial Mn–N(pyridyl) bonds Mn(2)–N(1C) and Mn(2)–N(1D) of 2.071(10) and 2.036(10) Å [average 2.05(2) Å]

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(29) See, for example: Glerup, J.; Goodson, P. A.; Hodgson, D. J.; Michelsen, K.; Nielsen, K. M.; Weihe, H. *Inorg. Chem.* **1992**, *31*, 4611–4616.

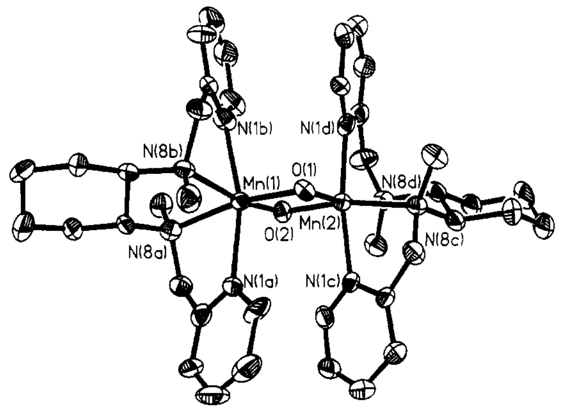

Figure 2. View of the binuclear bis(μ-oxo)bis[*N,N'*-bis(2-pyridylmethyl)-*N,N'*-dimethyl-(−)$_D$-1,2-cyclohexanediamine]dimanganese(III,IV) cation, [(bispicMe$_2$(−)chxn)MnO$_2$Mn(bispicMe$_2$(−)chxn)]$^{3+}$ (**4**).

Table 7. Selected Bond Lengths (Å) and Angles (deg) for **4**

Bond Lengths			
Mn(1)–Mn(2)	2.693(2)	Mn(1)–O(1)	1.860(7)
Mn(1)–O(2)	1.855(7)	Mn(1)–N(1A)	2.253(9)
Mn(1)–N(8A)	2.127(10)	Mn(1)–N(1B)	2.246(10)
Mn(1)–N(8B)	2.143(9)	Mn(2)–O(1)	1.787(7)
Mn(2)–O(2)	1.800(7)	Mn(2)–N(1C)	2.071(10)
Mn(2)–N(8C)	2.113(10)	Mn(2)–N(1D)	2.036(10)
Mn(2)–N(8D)	2.125(9)		

Bond Angles			
Mn(1)–O(1)–Mn(2)	95.1(3)	Mn(1)–O(2)–Mn(2)	94.9(3)
O(1)–Mn(1)–O(2)	83.1(3)	O(1)–Mn(1)–N(1A)	91.2(4)
O(2)–Mn(1)–N(1A)	100.2(4)	O(1)–Mn(1)–N(8A)	166.3(3)
O(2)–Mn(1)–N(8A)	97.8(3)	N(1A)–Mn(1)–N(8A)	75.3(4)
O(1)–Mn(1)–N(1B)	99.5(4)	O(2)–Mn(1)–N(1B)	92.0(4)
N(1A)–Mn(1)–N(1B)	164.7(4)	N(8A)–Mn(1)–N(1B)	94.1(4)
O(1)–Mn(1)–N(8B)	98.5(3)	O(2)–Mn(1)–N(8B)	167.6(4)
N(1A)–Mn(1)–N(8B)	92.1(4)	N(8A)–Mn(1)–N(8B)	83.6(4)
N(1B)–Mn(1)–N(8B)	75.6(4)	O(2)–Mn(2)–O(1)	86.8(3)
O(1)–Mn(2)–N(1C)	94.7(4)	O(2)–Mn(2)–N(1C)	90.9(4)
O(1)–Mn(2)–N(8C)	95.9(3)	O(2)–Mn(2)–N(8C)	168.8(4)
N(1C)–Mn(2)–N(8C)	78.0(4)	O(1)–Mn(2)–N(1D)	91.3(4)
O(2)–Mn(2)–N(1D)	97.2(4)	N(1C)–Mn(2)–N(1D)	170.2(4)
N(8C)–Mn(2)–N(1D)	93.7(4)	O(1)–Mn(2)–N(8D)	170.3(4)
O(2)–Mn(2)–N(8D)	96.1(4)	N(1C)–Mn(2)–N(8D)	94.6(4)
N(8C)–Mn(2)–N(8D)	83.1(4)	N(1D)–Mn(2)–N(8D)	79.2(4)

