3612 *Inorg. Chem.* **1994,** *33,* 3612–3615

An Unusual Chainlike Tetranuclear Manganese(II) Complex Displaying Ferromagnetic Exchange

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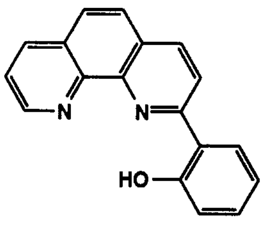
Received February 14, 1994

Introduction

Polynuclear complexes of manganese are currently receiving much attention as models for the active sites of metalloproteins such as the catalases[1] and the water-oxidizing center of photosystem II.[2] In addition, their magnetic behavior is of interest, particularly in regard to formation of materials displaying properties such as ferromagnetism, very high magnetic moments,[3] or spin frustration.[4] We have been interested in the preparation and study of polynuclear transition-metal complexes which display magnetic and/or electrochemical interactions between the metal centers,[5,6] and we report here the preparation, X-ray structure, and variable-temperature magnetic susceptibility of $[Mn_4L_6][ClO_4]_2$ (**1**), an unusual tetranuclear Mn(II) complex with a chainlike structure containing two phenolate bridges between each adjacent pair of Mn(II) ions.



HL

Experimental Section

General Details. HL[1] was prepared as described earlier.[5] Fast-atom bombardment mass spectra were recorded on a VG-Autospec instrument. Magnetic susceptibilities were measured in the liquid nitrogen range using a Faraday balance calibrated with $HgCo(NCS)_4$ as described previously[7] and in the liquid helium range with a SQUID magnetometer. EPR spectra were recorded on a Bruker ESP-300E spectrometer.

Table 1. Crystallographic Data for **1**

formula:	fw: 2317.79
$C_{108}H_{66}Cl_2N_{12}O_{14}Mn_4 \cdot 3MeCN_3 \cdot 2Et_2O$	cryst system: monoclinic
$a = 18.645(5)$ Å	space group: $P2_1/c$
$b = 22.056(8)$ Å	$T = 20$ °C
$c = 27.119(12)$ Å	$\lambda = 0.710\,73$ Å
$\beta = 94.56(3)°$	$\rho_{calc} = 1.385$ g cm^{-3}
$V = 11117(7)$ Å^3	$\mu = 5.65$ cm^{-1}
$Z = 4$	$R_w = 0.24$ ($R = 0.069$)[a]

[a] $R_w = [\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2]^{1/2}$ where $w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$ ($a = 0.0810$; $b = 36.4695$) and $P = [\max(F_o^2,0) + 2F_c^2]/3$. The structure was refined on F_o^2 using all data; the value in parentheses is given for comparison with older refinements based on F_o with a typical threshold of $F \geq 4\sigma(F)$ and $R = \sum||F_o| - |F_c||/\sum|F_o|$.

Preparation of $[Mn_4L_6][ClO_4]_2$ (1). A stirred mixture of HL (0.27 g, 1 mmol), $Mn(CH_3CO_2)_2 \cdot 4H_2O$ (0.25 g, 1 mmol), and $Na(CH_3CO_2)$ (0.16 g, 2 mmol) in methanol (20 cm^3) was heated to reflux in air for 5 min, affording a dark brown solution, which was then allowed to cool. An aqueous solution of $NaClO_4$ was added dropwise until precipitation was complete; the yellow solid was extracted into CH_2Cl_2, and this phase was separated from the aqueous phase, dried ($MgSO_4$), and evaporated to dryness to yield **1** (0.20 g, 60%), which was recrystallized from acetonitrile/ether. Caution! Metal complexes containing perchlorate are potentially explosive. Although we experienced no problems, **1** was treated with due caution, particularly when dry. Anal. Calcd for $C_{108}H_{66}N_{12}Mn_4Cl_2O_{14}$: C, 63.4; H, 3.2; N, 8.2. Found: C, 62.9; H, 3.4; N, 7.9. MS (FAB, 3-nitrobenzyl alcohol matrix): *m/z* 1946 (1%, $Mn_4L_6ClO_4$), 1847 (1%, Mn_4L_6), 1402 (1%, $Mn_4L_4ClO_4$), 1348 (5%, $Mn_3L_4ClO_4$), 1022 (1%, $Mn_2L_3ClO_4$), 923 (75%, Mn_2L_3), 597 (8%, MnL_2), 326 (100%, MnL).

