A Novel Tetranuclear $[Cr^{III}{}_2Mn^{III}{}_2(\mu_3\text{-}O)_2]^{8+}$ Core with an $S_T = 0$ Spin Ground State†

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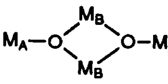
The reaction of $[Cr^{III}L(MeOH)_3]^{3+}$ ions with Mn^{III}(salox) units (L = 1,4,7-trimethyl-1,4,7-triazacyclononane; salox = salicylaldehyde oxime) produced *in situ* in methanol, yielded, in the presence of a small amount of triethylamine and $NaClO_4$, the complex $[L_2Cr^{III}{}_2(\mu\text{-}OMe)_2(\mu_3\text{-}O)_2(salox)_2Mn^{III}{}_2][ClO_4]_2{\cdot}3H_2O$. It has been characterized on the basis of elemental analysis, IR spectroscopy and variable-temperature (4–278 K) magnetic susceptibility measurements. The molecular structure established by X-ray diffraction consists of a $[Cr^{III}{}_2(\mu_3\text{-}O)_2Mn^{III}{}_2]^{8+}$ butterfly core with the chromium(III) ions representing the wing-tips, and high-spin manganese(III) ions the 'body' ions in the tetranuclear core. The magnetic susceptibility measurements revealed a diamagnetic ($S_T = 0$) ground state with antiferromagnetic exchange interactions $J_{CrMn} = -11.7$ cm^{-1} and $J_{MnMn} = -13.0$ cm^{-1}. The ground state is the result of spin frustration of the 'body' manganese(III) ions. In other words, owing to the topology of the tetranuclear complex, which can be viewed as being made up of two edge-shared triangular units, the ground state represents the lowest possible spin state for this electronic configuration when both interactions are antiferromagnetic.

Studies of exchange-coupled clusters of transition-metal ions are relevant to many different scientific areas, ranging from chemistry to solid-state physics and biology, because of their potential impact in material science, catalysis and metallobiochemistry. The current interest in the chemistry of polynuclear systems with two or more metal ions bridged by oxygen-donor ligands is mainly due to the growing awareness of the existence of oxo/hydroxo-bridged metal units in a variety of metalloproteins.[1–16] There are several intriguing features associated with oxohydroxo polynuclear metal complexes. First, they can have unusual electronic structures.[17] Secondly they may be building blocks for molecular-based magnetic materials.[18] In general, molecules which have large number of unpaired electrons should serve, because of their topology, as good starting points for constructing magnetic molecular materials. Even though the pairwise exchange interactions in these complexes are found almost always to be antiferromagnetic, spin frustration in a polynuclear complex can result in ground states having a relatively large number of unpaired electrons.[19] Although spin frustration is a well known magnetic exchange phenomenon for extended lattices,[20] its application to the magnetochemistry of discrete polynuclear complexes is not widely recognized.[21]

At present the study of the exchange interaction between paramagnetic metal centres through various bridging ligands is an active research field in co-ordination chemistry with the aim of understanding fundamental factors governing the magnetic properties of transition-metal compounds.[22–26] Relatively few magnetic studies dealing with tetranuclear systems have been reported in contrast to the large number of studies dealing with tri- and bi-nuclear systems, primarily due to a lack of fully structurally characterized compounds and to the increased complexity involved with theoretical treatments of large spin systems. Most of these studies are concerned with homotetranuclear complexes,[27–41] although a few have treated heterometallic systems.[42–46] New exchange pathways can be expected for heteropolynuclear complexes, where unusual sets of magnetic orbitals can be brought in close proximity; hence, investigations of heteropolynuclear complexes might be more informative in comparison to those of homopolynuclear complexes. The heteropolymetallic systems are of interest to both biologists and bioinorganic chemists investigating the structure and function of polynuclear metal centres in proteins, and physicists or physical inorganic chemists searching for new magnetic materials. Unfortunately, the field of heteropolynuclear complexes with different paramagnetic centres is still limited today by the difficulty in the synthesis and complete structural characterization of new compounds.

In studying the co-ordination chemistry of ternary systems[46] containing the tridentate cyclic amine 1,4,7-trimethyl-1,4,7-triazacyclononane (L) and an oxime, *viz.* salicylaldehyde oxime (H_2salox), we have prepared a novel $[Cr_2Mn_2(\mu_3\text{-}O)_2]^{8+}$-core-containing tetranuclear complex, $[L_2Cr^{III}{}_2(\mu\text{-}OMe)_2(\mu_3\text{-}O)_2(salox)_2Mn^{III}{}_2][ClO_4]_2{\cdot}3H_2O$ **1**, in which the metals are disposed in a butterfly-type arrangement. The concern of this work is the uncommon motif **A** where M_A and M_B represent Cr^{III} and Mn^{III}, respectively. Apart from **1**, there are several crystallographically characterized tetranuclear compounds with paramagnetic ions in the literature,[27–54] but only a few examples[30,33,38,40,46,47] with the 'butterfly' core structure.



A

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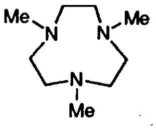
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.