actually slightly *shorter* than the equatorial Mn(2)–N(amine) bonds Mn(2)–N(8C) and Mn(2)–N(8D) of 2.113(10) and 2.125(9) Å [average 2.119(9) Å]. This lengthening of the equatorial bonds is expected for an isotropic manganese(IV) center and can be attributed to the *trans* influence of the μ-oxo ligands. Additionally, the Mn(2)–O bonds of 1.787(7) and 1.800(7) Å are approximately 0.06 Å shorter than the corresponding Mn(1)–O distances of 1.860(7) and 1.855(7) Å. All of these observations are consistent with the assignment of the atom Mn(2) as the *localized* d^3 Mn(IV) center of the dimer.

Conversely, the geometry at Mn(1) is significantly axially elongated, with the axial Mn–N(pyridyl) bonds Mn(1)–N(1A) and Mn(1)–N(1B) of 2.253(9) and 2.246(10) Å [average 2.250(4) Å] approximately 0.12 Å *longer* than the equatorial Mn(1)–N(amine) bonds Mn(1)–N(8A) and Mn(1)–N(8B) of 2.127(10) and 2.143(9) Å [average 2.135(11) Å]. This difference is very similar to that observed above in the structure of the Mn(III) dimer **3** and is entirely consistent with the assignment of the atom Mn(1) as the *localized* d^4 Mn(III) site. The Mn···Mn separation in the dimer of 2.693(2) Å is again comparable to that above in the (III,III) complex and in related systems, as are the bridging Mn–O–Mn angles of 95.1(3) and 94.9(3)°.[2-19]

Two of the three independent perchlorate ions in the structure are reasonably ordered at this temperature, although there is the usual high apparent librational motion associated with the oxygen atoms, and one of them is almost certainly experiencing some disorder which we were unable to fit to any reasonable model.

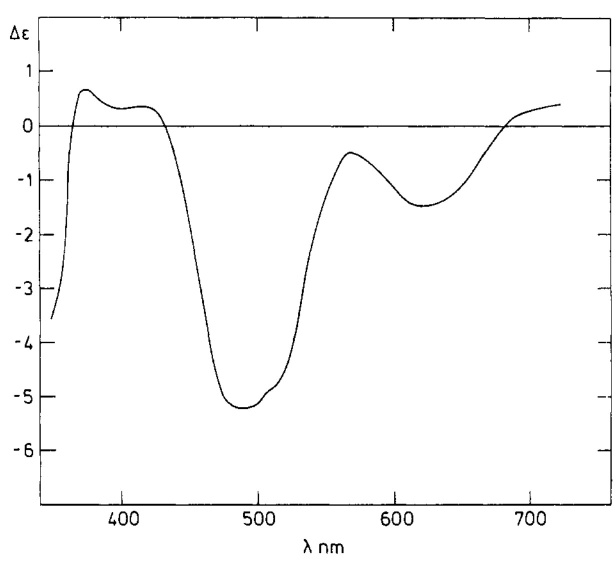

Figure 3. Circular dichroism spectrum (visible region) of the (III,IV) [(bispicMe$_2$(−)chxn)MnO$_2$Mn(bispicMe$_2$(−)chxn)]$^{3+}$ cation (**4**).

Electronic Spectroscopy. The electronic spectra of the complexes are reported in the synthetic section. The spectra of the (III,IV) complexes consist of two intense bands in the UV region (near 380 and 430 nm) and two bands of moderate intensity in the visible region (near 552 and 659 nm). The (IV,IV) complexes have spectra which also contain two intense bands in the UV region (near 410 and 470 nm), two bands of moderate intensity in the visible region (near 530 and 630 nm), and one weak but clearly evident band near 790 nm. As has been observed before,[8] the maximum near 630 nm is very broad and shows a low-energy shoulder near 700 nm. In contrast, in the visible region the (III,III) spectrum shows a sharp band at 492 nm with a high-energy shoulder at 475 nm, a barely discernible low-energy shoulder at 575 nm, and a very weak, very broad band centered at 760 nm.

