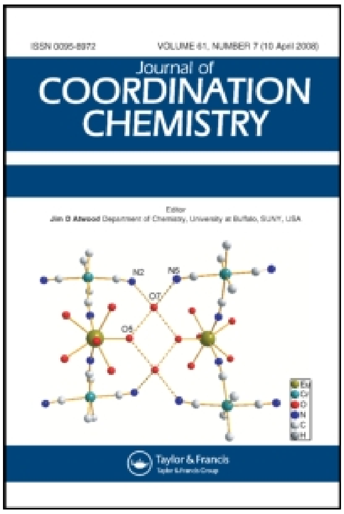

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Novel Mixed-Valence μ-Oxo-Bridged Trinuclear Manganese Complexes $[Mn_3O(O_2CR)_6L_3]$ (R=4-Cl-$C_6H_4OCH_2$, 3-Cl-C_6H_5, $BrCH_2$, L=3-Methylpyridine or Water): Structures and Magnetic Properties

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NOVEL MIXED-VALENCE μ-OXO-BRIDGED TRINUCLEAR MANGANESE COMPLEXES $[Mn_3O(O_2CR)_6L_3]$ (R=4-Cl–$C_6H_4OCH_2$, 3-Cl–C_6H_5, $BrCH_2$, L=3-METHYLPYRIDINE OR WATER): STRUCTURES AND MAGNETIC PROPERTIES

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Preparation of three new mixed-valence oxo-centered trinuclear manganese complexes $[Mn_3O(O_2CR)_6L_3]$ (R=4-Cl–$C_6H_4OCH_2$, **1**, 3-Cl-C_6H_5, **2**, $BrCH_2$, **3**; L=3-methylpyridine or water), by reaction of N-*n*-Bu_4MnO_4 with appropriate reagents in ethanol and 3-methelpyridine is reported. The crystal structure of **1** has shown to have an oxo-centered Mn_3O unit with peripheral ligands provided by bridging carboxylate and terminal 3-methylpyridine groups, and with an approximate 3-fold symmetry axis for the whole cluster. Variable temperature magnetic susceptibilities of the complexes in the range 1.5–300 K have been measured and are interpreted in terms of the Kambe vector-coupling method and Van Vleck equation; J (cm^{-1}), J' (cm^{-1}), g, and R parameters obtained are -8.2, -10.9, 2.04, 2.15×10^{-3} (**1**); -7.3, -11.1, 2.20, 3.32×10^{-3} (**2**); -2.1, -4.1, 1.97, 2.34×10^{-3} (**3**). There is weak antiferromagnetic exchange between manganese ions. Effects of bridging and terminal ligands on the J, J' values and spin ground state are discussed.

Keywords: Mixed valence; Trinuclear manganese; Crystal structure; Magnetism; Spin coupling

INTRODUCTION

During recent years, there has been continuous interest in trinuclear oxo-centered manganese complexes with mixed-valence states [1–10]. Many interesting aspects of these complexes were studied, such as magnetochemistry [1–3], electron localization and delocalization [4], and spin ground state variability [5,6]. Thus, a great number of μ-oxo-bridged mixed-valence trinuclear manganese complexes with the different bridging and terminal ligands have been reported. Mixed valence trinuclear manganese complexes have been synthesized and characterized. Although structures are similar, all

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having an oxo-centred trinuclear manganese core, they reveal different spin ground states, taking several values from a theoretical range from $S=1/2$ to $S=13/2$. In order to shed light on the reason why complexes with the same trinuclear sketeton show the different spin ground states, we have synthesized three new mixed-valence trinuclear manganese complexes with the different bridging and terminal ligands, $[Mn_3O(O_2CR)_6L_3]$ (R=4-Cl–$C_6H_4OCH_2$, **1**, 3-Cl–C_6H_5, **2**, $BrCH_2$, **3**; L=3-methylpyridine or water), and measured their variable temperature magnetic susceptibilities. As a part of our studies of magnetic properties of polynuclear manganese complexes, effects of bridging and terminal ligands on magnetic properties are discussed.

EXPERIMENTAL

Materials and Methods

Caution: Appropriate care should be taken in the use of organic permanganates and perchlorates.

All manipulations were performed under aerobic conditions. Reagent grade solvents were used without further purification. N-*n*-Bu_4MnO_4 was synthesized according to the literature [11].