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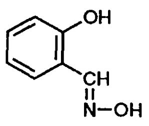


H_2salox

Experimental

The complex [$CrBr_3L$] was prepared as described in the literature.[55] All other reagents were used as received. Elemental microanalyses were performed by the Microanalytical Laboratory, Ruhr-Universität Bochum. Chromium was determined spectrophotometrically as chromate. Manganese was also determined spectrophotometrically by using pyridine-2,6-dicarboxylic acid as described in the literature.[56] Perchlorate anion was determined gravimetrically as tetraphenylarsonium perchlorate. Physical measurements were performed as previously outlined.[57]

Preparation of Complex **1**.—*Solution* 1. To a suspension of [$CrBr_3L$] (0.46 g, 1 mmol) in methanol (30 cm^3) was slowly added $AgClO_4 \cdot H_2O$ (0.62 g, 2.8 mmol) with stirring. The suspension was refluxed under dry conditions for 30 min; during this time a blue-violet solution with concomitant formation of AgBr resulted. The precipitated AgBr was filtered off, and the clear blue-violet solution added to solution 2 as described below.

Solution 2: 'Manganse(III) acetate' (1 mmol, 0.27 g) was added to a solution of salicylaldehyde oxime (0.135 g, 1 mmol) in methanol (30 cm^3) under vigorous stirring. The resulting suspension was stirred at room temperature for 0.5 h to yield a dark brown solution.

The mixture of the solutions 1 and 2 was refluxed for 1 h in the presence of triethylamine (1 cm^3) and then filtered to remove some green solid, presumably [Mn(Hsalox)$_3$]. Sodium perchlorate monohydrate (0.4 g) was added to the clear solution and the dark brown solution was kept at ambient temperature. After 12 h the dark brown crystals were filtered off and air-dried. Yield: 300 mg ($\approx$51%) (Found: C, 34.5; H, 5.50; Cr, 8.70; Mn, 9.20; N, 9.50; ClO_4, 17.0. Calc. for $C_{34}H_{64}Cl_2Cr_2Mn_2N_8O_{19}$: C, 34.80; H, 5.50; Cr, 8.85; Mn, 9.35; N, 9.55; ClO_4, 16.95%).

CAUTION: Although we experienced no difficulties, the unpredictable behaviour of perchlorate salts necessitates extreme caution in their handling.

Crystal Structure Determination.—A dark brown crystal of the tetranuclear complex **1** with dimensions 0.08 × 0.15 × 0.55 mm was mounted on a Siemens R3m/V diffractometer. Preliminary examination showed that it belonged to the monoclinic crystal system, space group *C*2/*c*. The lattice parameters were obtained at 23 °C by least-squares refinement of the angular settings ($12 \leqslant 2\theta \leqslant 30°$) of 30 reflections. The data are summarized in Table 1. 6121 Intensities were collected using ω–2θ scans in the range $3 \leqslant 2\theta \leqslant 55°$, $0 \leqslant h \leqslant 35$, $0 \leqslant k \leqslant 15$ and $-23 \leqslant l \leqslant 23$. Three standard reflections were monitored every 400 measurements and showed 6% decrease; the intensities were adjusted accordingly. Lorentz polarization correction and an empirical absorption correction[58] *via* ψ scans were applied. The scattering[59] factors for neutral non-hydrogen atoms were corrected for both the real and imaginary components of anomalous dispersion. The structure was solved by comparison of cell constants with those of the isotypic Cr_2Fe_2 complex[46] using the heavy-atom coordinates as starting parameters (SHELXTL PLUS).

The structure was refined by a least-squares technique, the function minimized being $\Sigma w(|F_o| - |F_c|)^2$ where $w^{-1} = \sigma^2(F) + 0.0001F^2$. Idealized positions of H atoms bound to carbon atoms were calculated (C–H 0.96 Å) and included in the refinement cycle with a common isotropic thermal parameter (U_{iso} = 0.080 $Å^2$). Atoms Mn, Cr, N, O, Cl and C(17) were refined anisotropically. The perchlorate anions were heavily disordered at least over two sites; the O atom positions could not be completely resolved. Final positional parameters are presented in Table 2, selected interatomic distances and angles in Table 3.

Table 1 Crystallographic data for complex **1**

Formula	$C_{34}H_{64}Cl_2Cr_2Mn_2N_8O_{19}$
M	1173.7
Crystal size/mm	0.08 × 0.15 × 0.55
Colour	Red-brown
Crystal system	Monoclinic
Space group	*C*2/*c*
a/Å	27.279(10)
b/Å	11.740(3)
c/Å	18.008(5)
β/°	121.00(1)
U/$Å^3$	4943.4
Z	4
D_c/g cm^{-3}	1.578
λ(Mo-Kα)/Å	0.710 73
μ/mm^{-1}	1.23
Transmission factors (minimum, maximum)	0.897, 1.000
2θ range/°	3–55
F(000)	2436
No. of unique data	5719
No. of data with $I/\sigma(I) \geqslant 2.0$	1723
Residual peaks (maximum, minimum)/e $Å^{-3}$	0.67, −0.51
R	0.088
R'	0.084

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

The dark brown solution obtained from manganese(III) acetate and salicylaldehyde oxime in methanol reacted with the LCr^{3+} unit to afford after addition of perchlorate anion in the presence of triethylamine dark brown crystals of [$L_2Cr_2(\mu\text{-OMe})_2(\mu_3\text{-O})_2$(salox)$_2Mn_2$][$ClO_4$]$_2 \cdot 3H_2O$ in reasonable yield. The purpose of adding triethylamine is to provide a basic medium for deprotonation of the OH groups present in H_2salox. The tetranuclear complex is sparingly soluble in water with decomposition {precipitation of a green solid, which according to IR spectroscopy is [Mn(Hsalox)$_3$]}, but reasonably soluble in organic solvents such as acetone, alcohols, acetonitrile and nitromethane.