Crystal Structure Determination of $1 \cdot 3MeCN \cdot 2Et_2O$. Orange crystals suitable for X-ray diffraction were grown from acetonitrile/ether by vapor diffusion. A crystal of approximate dimensions 0.40 × 0.45 × 0.52 mm was mounted in a capillary tube filled with mother liquor to prevent loss of solvent of crystallization.

Crystallographic data are summarized in Table 1. Intensity data were collected using a Siemens R3m/V diffractometer, in the range $2\theta \leq 40°$ by the Wyckoff ω-scan technique with index ranges $0 \leq h \leq 17$, $0 \leq k \leq 21$, $-26 \leq l \leq 26$. A total of 10 793 data reflections were collected of which 10 338 were unique. The data were corrected for Lorentz, polarization, and X-ray absorption effects, the last by an empirical method based on azimuthal scan data. Systematic monitoring of three check reflections at regular intervals showed no significant crystal decay. The structure was solved by conventional heavy atom methods, and successive difference Fourier syntheses were used to locate all non-hydrogen atoms. Initial calculations were performed on a DEC micro-Vax II computer with the SHELXTL PLUS system of programs. The final least-squares refinements (on all F^2 data) were carried out on a Silicon Graphics Indigo R4000 computer using SHELXL-93. Refinement converged at $R_w = 0.24$. For comparison with more conventional refinements against F, $R = 0.069$ for 3723 data [$F \geq 4\sigma(F)$]. The final atomic coordinates are given in Table 2, and selected bond lengths and angles, in Table 3.

Results and Discussion

The FAB mass spectrum and elemental analysis of the product obtained from reaction of HL with $Mn(CH_3CO_2)_4 \cdot 4H_2O$ followed by precipitation with sodium perchlorate suggested, unexpectedly, that a tetranuclear complex had formed; this was subsequently confirmed by X-ray crystallography (Figure 1). The complex cation contains a chain of four crystallographically independent Mn(II) ions, with two phenolate groups bridging each adjacent pair of Mn(II) ions. All metal ions are six-coordinate. The two

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Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for **1**