Complexes 1, 2 and 3

8.15 mmol of $Mn(O_2CCH_3)_2 \cdot H_2O$ and 61.4 mmol of 4-chlorophenoxyacetic acid (or 3-chloro-benzoic acid, bromo-acetic acid) were dissolved in a solvent mixture of absolute ethanol and 3-methylpyridine, and then 1.15 mmol of solid N-*n*-Bu_4MnO_4 was added in small portions, forming a brown–green precipitate. The precipitate was filtered off, washed with cold ethanol and ether, and dried in vacuum. Layering a CH_2Cl_2 solution using hexane gave small microcrystals of the products after several days. Crystals were filtered off and dried under vacuum to give **1** : 1.9 g, 38% based on Mn, Found: C, 50.45; H, 3.39; N, 2.13%; $C_{66}H_{57}Mn_3N_3O_{19}Cl_6$ requires C, 50.35; H, 3.62; N, 2.67%; FT-IR (ν/cm^{-1}): 1643vs, 1596m, 1582m, 1441m, 1419vs, 1414vs, 1287m, 1259s; 1229vs, 1172s, 1066m, 820m, 693s, 645m, 633s; **2** : 1.8 g, 42% based on Mn, Found: C, 50.11; H, 3.27; N, 2.69%; $C_{43}H_{35.5}Mn_3N_{2.5}O_{10}Cl_6$ requires C, 50.12; H, 3.18; N, 2.56%; FT-IR (ν/cm^{-1}): 1625m, 1567m, 1483s, 1423m, 1387vs, 1267s, 1070s, 760m, 735m, 700m, 677s, 658s, 464s; **3** : 1.35 g, 33% based on Mn, Found: C, 27.67; H, 2.73; N, 3.14%; $C_{36}H_{27}Mn_3N_3O_{13}Br_6$ requires C, 27.57; H, 2.68; N, 3.22%; FT-IR (ν/cm^{-1}): 3416m, 3116s, 3053s, 2928s, 1638vs, 1504s, 1410vs, 1214m, 1185s, 671m, 696m.

Physical Measurements

C, H and N analyses were carried out using a Carlo Erba 1106 instrument. Infrared spectra (400–4000 cm^{-1}) were recorded using KBr pellets in a Nicolet 7199B spectrophotometer. Magnetic susceptibility measurements were carried out using a Quantum Design Maglab System 2000 Squid magnetometer in the temperature range 1.5–300 K at an applied field of 10 kG. Magnetization measurements were carried out with a Quantum Design MPMS-7 magnetometer operating at 5 K between 0 and

65 kG. Pascal's constants were used to estimate diamagnetic corrections for each complex. Fitting was carried out by using the nonlinear regression analysis.

X-ray Crystallography

Diffraction data were collected at 293 K on a Enraf Nonius CAD4 four-circle diffractometer with graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å) using the ω–2θ scan technique. For complex **1** cell parameters were determined from 25 reflections with 2θ angles ranging between 20.06° and 30.80°. Some 14 507 intensity data, of which 7095 were unique, were collected in the range $0° \leq 2\theta \leq 53°$. The crystal structure was solved by direct methods. All nonhydrogen atoms were refined anisotropically by full-matrix least-squares methods. Hydrogen atoms were added geometrically and not refined. All calculations were performed on a 586 PC using SHELX-97 with refinement based on F^2. A summary of crystallographic data and refinement parameters is given in Table I. Final atomic coordinates are given in Table II. Additional materials available from the Cambridge Crystallographic Data Centre comprise complete lists of atomic coordinates, thermal parameters and bond lengths and angles (CCDC-125206).

TABLE I Crystal data and structure refinement details for complex **1**

Empirical formula	$C_{66}H_{57}Mn_3N_3O_{19}Cl_6$
Formula weight	1573.67
Color	Red–brown
Temperature	293(2)K
Wave length	0.71073Å
Radiation	MoKα
Crystal group	$P\bar{1}$
Space group	Triclinic
Unit dimensions	$a = 15.344(3)$ Å $b = 15.990(3)$ Å $c = 16.801(3)$ Å $\alpha = 65.03(3)°$ $\beta = 80.26(3)°$ $\gamma = 70.68(3)°$
V	3524.3(11) Å^3
Z	2
Calculated density	1.483 Mg/m^3
Absorption coefficient	0.828 mm^{-1}
F(000)	1606
Crystal size	0.40 × 0.23 × 0.19 mm
θ range for data collection	1.34°–26.47°
Index ranges	$0 <= h <= 19, -18 <= k <= 20, -20 <= l <= 21$
Reflections/collected/unique	15070/14507 [R(int) = 0.0472]
Completeness to $2\theta = 26.47$	99.6%
Absorption correction	Psi-scan
Max. and min. Transmission	1.000 and 0.942
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	14507/0/884
Goodness-of-fit on F^2	1.080
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0774$, $wR2 = 0.1728$
R indices (all data)	$R1 = 0.1923$, $wR2 = 0.2494$
Extinction coefficient	0.0003(3)
Largest diff. Peak and hole	1.458 e.Å^{-3} and -1.005 e.Å^{-3}

$w = 1/[\sigma^2(Fo^2) + (0.0181P)^2 + 2.5082P]$ where $P = (Fo^2 + 2Fc^2)/3$.

TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **1**

Atom	*x/a*	*y/b*	*z/c*	*U*(eq)
Mn(1)	2836(1)	3673(1)	865(1)	36(1)
Mn(2)	2667(1)	5221(1)	−1206(1)	38(1)
Mn(3)	2108(1)	6029(1)	416(1)	38(1)
Cl(1)	3745(3)	3234(4)	−4651(3)	148(2)
Cl(2)	4318(2)	−1296(2)	2027(2)	99(1)
Cl(3)	1997(2)	11061(2)	−2587(3)	114(1)
Cl(4)	2143(3)	8534(3)	−5594(2)	137(2)
Cl(5)	3061(2)	499(2)	5383(2)	112(1)
Cl(6)	424(4)	7141(8)	3892(7)	362(7)
O(1)	2556(3)	4942(3)	12(3)	36(1)
O(2)	1833(3)	4424(4)	−1133(3)	50(1)
O(3)	2325(3)	3135(3)	98(3)	48(1)
O(4)	1164(4)	3387(4)	−1692(4)	62(2)
O(5)	3881(3)	4009(4)	−1062(3)	48(1)
O(6)	4135(3)	3269(3)	378(3)	44(1)
O(7)	5742(3)	2024(4)	97(4)	55(1)
O(8)	892(3)	6578(4)	−283(4)	52(1)
O(9)	1483(3)	6501(4)	−1557(3)	50(1)
O(10)	120(5)	8326(5)	−2319(4)	83(2)
O(11)	2816(3)	6920(3)	−649(3)	43(1)
O(12)	3506(3)	6071(3)	−1474(3)	45(1)
O(13)	4276(3)	7486(4)	−2574(3)	57(1)
O(14)	1566(3)	3859(4)	1468(3)	48(1)
O(15)	1344(3)	5289(3)	1530(3)	48(1)
O(16)	310(3)	3419(4)	2831(4)	58(2)
O(17)	3403(3)	3967(3)	1761(3)	47(1)
O(18)	3247(4)	5546(4)	1189(3)	52(1)
O(19)	4042(4)	5385(4)	2575(4)	68(2)
N(1)	3114(4)	2259(4)	1808(4)	44(1)
N(2)	2804(4)	5490(4)	−2564(4)	51(2)
N(3)	1542(4)	7268(5)	795(4)	51(2)
C(1)	3863(5)	1822(5)	2308(5)	49(2)
C(2)	4044(5)	917(6)	2942(5)	54(2)
C(3)	3431(6)	411(6)	3081(6)	66(2)
C(4)	2655(6)	834(6)	2590(6)	66(2)
C(5)	2520(5)	1741(6)	1962(5)	53(2)
C(6)	4916(7)	459(7)	3474(7)	84(3)
C(7)	2057(6)	5799(6)	−3033(6)	64(2)
C(8)	2095(8)	5942(7)	−3902(7)	76(3)
C(9)	2959(10)	5744(8)	−4297(7)	90(3)
C(10)	3722(8)	5424(8)	−3832(7)	81(3)
C(11)	3613(6)	5310(6)	−2967(6)	64(2)
C(12)	1389(16)	6192(16)	−4398(13)	91(7)
C(13)	4561(14)	5204(18)	−4288(14)	98(7)
C(14)	1983(5)	7915(6)	648(5)	56(2)
C(15)	1603(6)	8741(7)	818(7)	72(3)
C(16)	721(7)	8870(8)	1188(9)	100(4)
C(17)	264(7)	8214(9)	1332(9)	106(4)
C(18)	682(5)	7434(7)	1146(7)	70(3)
C(19)	2151(8)	9454(9)	627(9)	113(4)
C(20)	1913(5)	3569(6)	−612(5)	44(2)
C(21)	1452(6)	2993(7)	−815(5)	64(2)
C(22)	1813(6)	3328(6)	−2337(5)	51(2)
C(23)	1480(7)	3543(7)	−3130(6)	65(2)
C(24)	2057(8)	3514(8)	−3844(7)	86(3)
C(25)	3002(8)	3264(8)	−3762(7)	80(3)
C(26)	3339(7)	3062(7)	−2982(8)	80(3)
C(27)	2758(6)	3095(6)	−2268(6)	65(2)
C(28)	4346(5)	3427(5)	−417(5)	42(2)