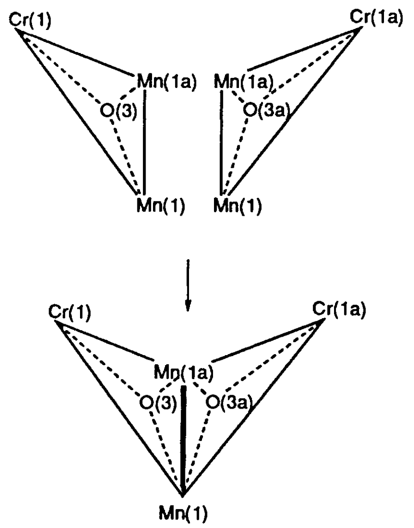
The fact that the metal ions have remained associated with their different ligands, originating from their respective starting materials, is evidenced from an aqueous solution of the complex in 1 mol dm^{-3} $HClO_4$, which is red-violet due to the presence of the [$CrL(OH_2)_3$]$^{3+}$ species which has an absorption maximum at 526 nm.

It is worth mentioning that besides ligand and ClO_4 absorptions, the IR spectrum of the tetranuclear complex exhibits a sharp band at 668 cm^{-1} probably due to the ν_{asym} vibration of the four modes of the $CrMn_2(\mu_3\text{-O})$ triangle.[60] The ν(CN) vibration is assigned to the medium-intense band at 1596 cm^{-1}. The complex shows a strong band at 1093 (antisymmetric stretch) and a sharp band at 625 cm^{-1} (antisymmetric bend), indicative of unco-ordinated perchlorate anions.

Structure of Complex **1**.—The structure of the cation in the complex is presented in Fig. 1. The geometrical centre of the

Table 2 Atomic coordinates (× 10^4) for complex **1**

Atom	*x*	*y*	*z*
Mn(1)	4703(1)	1716(2)	2925(1)
Cr(1)	3805(1)	742(2)	1309(2)
O(1)	4203(4)	130(9)	2485(6)
O(2)	3509(4)	2003(9)	1649(6)
O(3)	4539(4)	1520(8)	1784(5)
O(4)	4865(4)	1974(9)	4046(6)
N(1)	2969(6)	−35(15)	692(10)
N(2)	3509(5)	1458(12)	76(8)
N(3)	3993(7)	−693(12)	766(9)
N(4)	3907(6)	2344(11)	2472(8)
C(1)	2650(10)	651(22)	−72(17)
C(2)	2872(9)	1349(18)	−407(13)
C(3)	3724(8)	767(17)	−376(12)
C(4)	3979(10)	−239(21)	17(15)
C(5)	3540(10)	−1501(21)	598(15)
C(6)	3055(9)	−1214(19)	547(15)
C(7)	2694(7)	−7(17)	1215(11)
C(8)	3660(7)	2645(15)	109(10)
C(9)	4553(7)	−1233(15)	1386(11)
C(10)	3726(7)	2873(13)	2906(10)
C(11)	4116(6)	3219(14)	3818(9)
C(12)	3892(8)	4016(15)	4162(11)
C(13)	4230(7)	4345(15)	5024(11)
C(14)	4770(7)	3962(14)	5503(11)
C(15)	5012(7)	3163(14)	5213(10)
C(16)	4650(7)	2800(14)	4331(10)
C(17)	3999(8)	−330(15)	2992(10)
Cl(1)	2091(3)	1591(7)	2692(4)
O(11)	2256(10)	562(23)	2681(15)
O(121)	1984(15)	1768(29)	3325(22)
O(131)	1552(23)	1388(42)	2700(37)
O(141)	2146(13)	2316(26)	2118(20)
O(132)	1625(17)	1848(34)	1993(26)
O(142)	2533(11)	2142(22)	3414(17)
O(w1)	0	1214(15)	7500
O(w2)	996(9)	121(21)	3120(13)



Scheme 1

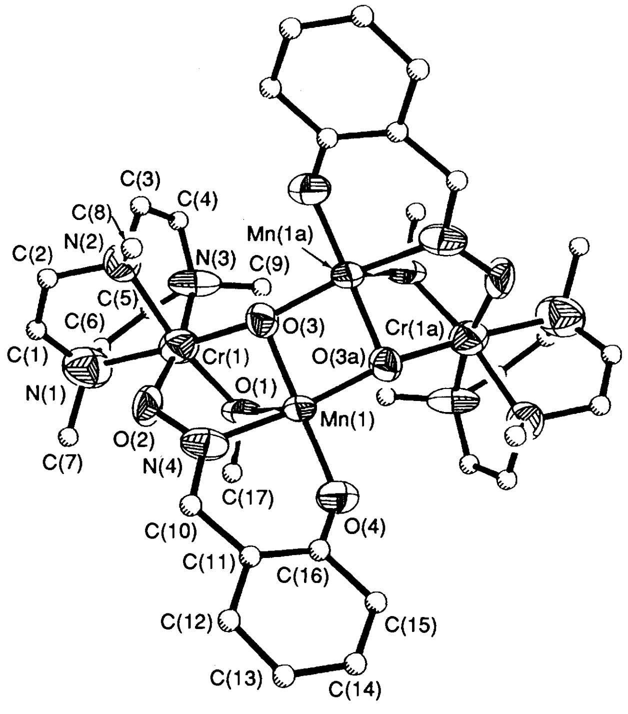
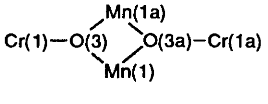


Fig. 1 Molecular structure of the tetranuclear cation in complex **1**, showing the atom-numbering scheme