As was the case with the ligands bispic(−)pn and bispic(−)chxn, it was only possible to isolate one isomer with bispicMe$_2$(−)chxn. The measurements of the optical rotation at the sodium D-line gave imprecise values near zero, but the (IV,IV) complex **5** was clearly a (−)$_D$ isomer. This was also the case for the corresponding complex with bispic(−)chxn, which was earlier mistakenly described as a (+)$_D$ isomer.[7]

In the case of the optically active binuclear bis(μ-hydroxo) complexes of chromium(III) with bispic(−)pn, we have earlier determined that the sign of the dominant CD-band in the visible region is negative for a ΔΔ isomer.[30] This is in agreement with the empirical rule that relates the sign of the dominant CD-band in the $^4A_{2g}$–$^4T_{2g}$ d–d absorption of the chromium(III) ion to the configuration around the metal atom.[31] In the present case of manganese, as is seen in Figure 3, the ΔΔ isomer of the (III,IV) complex **4** has a large negative band at approximately 490 nm. Negative bands are also dominant in the CD spectrum of the (IV,IV) complex **5**, which is shown in Figure 4. Since all of the optically active (III,IV) and (IV,IV) complexes have similar CD spectra, we suggest that all of them are ΔΔ isomers.

Magnetic Susceptibility. The temperature dependence of the magnetic susceptibility of powdered samples of the complexes **1–5** were measured in the range 4–296 K. The magnetic susceptibility data and effective magnetic moment of the (III,III) complex **3** are plotted as a function of temperature in Figure 5. As is shown in Figure 5, for the bispicMe$_2$en complex **3**, the effective magnetic moment at room temperature is approximately 2.72 μ_B, declining monotonically to a value of 0.36 μ_B at 30 K; the moment is essentially constant below 30 K.

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(30) Michelsen, K.; Pedersen, E. *Acta Chem. Scand.*, Ser. *A* **1983**, *A37*, 141–152.

(31) Mason, S. F. *Q. Rev. Chem. Soc.* **1963**, *17*, 20–66.

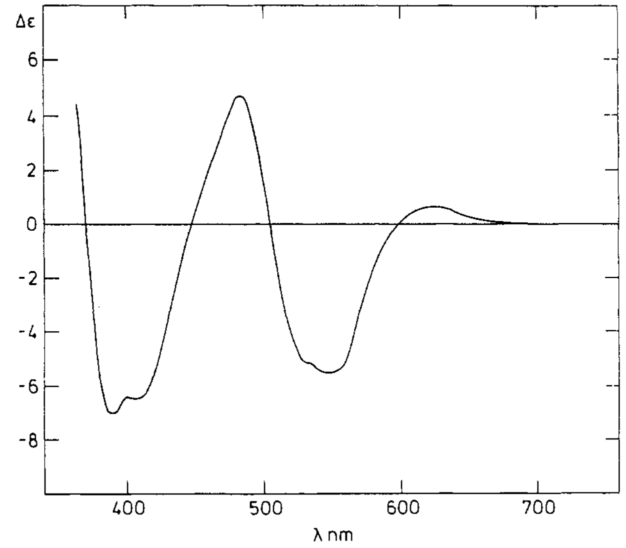

Figure 4. Circular dichroism spectrum (visible region) of the (IV,IV) $[(\text{bispicMe}_2(-)\text{chxn})\text{MnO}_2\text{Mn}(\text{bispicMe}_2(-)\text{chxn})]^{4+}$ cation (**5**).

The temperature dependence of the magnetic susceptibility was approximated by the expression

$$\chi_{\text{mol.exp}} \simeq \chi_{\text{mol.calc}} = -\frac{N}{H}\frac{\sum_i \frac{\partial E_i}{\partial H}\exp(-E_i/kT)}{\sum_i \exp(-E_i/kT)} + K + C/T$$

by minimization of the function

$$\sum_T \frac{[\chi'_{\text{mol.exp}}(T) - \chi'_{\text{mol.calc}}(T)]^2}{\sigma^2(\chi') + \left(\frac{\partial \chi}{\partial T}\right)^2 \sigma^2(T)}$$

within the framework of regression analysis. The term C/T accounts for the presence of small quantities of (presumably monomeric) paramagnetic impurities, while K accounts for temperature-independent paramagnetism (TIP) and for any minor deviations in the corrections for the diamagnetism of the atoms. The energies E_i of the components of the ground-state manifold were obtained from the following Hamiltonian operator with an isotropic Zeeman term

$$H = -2J\hat{S}_1\hat{S}_2 + g_1\mu_B S_1 H + g_2\mu_B S_2 H$$

where $S = S_1 + S_2$ and we have assumed that the g values for the two manganese atoms are identical; *i.e.*, we have set $g_1 = g_2$. Since we have two $S = 2$ d^4 centers in the complexes, the Heisenberg Hamiltonian gives rise to states with $S = 0, 1, 2, 3, 4$ with energies of 0, $-2J$, $-6J$, $-12J$, and $-20J$, respectively.