TABLE II Continued

Atom	*x/a*	*y/b*	*z/c*	*U*(eq)
C(29)	5289(5)	2834(6)	−624(5)	54(2)
C(30)	5377(5)	1267(5)	496(6)	51(2)
C(31)	4549(6)	1254(6)	282(6)	58(2)
C(32)	4241(6)	461(7)	744(7)	72(3)
C(33)	4728(6)	−303(6)	1414(7)	67(3)
C(34)	5559(7)	−301(6)	1617(6)	71(3)
C(35)	5872(6)	493(6)	1163(6)	64(2)
C(36)	871(5)	6816(5)	−1091(5)	44(2)
C(37)	−13(5)	7586(6)	−1521(6)	63(2)
C(38)	527(6)	8964(6)	−2285(7)	71(3)
C(39)	502(9)	9748(8)	−3064(7)	97(4)
C(40)	964(9)	10381(8)	−3153(8)	100(4)
C(41)	1412(7)	10254(7)	−2464(7)	73(3)
C(42)	1407(6)	9504(6)	−1684(7)	69(2)
C(43)	955(6)	8844(6)	−1580(6)	65(2)
C(44)	3346(5)	6772(5)	−1259(5)	38(2)
C(45)	3840(6)	7517(6)	−1775(5)	56(2)
C(46)	3741(6)	7737(5)	−3255(5)	53(2)
C(47)	2797(6)	7951(6)	−3193(6)	57(2)
C(48)	2309(7)	8187(7)	−3910(7)	79(3)
C(49)	2772(9)	8225(6)	−4690(6)	75(3)
C(50)	3726(9)	7999(7)	−4757(7)	83(3)
C(51)	4198(7)	7764(6)	−4032(6)	70(3)
C(52)	1154(5)	4519(6)	1746(5)	44(2)
C(53)	341(5)	4387(5)	2377(5)	55(2)
C(54)	956(5)	2788(5)	3441(5)	48(2)
C(55)	868(6)	1879(6)	3893(5)	66(2)
C(56)	1505(7)	1184(7)	4498(6)	75(3)
C(57)	2232(7)	1388(7)	4654(6)	69(2)
C(58)	2318(6)	2288(8)	4222(6)	75(3)
C(59)	1682(6)	3005(6)	3613(5)	63(2)
C(60)	3541(4)	4706(5)	1739(5)	43(2)
C(61)	4149(6)	4552(6)	2430(6)	64(2)
C(62)	3192(8)	5781(7)	2882(6)	71(3)
C(63)	3018(12)	6674(9)	2874(8)	125(5)
C(64)	2131(19)	7132(14)	3155(14)	176(11)
C(65)	1505(14)	6606(19)	3526(17)	180(12)
C(66)	1669(10)	5762(17)	3500(12)	173(9)
C(67)	2500(8)	5332(10)	3206(9)	107(4)

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

RESULTS AND DISCUSSION

Crystal Structure

An ORTEP projection of **1** is shown in Fig. 1. Mn coordination geometry is slightly distorted from octahedral consisting of the central oxygen atom, four oxygen atoms from bridging acetate groups and the nitrogen atom of a terminal 3-methylpyridine group. The overall structure is thus the common "basic carboxylate" type seen in many other complexes [1–5, 7–10]. Selected bond distances and angles for **1** are given in Table III. In molecule complex **1** the central-O-atom is slightly displaced from the plane of the Mn_3 triangle (0.0038 Å). The Mn(1)–O(1)–Mn(2) is 122.4(2)° and, Mn(1)–O(1)–Mn(3) is 118.3(2)° and Mn(2)–O(1)–Mn(3) is 119.3(2)°. Mn (1)–O(1), Mn(2)–O(1), Mn(3)–O(1) distances are 1.880(4), 1.891(4), and 2.000(4) Å, respectively.

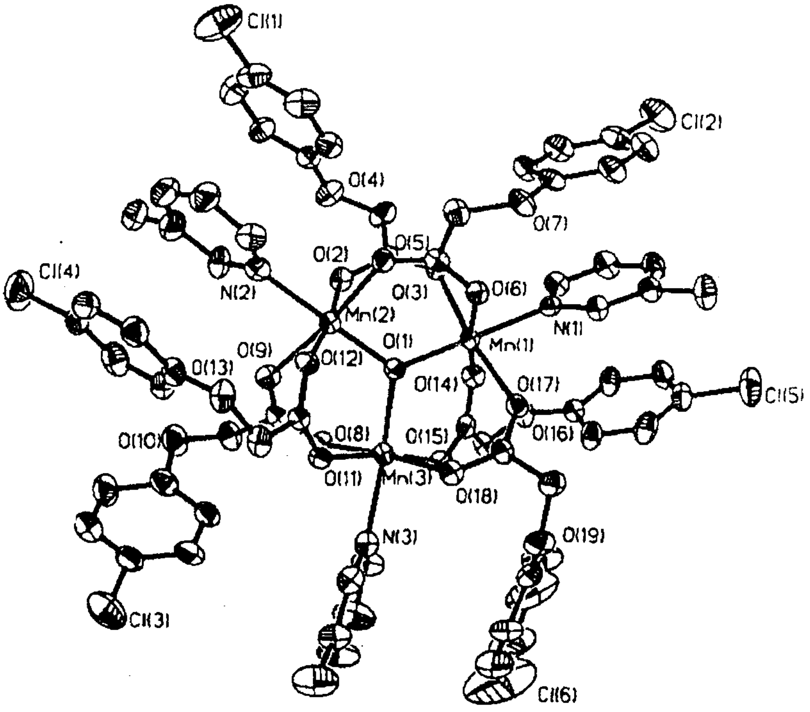

FIGURE 1 Structure of complex **1** (Hydrogen atoms are omitted for clarity).