Table 3 Selected bond distances (Å) and angles (°) for complex **1**

Cr(1)–O(2)	1.931(12)	Mn(1)–O(1)	2.200(11)
Cr(1)–O(1)	1.952(10)	Mn(1)–O(4)	1.857(11)
Cr(1)–O(3)	1.952(10)	Mn(1)–O(3)	1.877(10)
Cr(1)–N(1)	2.158(16)	Mn(1)–O(3a)	1.867(10)
Cr(1)–N(2)	2.108(13)	Mn(1)–N(4)	2.025(14)
Cr(1)–N(3)	2.138(17)	Mn(1)–O(w1)	2.790(11)
O(1)–Cr(1)–O(2)	91.6(5)	N(1)–Cr(1)–N(3)	82.5(7)
O(1)–Cr(1)–O(3)	79.9(4)	N(2)–Cr(1)–N(3)	83.4(6)
O(2)–Cr(1)–O(3)	79.9(4)		
O(1)–Cr(1)–N(1)	104.7(6)	O(1)–Mn(1)–O(3)	75.4(4)
O(2)–Cr(1)–N(1)	89.1(6)	O(1)–Mn(1)–O(4)	106.7(5)
O(3)–Cr(1)–N(1)	175.4(5)	O(3)–Mn(1)–O(4)	177.8(5)
O(1)–Cr(1)–N(2)	170.7(6)	O(1)–Mn(1)–N(4)	80.0(5)
O(2)–Cr(1)–N(2)	91.9(5)	O(4)–Mn(1)–N(4)	89.1(6)
O(3)–Cr(1)–N(2)	91.4(5)	O(3)–Mn(1)–N(4)	90.1(5)
N(1)–Cr(1)–N(2)	84.0(6)	O(1)–Mn(1)–O(3a)	112.9(4)
O(1)–Cr(1)–N(3)	94.4(5)	O(3)–Mn(1)–O(3a)	84.1(3)
O(3)–Cr(1)–N(3)	97.8(6)	O(4)–Mn(1)–O(3a)	96.0(5)
O(2)–Cr(1)–N(3)	170.7(4)	N(4)–Mn(1)–O(3a)	163.9(5)

Table 4 Bond distances (Å) and angles (°) within the $Cr^{III}_2Mn^{III}_2(\mu_3\text{-}O)_2$ core



Cr(1)–O(3)	1.952(10)	Cr(1) ··· Mn(1)	2.903(3)
Mn(1)–O(3)	1.877(10)	Cr(1) ··· Mn(1a)	3.745(5)
Mn(1a)–O(3)	1.867(10)	Mn(1) ··· Mn(1a)	2.742(7)
Mn(1)–O(3a)	1.867(10)	Cr(1) ··· Cr(1a)	5.664(3)
Mn(1)–O(3)–Mn(1a)	94.2(3)	Mn(1a)–O(3)–Cr(1)	156.6(6)
Mn(1)–O(3)–Cr(1)	98.6(6)		

cation lies on a two-fold rotation axis perpendicular to the central Mn_2O_2 rhomboid. The asymmetric unit thus consists of half of the cation and well separated ClO_4^- anions. The cation possesses a $Cr^{III}_2Mn^{III}_2(\mu_3\text{-}O)_2$ core. The metal geometry of the cluster may be described as a 'butterfly', based on two edge-sharing $CrMn_2(\mu_3\text{-}O)$ triangular units (Scheme 1) with the oxygen atoms O(3) slightly below (0.287 Å) the metal Mn_2Cr triangle. The Cr(1) ··· Mn(1) and Mn(1) ··· Mn(1a) distances are noticeably short, 2.903(3) and 2.742(7) Å, respectively. To our knowledge this is the shortest Mn ··· Mn distance reported for an inner Mn_2O_2 core.[34b] The distance between Cr(1) and Cr(1a) is 5.664(3) Å.

The dispositions of the μ_3-oxo groups are not completely symmetrical, but are consistent with all metals being in the trivalent oxidation level. The dihedral angle between the planes Mn(1)Mn(1a)Cr(1)O(3) and Mn(1)Mn(1a)Cr(1a)-O(3a) is 135.4° which is nearly the same as that in the corresponding $Cr_2Fe_2(\mu_3\text{-}O)_2$ core.[46] Selected bond distances and angles for the $Cr^{III}{}_2Mn^{III}{}_2(\mu_3\text{-}O)_2$ core and for the rest of the cation are given in Tables 4 and 3, respectively. The $(M_A)_2(M_B)_2O_2$ core is known in butterfly configuration for homotetranuclear complexes with $M_A = M_B = Mn^{III}$[33,34b,40,41] or Fe^{III}[30,38,47,49,50] and for the analogous $Cr_2Fe_2O_2$ complex.[46]

In addition to the two μ_3-oxo groups, there are two μ-bridging methoxy groups in the tetranuclear complex. A methoxy oxygen O(1) bridges Cr(1) and Mn(1) in an asymmetrical manner, the bond length Cr(1)–O(1) being shorter (1.952 Å) than that of Mn(1)–O(1) (2.200 Å). The atoms Mn(1)O(3)Mn(1a)O(3a) do not constitute a plane [deviations from the 'best' plane: Mn, ± 0.56; O(3), ± 1.14 Å]. It seems that the non-planarity is a consequence of the bridging methoxy groups. Specifically, the chromium and manganese ions that are methoxy bridged are apparently 'pulled' closer to one another, Cr(1) ••• Mn(1) 2.903(3) Å, than are those without methoxy bridging, Cr(1) ••• Mn(1a) 3.745(5) Å.