	x	*y*	*z*	*U*(eq)^a		*x*	*y*	*z*	*U*(eq)^a
Mn(1)	4690(1)	2711(1)	2575(1)	65(1)	C(323)	957(8)	410(6)	1626(5)	78(4)
Mn(2)	3154(1)	1900(1)	2447(1)	58(1)	C(324)	1192(9)	−21(6)	1987(6)	89(5)
Mn(3)	1403(1)	2227(1)	2340(1)	55(1)	C(325)	1422(8)	147(6)	2448(5)	83(5)
Mn(4)	401(1)	3272(1)	2867(1)	59(1)	C(326)	1445(7)	767(6)	2580(5)	69(4)
N(111)	5788(5)	2375(4)	2405(4)	79(3)	C(331)	2021(7)	1512(6)	3214(5)	67(3)
C(112)	6081(7)	2426(5)	1974(5)	90(5)	C(332)	1667(8)	962(6)	3086(5)	76(4)
C(113)	6722(7)	2129(6)	1869(5)	97(5)	C(333)	1519(9)	566(6)	3472(5)	102(5)
C(114)	7056(7)	1782(5)	2230(6)	94(4)	C(334)	1682(10)	732(8)	3954(6)	114(5)
C(115)	6785(7)	1713(5)	2684(5)	91(4)	C(335)	2059(9)	1256(8)	4074(5)	100(5)
C(116)	6140(6)	2016(5)	2770(5)	78(4)	C(336)	2237(8)	1643(7)	3712(5)	90(4)
C(117)	7119(7)	1351(5)	3080(6)	95(4)	O(331)	2212(4)	1895(4)	2865(3)	63(2)
C(118)	6822(7)	1308(5)	3504(6)	99(5)	N(411)	−800(5)	3273(5)	2870(4)	62(3)
N(121)	5201(5)	2278(4)	3285(4)	72(3)	C(412)	−1168(7)	3072(6)	3237(5)	70(4)
C(122)	5825(6)	1973(5)	3227(5)	78(4)	C(413)	−1915(7)	2999(7)	3187(5)	82(5)
C(123)	6172(7)	1615(5)	3594(5)	84(4)	C(414)	−2268(7)	3125(7)	2748(5)	83(5)
C(124)	5845(7)	1576(5)	4042(5)	92(4)	C(415)	−1916(7)	3353(6)	2352(5)	71(4)
C(125)	5233(7)	1876(5)	4103(5)	97(4)	C(416)	−1159(6)	3406(6)	2421(5)	61(3)
C(126)	4906(6)	2236(5)	3712(5)	83(4)	C(417)	−2266(7)	3514(7)	1883(5)	87(5)
C(131)	3700(7)	2715(6)	3406(5)	77(4)	C(418)	−1887(8)	3746(7)	1534(5)	94(5)
C(132)	4240(6)	2565(5)	3779(4)	90(4)	N(421)	−41(6)	3740(5)	2158(4)	68(3)
C(133)	4184(8)	2815(6)	4259(5)	94(4)	C(422)	−752(7)	3657(6)	2047(5)	64(3)
C(134)	3602(9)	3147(7)	4360(5)	100(5)	C(423)	−1121(7)	3811(6)	1595(5)	76(4)
C(135)	3058(8)	3269(7)	3998(6)	101(5)	C(424)	−692(8)	4051(7)	1242(5)	91(5)
C(136)	3103(7)	3052(6)	3519(5)	91(4)	C(425)	15(8)	4122(7)	1346(5)	87(5)
O(131)	3755(4)	2515(4)	2940(3)	69(3)	C(426)	347(7)	3975(6)	1816(5)	66(3)
N(141)	4833(7)	3670(5)	2818(5)	92(4)	C(431)	1561(7)	3679(6)	2241(5)	75(4)
C(142)	4971(10)	3858(7)	3286(6)	120(6)	C(432)	1123(7)	4069(6)	1924(5)	77(3)
C(143)	4948(9)	4458(8)	3430(6)	113(5)	C(433)	1455(8)	4565(6)	1722(6)	90(4)
C(144)	4776(12)	4893(7)	3085(7)	125(7)	C(434)	2164(9)	4684(7)	1805(7)	111(6)
C(145)	4633(9)	4732(6)	2590(6)	103(5)	C(435)	2593(8)	4307(8)	2118(7)	110(6)
C(146)	4654(9)	4108(6)	2467(5)	91(4)	C(436)	2306(7)	3798(7)	2317(6)	96(5)
C(147)	4491(11)	5156(6)	2198(7)	115(6)	O(431)	1294(4)	3183(4)	2443(3)	61(3)
C(148)	4324(9)	4968(6)	1739(6)	104(5)	N(441)	715(6)	4122(5)	3273(4)	67(3)
N(151)	4542(6)	3302(5)	1880(4)	73(3)	C(442)	748(8)	4675(6)	3081(5)	82(4)
C(152)	4510(8)	3910(6)	1971(5)	87(4)	C(443)	979(8)	5183(6)	3363(6)	83(4)
C(153)	4324(10)	4341(6)	1607(6)	98(5)	C(444)	1171(9)	5104(6)	3851(5)	94(5)
C(154)	4172(10)	4112(7)	1130(6)	116(6)	C(445)	1181(8)	4528(6)	4067(5)	82(4)
C(155)	4212(8)	3514(6)	1032(5)	89(5)	C(446)	932(7)	4038(6)	3765(5)	67(3)