Different Mn–O distances indicate the complex **1** is in a valence-trapped state. The Mn(3)–O(1) distance is longest as expected for a lower oxidation state, so we can preliminarily assign Mn(3) to Mn(II) and Mn(1) and Mn(2) to Mn(III) ions. Average values for the other five Mn(1,2,3)–O distances are Mn(1)–O, 2.049, Mn(2)–O, 2.060, Mn(3)–O, 2.096 Å, respectively. The four metal-carboxylate oxygen distances surrounding Mn (3) are all close to each other but these distances for Mn(1) and Mn(2) are found to be a pair of longer and a pair of shorter bonds respectively. In reported $Mn_3^{III}O$ complexes [3,4], the same distortion phenomena are observed. It is well-known that the Mn(III) ion (d^4) shows stronger John–Tellor effects than Mn(II) (d^5), we can further confirm Mn(3) as Mn(II) ion. Table IV is a summary of structure features for some reported mixed valence oxo-centred trinuclear manganese complexes. From Table IV the Mn (II)–O(1) length of 2.000 Å in **1** is a little shorter than Mn(II)–(μ–O) lengths of complexes **9** [8], and **14–18** [4, 5, 7,10], but is close to that of complex **10** [5]. The Mn(1)–Mn(2) distance of 3.3033 Å is shorter than the Mn(1,2)–Mn (3) distances (3.3317 and 3.3574 Å). In other words, the Mn (III)–Mn (II) distances of complex **1** are shorter than the Mn(III)-Mn(II) distances of known $Mn_3^{2III+II}O$ complexes. However, the Mn(III)-Mn(III) distances of **1** are longer than that of known $Mn_3^{2III+II}O$ complexes. So far as the terminal ligands are concerned, three terminal 3-methylpyridine rings in complex **1** are almost perpendicular to the Mn_3 plane, with dihedral angles of 73.95, 71.90 and 69.36°, respectively. This is different to the case with $Mn_3O(O_2CMe)_6(pry)_3$, reported in [8], where the three terminal pyridine rings are essentially coplanar with the Mn_3 plane.

TABLE III Selected bond distances (Å) and bond angles (°) for **1**

Mn(1)–O(1)	1.880(4)	Mn(2)–O(9)	2.172(5)
Mn(1)–O(6)	2.026(5)	Mn(3)–O(1)	2.000(4)
Mn(1)–O(14)	2.028(5)	Mn(3)–O(18)	2.089(5)
Mn(1)–N(1)	2.090(6)	Mn(3)–O(8)	2.102(5)
Mn(1)–O(17)	2.133(5)	Mn(3)–O(15)	2.141(5)
Mn(1)–O(3)	2.177(5)	Mn(3)–O(11)	2.150(5)
Mn(2)–O(1)	1.891(4)	Mn(3)–N(3)	2.196(7)
Mn(2)–O(12)	2.037(5)	Mn(1)–Mn(2)	3.3033(20)
Mn(2)–O(2)	2.042(5)	Mn(1)–Mn(3)	3.3317(17)
Mn(2)–N(2)	2.124(7)	Mn(2)–Mn(3)	3.3574(17)
Mn(2)–O(5)	2.158(5)		
O(1)–Mn(1)–O(6)	94.48(19)	N(2)–Mn(2)–O(5)	85.8(2)
O(1)–Mn(1)–O(14)	94.2(2)	O(1)–Mn(2)–O(9)	95.5(2)
O(6)–Mn(1)–O(14)	171.2(2)	O(12)–Mn(2)–O(9)	89.44(19)
O(1)–Mn(1)–N(1)	178.4(2)	O(2)–Mn(2)–O(9)	89.3(2)
O(6)–Mn(1)–N(1)	86.6(2)	N(2)–Mn(2)–O(9)	85.9(2)
O(14)–Mn(1)–N(1)	84.8(2)	O(5)–Mn(2)–O(9)	171.6(2)
O(1)–Mn(1)–O(17)	95.41(19)	O(1)–Mn(3)–O(18)	94.1(2)
O(6)–Mn(1)–O(17)	88.2(2)	O(1)–Mn(3)–O(8)	90.7(2)
O(14)–Mn(1)–O(17)	92.7(2)	O(18)–Mn(3)–O(8)	174.7(2)
N(1)–Mn(1)–O(17)	85.8(2)	O(1)–Mn(3)–O(15)	94.01(18)
O(1)–Mn(1)–O(3)	93.70(19)	O(18)–Mn(3)–O(15)	90.7(2)
O(6)–Mn(1)–O(3)	90.3(2)	O(8)–Mn(3)–O(15)	86.6(2)
O(14)–Mn(1)–O(3)	87.3(2)	O(1)–Mn(3)–O(11)	93.26(17)
N(1)–Mn(1)–O(3)	85.1(2)	O(18)–Mn(3)–O(11)	88.8(2)
O(17)–Mn(1)–O(3)	170.86(19)	O(8)–Mn(3)–O(11)	93.3(2)
O(1)–Mn(2)–O(12)	94.42(19)	O(15)–Mn(3)–O(11)	172.73(19)
O(1)–Mn(2)–O(2)	94.05(19)	O(1)–Mn(3)–N(3)	176.1(2)
O(12)–Mn(2)–O(2)	171.5(2)	O(18)–Mn(3)–N(3)	89.7(2)
O(1)–Mn(2)–N(2)	178.3(2)	O(8)–Mn(3)–N(3)	85.5(2)
O(12)–Mn(2)–N(2)	86.6(2)	O(15)–Mn(3)–N(3)	86.5(2)
O(2)–Mn(2)–N(2)	84.9(2)	O(11)–Mn(3)–N(3)	86.2(2)
O(1)–Mn(2)–O(5)	92.87(19)	Mn(1)–O(1)–Mn(2)	122.4(2)
O(12)–Mn(2)–O(5)	88.85(19)	Mn(1)–O(1)–Mn(3)	118.3(2)
O(2)–Mn(2)–O(5)	91.2(2)	Mn(2)–O(1)–Mn(3)	119.3(2)