The co-ordination geometry of the 'wing-tip' chromium ions, Cr(1) and Cr(1a), is distorted octahedral with three nitrogen atoms N(1), N(2) and N(3) from the facially co-ordinated tridentate macrocyclic amine (L) and three oxygen atoms [O(2) from the deprotonated oxime group, O(1) from the μ-bridging methoxy and O(3) from the μ_3-bridging oxo-group], resulting in *fac*-CrN_3O_3 chromophores. The Cr–N [average 2.13(3) Å] and Cr–O [average 1.94(1) Å] distances are comparable to literature values[55] for chromium(III) complexes with this macrocyclic amine. A deviation from the idealized octahedral geometry is found for the ligand L, the N–Cr–N angles ranging between 82.5 and 84°, whereas the O–Cr–O angles fall between 79.9 and 91.6°. The chromium ion is displaced by 0.079 Å from the mean basal plane comprising N(1)N(3)O(2)O(3) atoms toward the apical oxygen atom O(1) of the methoxy group.

The ligand L exhibits no unexpected features. Comparatively short C–C bond lengths [average 1.34(2) Å] between the methylene groups may be attributed to the effects of libration.

The 'body' manganese ions, Mn(1) and Mn(1a), are bridged by two oxo groups, O(3) and O(3a). Each Mn is co-ordinated to three oxygens [O(3), O(3a) and the phenolate O(4)], and imine nitrogen N(4) from an oxime in the basal plane. A methoxy oxygen O(1) occupies the fifth position and the sixth co-ordination position may be envisaged to be occupied by the water molecule O(w1) at a distance of 2.790 Å resulting in a very weak bonding between it and Mn(1). Probably this long $Mn–OH_2$ bonding is a consequence of the so-called 'magnetic Jahn-Teller effect' (see later). The Mn–O bond lengths fall in the range 1.857–1.877 Å and are considered as normal covalent bonds. The axial Mn(1)–O(1) bond is longer, 2.20 Å, as expected for tetragonally distorted Mn^{III}. Atom Mn(1) is 0.147 Å out of the best basal plane comprising N(4)O(4)O(3a)O(3) in the direction of the bridging methoxy oxygen O(1). The Mn–N and Mn–O bond distances are consistent with a d^4 high-spin electronic configuration for the manganese(III) centres.

The structural data concerning the salicylaldehyde oxime parts of the complex are in good agreement with previous studies[61] dealing with compounds of the same ligand and do not warrant comment.

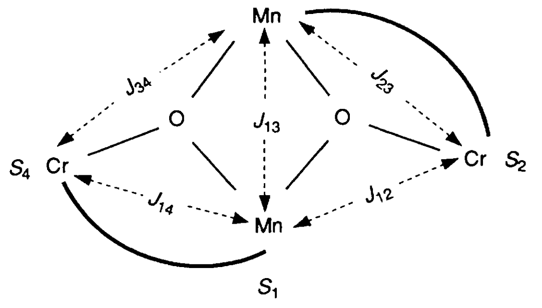
Magnetic Susceptibility.—Magnetic susceptibility data for polycrystalline samples of the complex were collected in the temperature range 4.3–278.5 K, and the data are displayed in Fig. 2. The molar paramagnetic susceptibility increases with decreasing temperature and reaches a maximum around ≈17 K, below which it starts to decrease. The effective magnetic moment μ_{eff} per $Cr^{III}{}_2Mn^{III}{}_2$ cluster decreases with decreasing temperature from 5.837 μ_B at 278.5 K to an essentially diamagnetic value of 0.935 μ_B at 4.3 K; the residual non-zero moment is mainly due to an amount of paramagnetic impurity ($S = \frac{4}{2}$). The shapes of both plots reveal a behaviour typical for antiparallel spin coupling. The data clearly indicate that this complex possesses a well separated electronic ground state with total spin $S_T = 0$. A ground state of zero net spin can be qualitatively rationalized in terms of an antiferromagnetic coupling of two $Cr^{III}Mn^{III}$ pairs ($S_{Cr} = \frac{3}{2}$, $S_{Mn} = \frac{4}{2}$). For a system of two chromium(III) and two high-spin manganese(III) ions disposed in a butterfly-type arrangement the overall spin degeneracy (400) is distributed over 60 spin states with S_T values ranging from 0 to 7.

The experimental magnetic data were simulated several times, in general with two different least-squares-fitting computer programs. (1) A full-matrix diagonalization approach including magnetic exchange coupling ($-2JS_iS_j$), Zeeman splitting and axial single-ion zero-field splitting ($DS_z{}^2$) of Mn^{III} ($S = 2$) was employed. After each diagonalization the energies (E_i) and magnetic moments [$\delta(E_i)/\delta(H)$] of each state were used to calculate the molar paramagnetic susceptibility as a function of temperature. (2) A theoretical expression for χ_M as a function of temperature was derived from the van Vleck susceptibility equation combined with the following Kambe vector-coupling scheme: $S_T = S_{Mn} + S_{Cr}$ where $S_{Mn} = S_{Mn(1)} + S_{Mn(3)}$ and $S_{Cr} = S_{Cr(2)} + S_{Cr(4)}$.

The main results of the different simulations are as follows.

(*a*) Under similar conditions, both fitting procedures yield, as expected, the same exchange coupling constants.