For the bispicMe$_2$en complex **3**, the fitting leads to a value of $2J = -201(1)$ cm^{-1} with $g = 1.989(4)$ and $C = 0.0134$, which can be translated as 0.3% monomeric manganese(II) impurity or 3.6% dimanganese(III,IV) impurity. The observed $2J$ value for **3** is comparable to, but larger in magnitude than, that of $2J = -172.8$ cm^{-1} observed for the 6-Mebispicen (III,III) complex.[10]

The magnetic susceptibility data for the (IV,IV) complexes **2** and **5** are also consistent with those expected for a singlet ground state. For **2**, the effective magnetic moment decreases from 2.21 μ_B at 295 K to 0.2 μ_B at 4.1 K; very similar results are obtained for **5**. The fit to the above model for complex **2** gives values of $2J = -205(1)$ cm^{-1}, $g = 1.859(4)$, and $C = 0.01$, which correspond to 0.02% monomeric manganese(II) impurity or 2.8% dimanganese(III,IV) impurity. For complex **5**, the values are $2J = -211(1)$ cm^{-1}, $g = 1.86(1)$, and $C = 0.06$, which corresponds to 1.3% manganese(II) or 16% of dimanganese(III,IV). These $2J$ values are again comparable to the broad range of values reported for other (IV,IV) complexes of this type.[4,6–8,12b,17–19]

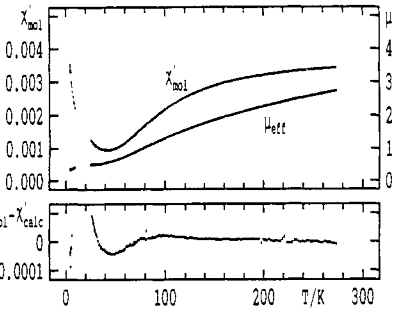

Figure 5. Magnetic susceptibility (left scale) and effective magnetic moment (right scale) for the (III,III) complex $[(\text{bispicMe}_2\text{en})\text{MnO}_2\text{Mn}(\text{bispicMe}_2\text{en})](\text{ClO}_4)_2$ (**3**). The lower curve shows the fit of the susceptibility data to the values calculated using the parameters $g = 1.989$ and $2J = -201.2$ cm^{-1}.

The susceptibility data for the (III,IV) complexes **1** and **4** are again consistent with those observed for analogous systems.[2–8,11–17] For the bispicMe$_2$en complex **1**, the effective magnetic moment declines gradually from 2.47 μB at 295 K to 1.69 μ_B at 4.1 K; very similar results are obtained for **4**, the values being 2.65 to 1.74. These low temperature values are similar to the spin-only value of $\sqrt{3}\mu_B$ expected for a doublet ground state. For complex **1**, the fit to the above model gives $2J = -320(2)$ cm^{-1}, $g = 2.04(1)$, and $C = 0.005$ (corresponding to 0.01% monomeric manganese(II) impurity). For complex **4**, the values are $2J = -293(5)$ cm^{-1}, $g = 1.98(2)$, and $C = 0.07$ (1.6% manganese(II) impurity).

EPR Spectra. The EPR spectrum of a frozen glass of the (III,IV) complex **4** dissolved in NMF (*N*-methylformamide) is typical of a dinuclear bis(μ-oxo)dimanganese(III,IV) complex and shows 16 lines with some anisotropy.[8] The EPR spectra recorded at low temperatures on solid samples of the (IV,IV) complexes **2** and **5** show a broad band centered around $g = 2$ on top of which are seen the 16-line signal characteristic of the (III,IV) complexes. Similarly, in the solid spectrum at low temperatures of the (III,III) complex **3** is seen the 16-line signal characteristic of the (III,IV) complex on top of a broad signal. On the basis of both the magnetic susceptibility and the EPR results, we must conclude that it is very difficult to prepare samples of the (III,III) and (IV,IV) complexes which do not contain small quantities of (III,IV) and/or Mn(II) impurities.

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Supplementary Material Available: Tables S1–S3 (hydrogen atom parameters for complexes **1**, **3**, and **4**) and Tables S4 and S5 (anisotropic thermal parameters for complexes **3** and **4**) (11 pages). For ordering information, see any current masthead page. Listings of observed and calculated structure amplitudes are available from D.J.H.