TABLE IV Distances (Å) Mn–Mn and Mn–(μ_3–O) in mixed valence oxo-centred trinuclear manganese complexes

	Mn(III)–μ_3–O	*Mn(III)–μ_3–O*	*Mn(II)–μ_3–O*	*Mn(III)–Mn(III)*	*Mn(III)–Mn(II)*	*Mn(III)–Mn(II)*	*Ref.*
1[Mn$_3$O(P–Cl–C$_6$H$_4$OCH$_2$CO$_2$)$_6$ (3-Me–pyr)$_3$]	1.880(5)	1.891(4)	2.000(4)	3.3033	3.3574	3.3317	This work
9[Mn$_3$O(O$_2$CC$_6$H$_5$)$_6$ (pyr)$_2$(H$_2$O)]·0.5MeCN	1.817(14)	1.822(14)	2.154(13)	3.218(4)	3.418(5)	3.396(5)	8
10[Mn$_3$O(2-F–benzoato)$_6$ (pyr)$_3$]	1.871(3)	1.871(3)	1.990(6)	3.253(3)	3.338(5)		5
14[Mn$_3$O(3-Cl–benzoato)$_6$ (pyr)$_2$(H$_2$O)]	1.831(9)	1.835(9)	2.064(10)	3.201(3)	3.364(5)	3.362(5)	5
15[Mn$_3$O(3Br–benzoato)$_6$ (pyr)$_2$(H$_2$O)]	1.824(10)	1.83(10)	2.066(12)	3.202(3)	3.362(7)	3.34(7)	5
16[Mn$_3$O(O$_2$CPh)$_6$ (pyr)$_3$]	1.817(8)	1.855(10)	2.089(8)	3.23(4)	3.389(4)	3.359(5)	10
17[Mn$_3$O(O$_2$CCH$_3$)$_6$ (3-Cl-pyr)$_3$]–(pyr)	1.863(4)	1.864(4)	2.03(4)				7
18[Mn$_3$O(O$_2$CCMe$_3$)$_6$ (pyr)$_3$]	1.813(3)	1.848(3)	2.171(3)				4

Magnetic Properties

Variable temperature magnetic susceptibility data for microcrystalline samples of **1**, **2** and **3** were recorded from higher temperatures to 1.5 K. These data, in conjunction with the calculated susceptibility values resulting from the least-squares fit to the appropriate theoretical equation, are shown in Fig. 2. For complex **1** the value of $\chi_m T$ is $7.1\,\mathrm{cm^3\,mol^{-1}\,K}$ at 256 K and decreases with decreasing temperature, reaching $0.4\,\mathrm{cm^3\,mol^{-1}\,K}$ of $\chi_m T$ at 1.8 K. This behaviour obviously indicates an overall weak antiferromagnetic coupling interaction. The properties of complex **2** are very similar: $\chi_m T$ varies from $8.5\,\mathrm{cm^3\,mol^{-1}\,K}$ at 276.5 K to $0.6\,\mathrm{cm^3\,mol^{-1}\,K}$ at 2.14 K. For complex **3** the value of $\chi_m T$ is $8.9\,\mathrm{cm^3\,mol^{-1}\,K}$ at 299.7 K and decreases with decreasing temperature, reaching $2.1\,\mathrm{cm^3\,mol^{-1}\,K}$ at 4.98 K. The spin Hamiltonian