(*b*) Assuming the exchange interaction between the chromium(III) centres to be negligible, there are three exchange coupling constants, $J_{14} = J_{23}$, $J_{12} = J_{34}$ and J_{13}, as pictured in Scheme 2, where the arcs represent bridging methoxy groups. The three exchange coupling constants, g and P, *i.e.* the amount of paramagnetic impurity ($S = 2$), were allowed to vary independently in the full-matrix diagonalization program to optimize the agreement. A good fit was found with the following fit-parameters $J_{12} = J_{34} = -12.5$, $J_{14} = J_{23} = -12.0$, $J_{13} = -12.6$ cm^{-1}; $g = 1.71$, $P = 3.9\%$. This result clearly demonstrates that the two exchange coupling constants between the



Scheme 2

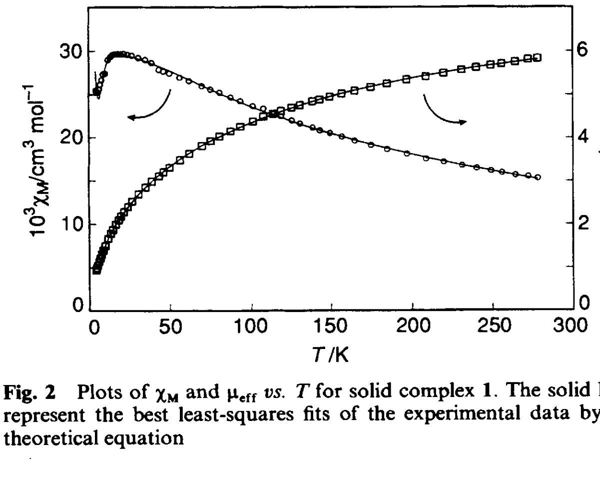


Fig. 2 Plots of χ_M and μ_{eff} *vs.* T for solid complex 1. The solid lines represent the best least-squares fits of the experimental data by the theoretical equation

chromium(III) and manganese(III) centres (*i.e.* $J_{14} = J_{23}$ and $J_{12} = J_{34}$) with and without the methoxide bridging are not significantly different. In other words, the coupling between the centres can reasonably be assumed to be equivalent for all four pairs, *i.e.* $J_{CrMn} = J_{12} = J_{23} = J_{34} = J_{14}$, regardless of the methoxide bridging and is designated as J_{CrMn} for the rest of the discussion. Thus two exchange coupling constants J_{CrMn} and J_{MnMn} ($=J_{13}$) can safely be used to describe the magnetic interactions for this heterotetranuclear butterfly core. A similar 'two-*J*' magnetic exchange model was applied previously to analyse the magnetic properties of several structurally related complexes $[Fe_4(\mu_3\text{-}O)_2]^{8+}$,[30,38] $[Mn_4(\mu_3\text{-}O)_2]^{8+}$ [33,40] and $[Cr_2Fe_2(\mu_3\text{-}O)_2]^{8+}$.[46]

(*c*) Fortunately, the values of J_{CrMn} and J_{MnMn} are not very dependent on the values of *D*, the axial zero-field splitting for Mn^{III}, but the quality of fit, particularly for the low-temperature data, is very much dependent on the use of *D* in the fitting procedure. Since from susceptibility data it is not possible to determine *D* values with accuracy, we neglected the zero-field splitting term in the best-fit plot shown in Fig. 2.

(*d*) The quality of the fit could always be improved by including a small amount of monomeric ($S = 2$) paramagnetic impurity.

(*e*) To fit particularly the low-temperature data, it was necessary to consider a constant θ in the van Vleck equation.

The best fits shown as the solid lines in Fig. 2 were obtained by using the van Vleck susceptibility equation combined with the Kambe vector coupling to calculate the theoretical values of χ_M. In this model the effects of nearest-neighbour isotropic spin–spin coupling are evaluated by using the Hamiltonian (1) where

$$H = -2J_{CrMn}(S_1 \cdot S_2 + S_2 \cdot S_3 + S_3 \cdot S_4 + S_4 \cdot S_1) - 2J_{MnMn}S_1 \cdot S_3 \quad (1)$$

$S_1 = S_3 = \frac{4}{2}$ and $S_2 = S_4 = \frac{3}{2}$. A correction for a small amount of paramagnetic impurity, $P(S = \frac{4}{2})$, was also taken into account by adding a Curie-law expression to the formula derived from the above Hamiltonian. The expression used was (2) where *P* is the amount of paramagnetic ($S = \frac{4}{2}$) impurity,

$$\chi_{calc}^{Cr_2Mn_2} = (1 - P)\left[\frac{C}{T - \theta} f(J_{CrMn}, J_{MnMn}, T)\right] + P\frac{C}{T} \quad (2)$$

$C = Ng^2\mu_B{}^2/k$ and $f(J_{CrMn}, J_{MnMn}, T)$ is derived from the theoretical equation. The experimental values of χ (and μ_{eff} per molecule) have been fitted by this equation, treating J_{CrMn}, J_{MnMn}, *g*, θ and *P* as adjustable parameters. The agreement between the calculated and observed magnetic susceptibilities is very good (Fig. 2) with a relative standard deviation $r = \{n^{-1}\Sigma[(\chi_{meas} - \chi_{calc})/\chi_{meas}]^2\}^{\frac{1}{2}}$ of 1.88%. The best-fit parameters obtained are $J_{CrMn} = -11.7$ cm^{-1}, $J_{MnMn} = -13.0$ cm^{-1}, $g = 1.71$, $\theta = -3.0$ K and $P = 3.74\%$. The fit confirms the observation of net antiferromagnetic coupling described before. The unusually low *g* value may result from the assumption that all of the spin states have the same *g* value. It is worth mentioning that low *g* values for similar complexes have been reported.[33,34a]

By using the spin-projection technique[24] the *g* tensor associated with different states can be related to local spins g_{Cr} and g_{Mn} and the values for some of the low-lying multiplets for the different states, labelled as $g_{S_T,S_{Cr},S_{Mn}}$, are $g_{|1,3,2>} = 2g_{Cr} - g_{Mn}$, $g_{|1,33>} = \frac{1}{2}g_{Cr} + \frac{1}{2}g_{Mn}$, $g_{|1,3,4>} = -\frac{3}{2}g_{Cr} + \frac{5}{2}g_{Mn}$ and $g_{|2,3,1>} = \frac{4}{3}g_{Cr} - \frac{1}{3}g_{Mn}$. To determine whether this fit is unique, a search in the form of a relative error surface for fitting the measured data by the theoretical expression was performed.