C(156)	4397(8)	3102(6)	1421(5)	77(4)	C(447)	1390(8)	4425(7)	4579(5)	88(5)
C(161)	4369(7)	1986(6)	1652(5)	69(4)	C(448)	1389(8)	3857(7)	4755(5)	86(4)
C(162)	4478(8)	2455(6)	1310(5)	73(4)	N(451)	588(6)	2998(5)	3664(4)	66(3)
C(163)	4700(8)	2294(7)	841(5)	84(4)	C(452)	891(7)	3441(6)	3964(4)	68(4)
C(164)	4837(9)	1711(8)	723(5)	96(5)	C(453)	1127(8)	3353(6)	4458(5)	77(4)
C(165)	4746(8)	1254(7)	1066(6)	86(5)	C(454)	1089(8)	2755(7)	4637(5)	87(4)
C(166)	4517(8)	1398(6)	1514(5)	76(4)	C(455)	786(8)	2316(6)	4346(5)	80(4)
O(161)	4134(4)	2105(3)	2095(3)	56(2)	C(456)	530(7)	2446(6)	3853(4)	68(4)
N(211)	3481(6)	1030(5)	2818(4)	72(3)	C(461)	121(7)	1938(6)	3038(4)	60(3)
C(212)	3705(7)	966(6)	3295(5)	74(4)	C(462)	138(7)	1985(6)	3551(4)	71(3)
C(213)	3845(8)	406(7)	3528(5)	90(5)	C(463)	−279(8)	1554(6)	3795(5)	85(4)
C(214)	3758(9)	−106(7)	3247(5)	92(5)	C(464)	−668(9)	1128(7)	3539(5)	94(5)
C(215)	3535(8)	−70(6)	2746(5)	77(4)	C(465)	−674(8)	1079(6)	3031(5)	84(4)
C(216)	3373(7)	506(6)	2539(5)	66(3)	C(466)	−288(8)	1494(6)	2776(5)	70(4)
C(217)	3437(9)	−584(6)	2432(5)	98(5)	O(461)	491(4)	2326(4)	2775(3)	56(2)
C(218)	3193(9)	−518(6)	1959(5)	88(5)	Cl(1)	6312(4)	3446(4)	608(3)	134(2)
N(221)	2974(6)	1140(4)	1865(3)	59(3)	O(1)	6595(17)	2861(17)	709(12)	380(21)
C(222)	3101(7)	577(6)	2037(4)	64(3)	O(2)	6901(15)	3696(16)	442(10)	379(21)
C(223)	3031(7)	50(6)	1743(5)	70(4)	O(3)	6149(10)	3559(10)	1063(7)	240(10)
C(224)	2737(9)	146(7)	1253(5)	93(5)	O(4)	5735(8)	3389(9)	259(5)	193(8)
C(225)	2632(8)	711(6)	1076(5)	84(5)	Cl(2)	1324(4)	8805(3)	401(2)	119(2)
C(226)	2738(8)	1219(6)	1384(5)	72(4)	O(5)	656(12)	9060(12)	383(9)	317(16)
C(231)	2464(7)	2349(6)	1458(4)	65(4)	O(6)	1581(17)	9016(15)	20(11)	415(24)
C(232)	2660(6)	1838(6)	1187(4)	57(3)	O(7)	1675(12)	8967(9)	815(8)	258(11)
C(233)	2767(8)	1925(7)	676(4)	78(4)	O(8)	1288(16)	8209(10)	360(9)	317(15)
C(234)	2675(9)	2473(8)	459(5)	89(5)	C(1)	8289(13)	2358(12)	838(9)	168(10)
C(235)	2466(9)	2965(7)	725(5)	87(5)	C(2)	8421(16)	1988(14)	1226(12)	175(14)
C(236)	2359(8)	2907(6)	1217(5)	77(4)	N(3)	8621(14)	1769(13)	1584(10)	207(11)
O(231)	2368(4)	2303(4)	1943(3)	57(2)	C(4)	3468(13)	8148(10)	1074(11)	165(12)
N(311)	802(6)	2067(5)	1602(4)	63(3)	C(5)	3452(23)	8237(26)	598(13)	300(26)
C(312)	570(8)	2498(6)	1284(5)	76(4)	N(6)	3499(24)	8220(24)	172(12)	391(26)
C(313)	267(8)	2375(7)	805(5)	84(5)	C(7)	1976(17)	6952(16)	478(13)	219(14)
C(314)	203(8)	1784(7)	658(5)	80(4)	C(8)	1503(22)	6622(24)	214(15)	255(21)
C(315)	447(8)	1321(7)	969(5)	75(4)	N(9)	1039(22)	6402(22)	−19(10)	309(20)
C(316)	750(7)	1472(6)	1452(5)	62(3)	C(20)	6940(23)	203(29)	1504(21)	426(43)
C(317)	456(9)	698(7)	815(5)	98(5)	C(21)	6967(35)	650(30)	1104(27)	472(48)
C(318)	668(9)	270(7)	1141(6)	90(5)	O(22)	6493(22)	182(16)	703(17)	402(23)
N(321)	1230(5)	1185(5)	2256(4)	61(3)	C(23)	6354(30)	−139(27)	139(21)	344(29)
C(322)	987(7)	1014(6)	1791(5)	65(4)	C(24)	5709(34)	29(40)	−110(31)	600(69)