$$H = -2[J_{12}(S_1S_2) + J_{23}(S_2S_3) + J_{31}(S_3S_1)]$$

was used to fit the observed results, assuming the two Mn(III) ions to be equivalent. There are two exchange parameters, $J = J_{12} = J_{31}$ for the Mn(II)–Mn(III) interaction and $J' = J_{23}$ for the Mn(III)–Mn(III) interaction. On the basis of this model, Hendrickson *et al.* have given a mathematical expression [8] for the molar paramagnetic susceptibility for such mixed valence trinuclear complexes. Magnetic susceptibility data for complexes **1–3** provided a fit to the theoretical equation (Fig. 2). Fitting parameters J, J' and g for **1–3** are given in Table V. From Table V it is found that though complexes **1–5** [3] have the same terminal ligands, their J and J' values

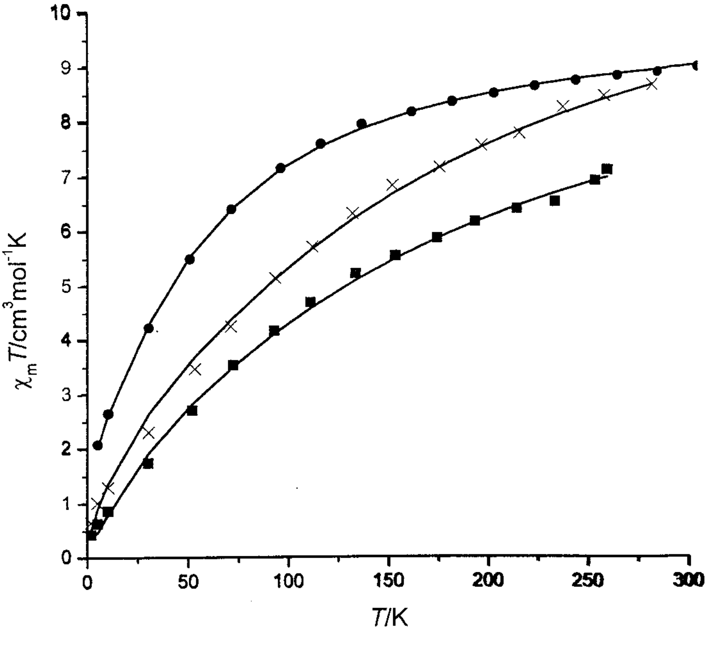

FIGURE 2 Temperature dependence of magnetic susceptibility for complexes **1**, **2**, **3** with experimental data (■), (×), (●), respectively. Solid lines result from a fit of the data to the appropriate theoretical equation.

TABLE V Ground states and parameters from least-squares fitting of magnetic susceptibility data

Compound	J/cm^{-1}	J'/cm^{-1}	g	J/J'	S	*Ref.*
1 $[Mn_3O(4\text{-Cl–}C_6H_4OCH_2CO_2)_6(3\text{-Me–pyr})_3]$	-8.2	-10.9	2.04	0.75	1/2	This work
2 $[Mn_3O(3\text{-Cl-}C_6H_4CO_2)_6(3\text{-Me–pyr})_3]$	-7.3	-11.1	2.20	0.66	1/2, 3/2	This work
3 $[Mn_3O(O_2CCH_2Br)_6(3\text{-Me–pyr})_3]$	-2.1	-4.1	1.97	0.51	3/2	This work
4 $[Mn_3O(O_2CC_6H_5)_6(3\text{-Me–pyr})_2(H_2O)]\cdot 2H_2O$	-5.8	-8.7	2.09	0.66	3/2	3
5 $[Mn_3O(O_2CCH_2Cl)_6(3\text{-Me–pyr})_2(H_2O)]$	-4.6	-8.2	2.09	0.56	3/2	3
6 $[Mn_3O(O_2CCH_3)_6(\text{pyr})_3]\cdot(\text{pyr})$	-5.2	-2.7	2.05	1.92	3/2	6
7 $[Mn_3O(O_2CCH_3)_6(\text{py})_3]\ (\text{pyr})_{0.7}$	-5.6	-6.4	2.07	0.88	1/2	8
8 $[Mn_3O(O_2CCH_3)_6(\text{pyr})_3]$	-7.7	-5.7	2.10	1.35	1/2	8
9 $[Mn_3O(O_2CC_6H_5)_6(\text{pyr})_2(H_2O)\cdot 0.5MeCN$	-6.5	-4.5	1.99	1.44	1/2	6
10 $[Mn_3O(2\text{-F–benzoato})_6(L)_3]$*	-8.5	-6.8	2.09	1.25	1/2	5
11 $[Mn_3O(2\text{-Cl–benzoato})_6(L)_3]$	-4.8	-2.9	2.08	1.65	3/2	5
12 $[Mn_3O(2\text{-Br–benzoato})_6(L)_3]$	-3.9	-2.4	2.05	1.62	3/2	5
13 $[Mn_3O(3\text{-F–benzoato})_6(L)_3]$	-7.1	-5.9	2.10	1.19	1/2	5
14 $[Mn_3O(3\text{-Cl–benzoato})_6(L)_3]$	-6.8	-5.5	2.10	1.13	1/2	5
15 $[Mn_3O(3\text{-Br–benzoato})_6(L)_3]$	-4.7	-3.4	2.05	1.38	1/2, 3/2	5