In Fig. 3 is shown a two-dimensional contour projection of the relative error surface for fitting the magnetic data of the complex as a function of both J_{MnMn} and J_{CrMn}. Only the region of smallest relative error is presented. It can be concluded that the above parameters do represent a well defined global minimum in the parameter space for this system, and allow us to estimate the error bars on the quoted J_{MnMn} and J_{CrMn} values as approximately ± 0.2 and ± 0.1 cm^{-1}, respectively.

Using the exchange coupling parameters J_{CrMn} and J_{MnMn} the energies of the low-energy states for the tetranuclear complex containing the $Cr^{III}{}_2Mn^{III}{}_2(\mu_3\text{-}O)_2$ core were calculated and are shown in Fig. 4. The energy of the ground state with $S_T = 0$, has arbitrarily been set at 0 cm^{-1}. The ground state is separated from the first excited state by an energy gap of 15.8 cm^{-1}. There are three spin states with $S_T = 1$ within 33.6 cm^{-1} of the ground state. The ground state with $S_T = 0$ results from spin frustration in a broad sense. The term 'spin frustration' describes an effect where the interplay of various exchange interactions in a

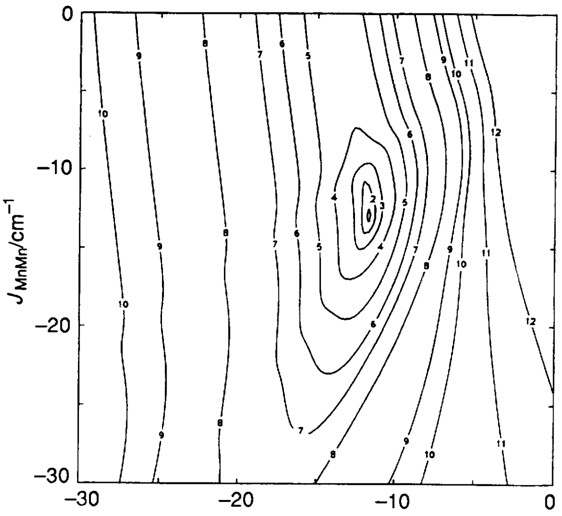


Fig. 3 Best-fit contour maps as functions of J_{CrMn} and J_{MnMn} for complex **1**

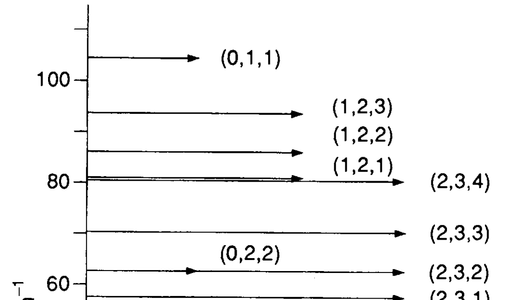


Fig. 4 Energy diagram of the low-energy states for complex **1**. The energy of the ground state $S_T = 0$ has arbitrarily been set at 0 cm^{-1}. The numbers in parentheses indicate the values of S_T, S_{Cr} and S_{Mn} for each state [$S_{Cr} = S_{Cr(2)} + S_{Cr(4)}$, $S_{Mn} = S_{Mn(1)} + S_{Mn(3)}$]; $J_{MnMn} = -13.0$, $J_{CrMn} = -11.7$ cm^{-1}

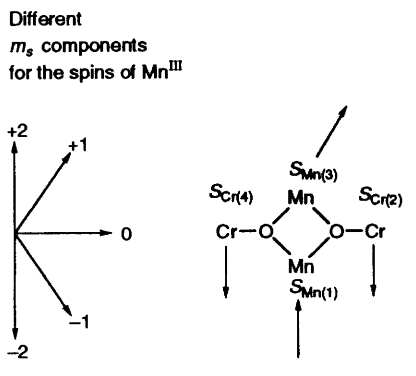
polynuclear complex causes a net spin-vector alignment which is different from that expected upon consideration of pairwise exchange interactions. It has been shown in detail by Hendrickson and co-workers[21,33,38,40] that in the case of spin frustration very subtle changes in the ratios of competing exchange interactions in a polynuclear transition-metal complex can have dramatic effects on the exact nature of the ground and low-lying spin states. It is the ratio of competing coupling pathways and not so much their absolute magnitude which characterizes the electronic structure of these complexes. Although the antiferromagnetic exchange interactions J_{CrMn} and J_{MnMn} in the present complex are greater than the corresponding exchange interactions J_{CrFe} and J_{FeFe} in the isostructural $[\mathrm{Cr^{III}{}_2Fe^{III}{}_2(\mu_3\text{-}O)_2}]^{8+}$ core with a ground state of $S_{\mathrm{T}} \neq 0$, described earlier,[46] the ratio $J_{\mathrm{CrMn}}/J_{\mathrm{MnMn}}$ in the present complex of 0.9:1 is smaller than $J_{\mathrm{CrFe}}/J_{\mathrm{FeFe}}$ of 1.42:1. The ground state of the present complex represents the smallest spin state possible for this electronic d^n configuration when both interactions are antiferromagnetic. This result is in accord with the analysis made by Hendrickson that, when competing exchange pathways are antiferromagnetic and are of similar magnitude, the complex will have a ground state with the smallest possible S_{T} value. The antiferromagnetic Cr ··· Mn and Mn ··· Mn interactions are of similar magnitude, -11.7 ± 0.1 cm^{-1} and -13.0 ± 0.2 cm^{-1}, respectively.