Table 2 (Continued)

	x	*y*	*z*	*U*(eq)[a]		*x*	*y*	*z*	*U*(eq)[a]
C(31)	5693(70)	4876(57)	84(49)	388(73)	C(44)	7812(63)	4627(49)	−381(40)	338(53)
C(32)	5225(46)	5265(40)	118(22)	211(32)	C(51)	9056(60)	5809(51)	−268(29)	400(52)
C(33)	6148(48)	5889(42)	196(21)	316(37)	C(52)	9801(73)	5325(43)	105(40)	215(39)
C(41)	6499(59)	4993(34)	−172(22)	229(31)	C(53)	7725(55)	5216(42)	−385(28)	254(37)
C(42)	7209(34)	4812(27)	−285(31)	171(27)	C(54)	10484(75)	4927(80)	140(41)	293(58)
C(43)	7054(61)	5213(50)	−18(36)	311(58)					

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

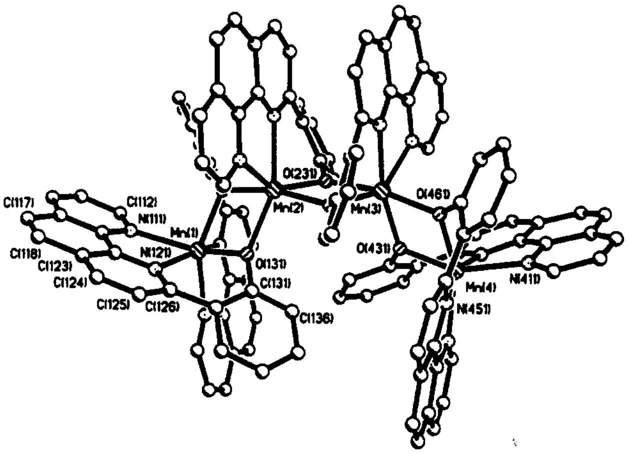

Figure 1. Structure of the complex cation $[Mn_4L_6]^{2+}$.

terminal Mn(II) centers are each coordinated by two terdentate ligands L to give *cis*-N_4O_2 donor sets; the two inner Mn(II) centers each have one associated terdentate ligand, with the other three sites occupied by bridging phenolate groups from the ligands attached to the metals on either side, giving *cis*-N_2O_4 donor sets. Table 2 gives the coordination-sphere bond lengths and angles and Mn–Mn separations. The bond lengths are unremarkable for Mn(II) species. The coordination geometries are highly distorted, a common feature of metal complexes which have no stereoelectronic preferences. That all four manganese ions are in oxidation state +2 is confirmed by the bond lengths and by the presence of two perchlorate counterions. The $(pyridyl)_2$-$(phenolate)_4$ donor set has been found around both Mn(II)[8] and Mn(III) centers[9] in other polynuclear complexes, but no reversible electrochemical processes were observed for **1**. The structure is reminiscent of $[Mn^{IV}_4(\mu\text{-}O)_6(bipy)_6]^{4+}$, which contains a chain of four manganese ions with two oxo bridges between each adjacent pair.[10]

The structure appears to be stabilized by aromatic π-stacking interactions between sections of the ligands. The phenanthroline fragments of the two inner ligands are nearly parallel (interplanar angle = 3.4°) and overlap substantially with an average interplanar separation of 3.4 Å in the overlapping region; likewise the phenol ring of each of the inner ligands stacks (average interplanar separation = 3.6 Å) with a phenol ring of one of the adjacent ligands on a terminal Mn(II) ion. The flexibility of the ligands allows these interactions to be optimized by substantial dihedral twists between the phenanthroline and phenol fragments.

The structure of **1** is in interesting contrast to the binuclear complexes of Cu(II) and Ni(II) with the same ligand.[5] Both $[Cu_2L_2(\mu\text{-}CH_3CO_2)]^+$ and $[Ni_2L_2(\mu\text{-}CH_3CO_2)(MeCN)_2]^+$ have $M_2(\mu\text{-phenolate})_2(\mu\text{-}1,3\text{-}CH_3CO_2)$ cores, with the metal ions in each case in the regular coordination geometries (axially elongated square-pyramidal and octahedral, respectively) to be expected for Cu(II) and Ni(II) complexes. This illustrates nicely how finely-balanced is the competition between the effects which control the complex structures. The lack of any geometric preference for the high-spin, d^5 Mn(II) ions permits a completely different structure in which the propensity of phenolate residues to bridge two metal centers and the presence of interligand π-stacking interactions are allowed to dominate.