*L indicates pyridine or water.

are different due to different bridging ligands. On the other hand, complexes **6–10** [5,6,8], with the common pyridine terminal ligand but with the different bridging ligands, also show the different J and J' values. Furthermore, comparing complex **2** with the isostructural complex **14** [5], shows both the J and J' values for 3-methylpyridine terminal ligands are larger than for pyridine terminal ligands. In comparing the Mn(III)–Mn(III) distances with the other complexes, characterized structurally, it is seen that though **1** has the longest Mn(III)–Mn(III) distance, the J' value is the largest. This unusual phenomenon is also observed in comparison with complexes **10, 14**, and **15** [5].

According to the relation between the J/J' value and the spin ground state, supposed by Hendrickson [6], the ground state of complex **3** is $S = 3/2$. For **1** however, the ground state is $S = 1/2$ (Table IV). This is confirmed by magnetization *vs.* magnetic field H plots at 5 K shown in Fig. 3. For **3**, the $M/N\beta$ value tends to 3, consistent with the $S = 3/2$ ground state. For **1**, the $M/N\beta$ value tends to 1, which corresponds to $S = 1/2$. It is interesting to note that for **2**, the value of $M/N\beta$ tends to 1.27 at 60 kG at 5 K, greater than the $S = 1/2$ ground state but lower than for the pure $S = 3/2$ ground state. Thus complex **2** has a mixed ground state [5]. In fact, the J/J' ratio of 0.66 almost represents the crossing point for the 1/2 and 3/2 ground states [5]. It should be pointed out that in the case of complex 4 [3] the J/J' value is also 0.66, and the value of $M/N\beta$ tends to 2.3 at 65 kG at 1.5 K; thus it has a ground state of $S = 3/2$ [3,5]. On the basis of angular moment coupling theory the ground states for the $Mn_3^{2III+II}O$ complexes may lie in a range of $S = 1/2$ to $S = 13/2$. Further, the ground state for the kind of these complexes is determined by spin frustration [12]. So-called "spin frustration" is a complicated magnetic phenomenon. It is the total effect of various exchange interaction in a polynuclear complex and causes a net vector alignment, differing from that expected on the basis of pair-wise exchange interactions. From Table IV, the spin ground state for the $Mn_3^{2III+II}O$ complexes is, indeed, very sensitive to the bridging and terminal ligand. As mentioned above, ground states with $S = 1/2$ [5,8], 3/2 [3,5,6] and 9/2 [2] have been found for these kind of complexes. The discovery of related new complexes with other ground states will be of interest.

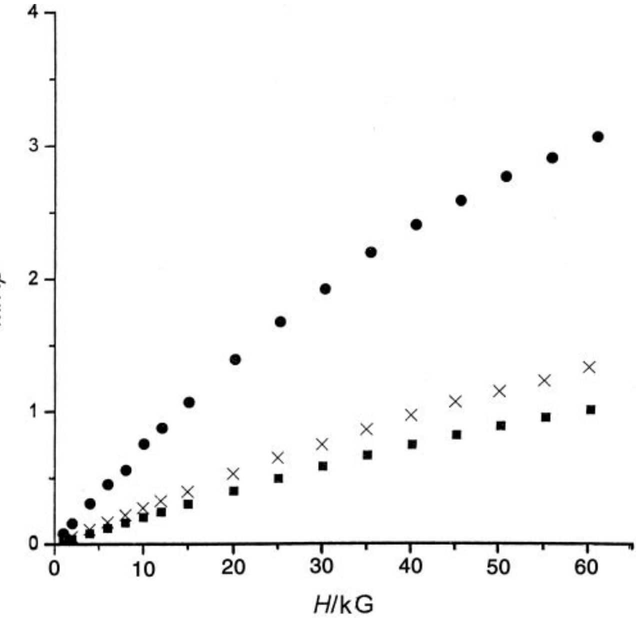

FIGURE 3 Plots of magnetization $M/N\beta$ *versus* magnetic field H (kG) for complexes **1**(■), **2**(×), **3**(●) at 5 K.

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