The ground state $S_{\mathrm{T}} = 0$ has component S_{Cr} and S_{Mn} values of 3 and 3, respectively. These values result from the different relative orientations of $S_{\mathrm{Cr(2)}}$, $S_{\mathrm{Cr(4)}}$, $S_{\mathrm{Mn(1)}}$ and $S_{\mathrm{Mn(3)}}$, which is represented in Scheme 3 as an overall spin alignment. On comparing the exchange coupling parameters between complex **1**, $[\mathrm{Cr^{III}{}_2Mn^{III}{}_2O_2}]^{8+}$, and the two other magnetically characterized examples of the $[\mathrm{Mn^{III}{}_2Mn^{III}{}_2O_2}]^{8+}$ cores,[33,40] we note that there is a factor of nearly two in the coupling between the two central di-μ-oxo-bridged manganese(III) ions in these hetero- and homo-tetranuclear complexes with $J_{\mathrm{MnMn}} = -13.0$ cm^{-1} for the $\mathrm{Cr_2Mn_2}$ complex and -23.5 and -24.6 cm^{-1} for the $\mathrm{Mn_2Mn_2}$ complexes with Mn–O–Mn angles of 94 and ≈96°, respectively. This difference in angles is manifested also, as expected, in the metal–metal separation. The Mn ··· Mn separation is remarkably shorter in **1**, 2.74 Å, than in the $\mathrm{Mn_4}$ complexes, ≈2.84 Å.

In the following we provide a qualitative rationale for the trend and nature of the magnetic interactions between the 'body' spin carriers, the central $\mathrm{Mn_2O_2}$ unit, in the isostructural $[\mathrm{Cr^{III}{}_2Mn^{III}{}_2O_2}]^{8+}$ and $[\mathrm{Mn^{III}{}_2Mn^{III}{}_2O_2}]^{8+}$ [33,40] complexes in the framework of the Goodenough–Kanamori rules for magnetic superexchange as elegantly and clearly outlined in Ginsberg's review.[62]

The sign of the intramolecular exchange coupling constant results from the sum of antiferromagnetic and ferromagnetic contributions given in equation (3). The structures of the central $\mathrm{Mn_2O_2}$ units in all three complexes may be described as resulting from two octahedrally co-ordinated manganese(III) ions sharing an edge comprised of two μ-oxo ligands. The manganese(III) centres (high spin, d^4) are tetragonally distorted, the electronic configurations of the localized metal orbitals being $(d_{yz},d_{xz})^2$, $(d_{xy})^1$, $(d_{z^2})^1$, $(d_{x^2-y^2})^0$ in order of increasing energy. It is then obvious that the interactions between the $(d_{yz},d_{xz})^2$ orbitals of the two manganese(III) ions and the orbitals of the bridging oxygen atoms provide the antiferromagnetic π pathways; similarly, antiferromagnetic σ pathways are available between the $(d_{xy})^1$ pairs *via* s and p orbitals of oxygen. The path $d_{z^2}|d_{z^2}$ involves orbitals weakly delocalized in the molecular plane, so its contribution is expected to be rather weak irrespective of its magnetic nature, with the Mn–O overlap being of the σ type. As the Mn–O–Mn angle is close to 90°, d_{z^2} electrons interact *via* a ferromagnetic pathway involving an orthogonality at the bridging oxygen atom. A weakly negative, J, *i.e.* a net antiferromagnetic interaction, is expected and is also observed (see above). The smaller Mn–O–Mn angle in **1** than that in the $\mathrm{Mn_4}$ complexes leads to stronger ferromagnetic interactions through the $d_{z^2}|d_{z^2}$ path resulting in a net weaker antiferromagnetic interaction in **1** than that in the $\mathrm{Mn_4}$ complexes [equation (3)]. This picture is consistent with the predictions made by Kahn[25] for dinuclear complexes.

$$J = J_{\mathrm{AF}} + J_{\mathrm{F}} \qquad (3)$$



Scheme 3

The most salient feature of the present work is the synthesis of a heterotetranuclear complex containing the butterfly core $[\mathrm{Cr^{III}{}_2Mn^{III}{}_2(\mu_3\text{-}O)_2}]^{8+}$ which is isostructural, but not isoelectronic, with a similar $[\mathrm{Cr^{III}{}_2Fe^{III}{}_2(\mu_3\text{-}O)_2}]^{8+}$ core. It seems that a 'two-J' model is sufficient to describe the magnetic properties of this core. The ground state for complex **1** is $S_{\mathrm{T}} = 0$ which results from the coupling of $S_{\mathrm{Cr}} = 3$ and $S_{\mathrm{Mn}} = 3$ due to spin frustration in a wider sense of the term. In contrast to the present complex, the ground state of $[\mathrm{Cr^{III}{}_2Fe^{III}{}_2(\mu_3\text{-}O)_2}]^{8+}$ is non-diamagnetic ($S_{\mathrm{T}} \neq 0$) and the low-lying magnetic states are very complicated.

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