Table 3. Selected Internuclear Distances (Å) and Angles (deg) for 1

Mn(1)–O(161)	2.084(8)	Mn(1)–O(131)	2.118(8)	Mn(1)–N(141)	2.226(11)	Mn(1)–N(111)	2.259(10)
Mn(1)–N(121)	2.289(11)	Mn(1)–N(151)	2.289(11)	Mn(2)–O(231)	2.118(8)	Mn(2)–O(131)	2.156(9)
Mn(2)–O(331)	2.164(8)	Mn(2)–O(161)	2.176(8)	Mn(2)–N(211)	2.230(10)	Mn(2)–N(221)	2.307(10)
Mn(3)–O(331)	2.121(8)	Mn(3)–O(431)	2.139(9)	Mn(3)–O(461)	2.157(8)	Mn(3)–O(231)	2.175(8)
Mn(3)–N(311)	2.242(10)	Mn(3)–N(321)	2.329(10)	Mn(4)–O(431)	2.107(8)	Mn(4)–O(461)	2.108(8)
Mn(4)–N(441)	2.230(10)	Mn(4)–N(411)	2.240(9)	Mn(4)–N(451)	2.245(10)	Mn(4)–N(421)	2.278(10)
Mn(1)⋯Mn(2)	3.372	Mn(2)⋯Mn(3)	3.333	Mn(3)⋯Mn(4)	3.356		

O(161)–Mn(1)–O(131)	76.9(3)	O(161)–Mn(1)–N(141)	146.9(4)	O(131)–Mn(1)–N(141)	98.0(4)
O(161)–Mn(1)–N(111)	94.3(3)	O(131)–Mn(1)–N(111)	145.3(4)	N(141)–Mn(1)–N(111)	106.5(4)
O(161)–Mn(1)–N(121)	114.2(3)	O(131)–Mn(1)–N(121)	79.9(3)	N(141)–Mn(1)–N(121)	96.6(4)
N(111)–Mn(1)–N(121)	73.3(4)	O(161)–Mn(1)–N(151)	80.2(3)	O(131)–Mn(1)–N(151)	116.8(4)
N(141)–Mn(1)–N(151)	73.0(4)	N(111)–Mn(1)–N(151)	94.1(4)	N(121)–Mn(1)–N(151)	161.0(4)
O(231)–Mn(2)–O(131)	115.8(3)	O(231)–Mn(2)–O(331)	78.0(3)	O(131)–Mn(2)–O(331)	94.7(3)
O(231)–Mn(2)–O(161)	101.1(3)	O(131)–Mn(2)–O(161)	74.2(3)	O(331)–Mn(2)–O(161)	167.4(3)
O(231)–Mn(2)–N(211)	143.4(4)	O(131)–Mn(2)–N(211)	98.7(4)	O(331)–Mn(2)–N(211)	87.9(4)
O(161)–Mn(2)–N(211)	99.6(4)	O(231)–Mn(2)–N(221)	78.9(3)	O(131)–Mn(2)–N(221)	157.1(4)
O(331)–Mn(2)–N(221)	105.9(3)	O(161)–Mn(2)–N(221)	86.1(3)	N(211)–Mn(2)–N(221)	72.7(4)
O(331)–Mn(3)–O(431)	108.9(3)	O(331)–Mn(3)–O(461)	102.5(3)	O(431)–Mn(3)–O(461)	75.0(3)
O(331)–Mn(3)–O(231)	77.7(3)	O(431)–Mn(3)–O(231)	94.6(3)	O(461)–Mn(3)–O(231)	169.2(3)
O(331)–Mn(3)–N(311)	145.4(4)	O(431)–Mn(3)–N(311)	103.0(4)	O(461)–Mn(3)–N(311)	98.3(3)
O(231)–Mn(3)–N(311)	86.8(4)	O(331)–Mn(3)–N(321)	79.0(3)	O(431)–Mn(3)–N(321)	166.3(3)
O(461)–Mn(3)–N(321)	92.5(3)	O(231)–Mn(3)–N(321)	98.1(3)	N(311)–Mn(3)–N(321)	72.7(4)
O(431)–Mn(4)–O(461)	76.7(3)	O(431)–Mn(4)–N(441)	99.2(4)	O(461)–Mn(4)–N(441)	150.5(4)
O(431)–Mn(4)–N(411)	146.7(4)	O(461)–Mn(4)–N(411)	95.2(4)	N(441)–Mn(4)–N(411)	102.7(4)
O(431)–Mn(4)–N(451)	115.6(4)	O(461)–Mn(4)–N(451)	80.8(3)	N(441)–Mn(4)–N(451)	74.7(4)
N(411)–Mn(4)–N(451)	94.3(4)	O(431)–Mn(4)–N(421)	80.2(4)	O(461)–Mn(4)–N(421)	112.1(4)
N(441)–Mn(4)–N(421)	95.7(4)	N(411)–Mn(4)–N(421)	73.0(4)	N(451)–Mn(4)–N(421)	162.3(4)
Mn(1)–O(131)–Mn(2)	104.2(4)	Mn(1)–O(161)–Mn(2)	104.7(4)	Mn(2)–O(231)–Mn(3)	101.8(3)
Mn(3)–O(331)–Mn(2)	102.1(4)	Mn(4)–O(431)–Mn(3)	104.5(4)	Mn(4)–O(461)–Mn(3)	103.8(4)

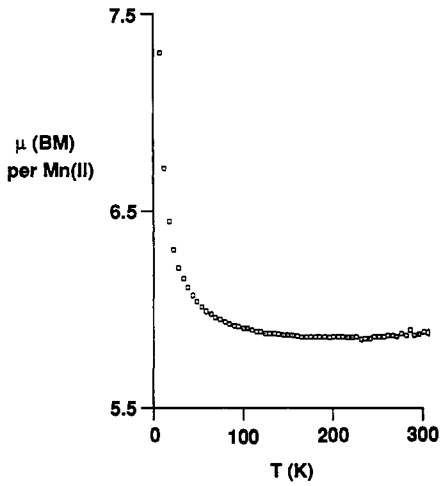

Figure 2. Magnetic moment of **1** [per Mn(II)] as a function of temperature.

The magnetic susceptibility of **1** was measured down to 4 K using a SQUID magnetometer, and marked magnetic exchange effects are present. The magnetic moment per Mn(II) ion is 5.80 μ_B at 300 K. This value is maintained as the temperature is decreased to 100 K but then rises to 7.30 μ_B at 4 K (Figure 2). The data fit a Curie–Weiss plot closely over the whole temperature range, giving a ferromagnetic Θ value of 2.28 K. This ferromagnetism must be due to exchange interactions within the complex, as the ligand bulk prevents any contacts between Mn(II) ions from different molecules. It appears that **1** may have an overall ground state with $S = 7$ (taking $g = 2.018$ from the EPR spectrum),[11] which implies a combination of ferromagnetic and antiferromagnetic interactions. This is not unreasonable; for the binuclear Mn(II) complexes with two phenolate bridges that have been structurally and magnetically characterized, both ferromagnetic[12] and antiferromagnetic exchanges[13] have been observed. The structural data for **1** show that the central $Mn_2(\mu\text{-}O)_2$ moiety has smaller Mn–O–Mn angles and longer Mn–O bonds than the outer ones, but further analysis is inappropriate in view of the paucity of data available for polynuclear manganese(II) complexes compared to, for example, binuclear copper(II) complexes, for which magnetism/structure correlations are well established.[14]

Acknowledgment. We thank the University of London Central Research Fund for the provision of magnetochemical apparatus, Dr. S. G. Carling and Professor P. Day (Royal Institution) for assistance with the low-temperature magnetic data, the SERC for funds to purchase the EPR spectrometer, and Dr. J. P. Maher (University of Bristol) for recording the EPR spectrum.

Supplementary Material Available: Textual X-ray experimental details and tables of crystallographic data, anisotropic thermal parameters, and bond distances and angles for $[Mn_4L_6][ClO_4]_2 \cdot 3MeCN \cdot 2Et_2O$ (17 pages). Ordering information is given on any current masthead page.

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