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Oxo-centred trinuclear acetate complexes containing mixed-metal clusters. Crystal structure of a chromium(III)iron(III)nickel(II) complex and magnetic properties of a dichromium(III)magnesium(II) complex ‡

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The crystal structure of $[Cr^{III}_{x}Fe^{III}_{2-x}Ni^{II}O(O_2CCH_3)_6(py)_3]\cdot py$ **1** ($x = ca.$ 0.7, py = pyridine), has been determined at 25 °C. Although the molecule has no crystallographically imposed symmetry, the metal atoms form an almost equilateral triangle, M · · · M 3.274(3), 3.284(4), 3.281(3) Å, with the O atom less than 0.006 Å from the M_3 plane, and the Cr, Fe, and Ni atoms extensively disordered over the three metal sites. The corresponding Cr_2Mg, Cr_2Ni, and Fe_2Ni complexes are isomorphous with **1**. The structure differs from that of the rhombohedral $Fe^{III}_2M^{II}$ (M^{II} = Mn, Fe, Co or Zn) and $Cr^{III}_2M^{II}$ (M^{II} = Mn, Fe or Co) analogues in the orientations of the pyridine rings. The planes of the pyridine ligands in **1** are approximately perpendicular to the M_3 plane, and the non-co-ordinated pyridine molecule lies approximately in this plane. (This contrasts with the rhombohedral complexes, where the ligand pyridine rings are approximately parallel with the M_3 plane and the non-co-ordinated pyridine lies with its plane on the three-fold axis of the M_3O system.) The magnetic susceptibility of $[Cr^{III}_2MgO(O_2CCH_3)_6(py)_3]\cdot py$ has been measured between 5 and 300 K, and fitted by use of an exchange hamiltonian $-2J\boldsymbol{S}_1\cdot\boldsymbol{S}_2$, giving $J_{CrCr} = -17\ cm^{-1}$, a value considerably smaller than that ($ca.$ $-26\ cm^{-1}$) of the Cr_2Ni and Cr_2Co analogues.

In a study some years ago of the magnetic properties of the mixed-metal trinuclear complexes $[Cr^{III}_2M^{II}O(O_2CCH_3)_6(py)_3]\cdot py$ and the analogous $Fe^{III}_2M^{II}$ and $Cr^{III}Fe^{III}M^{II}$ complexes (M^{II} = Mg, Mn, Fe, Co, Ni, or Zn; py = pyridine)[1] we noted that they fall crystallographically into two groups. The majority crystallise in the rhombohedral (trigonal) space group $R32$, with the central O atom necessarily on a site of three-fold symmetry. They are isomorphous with the mixed-valence $Mn^{III}_2Mn^{II}$ and $Fe^{III}_2Fe^{II}$ complexes, the crystal structures of which are known,[2,3a,b] and the crystal structures of three of these mixed-metal rhombohedral complexes, $[M_2CoO(O_2CCH_3)_6(py)_3]\cdot py$ (M = Mn,[4] Fe[3b] or Ru[3c]), have been reported. However, the Cr_2Mg, Cr_2Ni, CrFeNi, and Fe_2Ni complexes, which are also isomorphous, do not conform to this trigonal class, but crystallise with a monoclinic unit cell, space group Cc or $C2/c$.

We were intrigued by this difference, arising from a seemingly minor change at the atomic level. Further, our interpretation of the magnetic properties, in particular the unexpected effect of the divalent metal on the exchange interaction between the trivalent metal ions, was hampered by the absence of detailed information about the metal–oxygen bond lengths and angles. In the rhombohedral compounds it is obvious that the metal ions must be randomly distributed over the three equivalent metal sites in the molecule, and hence the individual co-ordination environments of the tri- and di-valent metals cannot be revealed by X-ray crystallography. Recently, extended X-ray absorption-edge fine-structure spectroscopy (EXAFS), an element-specific technique that does not depend on crystallographic order, has been successfully used to obtain limited information about the individual metal co-ordination environments in the rhombohedral $Cr^{III}_2Co^{II}$ complex, throwing some light on the magnetic properties, but the precision of the distances and angles obtained is considerably lower than that achievable by crystallography.[5] It seemed possible that in the monoclinic compounds the lower molecular symmetry (at most a mirror plane or two-fold axis) might reflect an ordered arrangement of the $M^{III}_2M^{II}$ triangles, which would permit a full crystallographic determination of the environments of the individual metal ions in these molecules. Our belief in this possibility was encouraged by the case of some monoclinic $Fe^{III}_2Fe^{II}$ complexes with substituted pyridine ligands, where the Fe–O bond lengths indicated a substantial degree of order in the di- and tri-valent ion positions.[6]

We have now determined the crystal structure of the monoclinic complex $[Cr^{III}_{x}Fe^{III}_{2-x}Ni^{II}O(O_2CCH_3)_6(py)_3]\cdot py$ **1** ($x = ca.$ 0.7). Unfortunately, we find no evidence for an ordered distribution of the different metal ions among the three metal sites in this molecule. The crucial difference between the monoclinic and the rhombohedral compounds turns out to be in the orientations of the pyridine ligands. The structure is reported below.

Our magnetic investigation of the mixed-metal $Fe^{III}_2M^{II}$ (M = Mg, Mn, Co, or Ni) and $Cr^{III}_2M^{II}$ (M = Co or Ni) complexes revealed a remarkable increase in the strength of the superexchange interaction between the two trivalent ions compared with that in the Fe^{III}_3 or Cr^{III}_3 complex.[1] Data for the complex $[Cr^{III}_2MgO(O_2CCH_3)_6(py)_3]\cdot py$ **2**, where the interpretation is particularly simple because only one exchange parameter is involved, were unfortunately not available at that time. We have now measured the magnetic susceptibility of this compound between 5 and 300 K, and the results, also reported below, turn out to deviate significantly from the above generalisation.

Experimental

The compounds were obtained as well formed single crystals in the manner described previously.[1]

Chemical analysis

Carbon, H, and N were determined by commercial microanalysis, Cr by oxidation to dichromate(VI) and titration against

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‡ *Non-SI unit employed*: $\mu_B \approx 9.27 \times 10^{-24}\ J\ T^{-1}$.

iron(II), and Mg by atomic absorption spectrometry {Found: C, 45.1; H, 4.52; Cr, 4.3; N, 6.6. $[Cr_{0.7}Fe_{1.3}NiO(O_2CCH_3)_6(py)_3]\cdot py$ **1** requires C, 45.0; H, 4.48; Cr, 4.3; N, 6.6. Found: C, 47.4; H, 4.74; Cr, 12.9; Mg, 3.2; N, 6.95. $[Cr_2MgO(O_2CCH_3)_6(py)_3]\cdot py$ **2** requires C, 47.2; H, 4.70; Cr, 12.8; Mg, 2.6; N, 6.9%}.

Crystallography

All measurements on complex **1** were made as previously described,[7] using a Rigaku AFC6S diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71069 Å) on a prismatic crystal having approximate dimensions 0.40 × 0.30 × 0.25 mm. Cell constants and an orientation matrix were obtained from a least-squares refinement based on the setting angles of 25 carefully centred reflections in the range $18.4 < 2\theta < 28.9°$. Reflection intensity data were collected at 22 °C by the ω–2θ scan technique. Scans of angular width $(1.63 + 0.30\tan\theta)°$ were made at 8.0° min^{-1} (in ω), together with stationary background counts on each side of the reflection. Of the 5571 reflections collected, 5141 were unique ($R_{int} = 0.040$), and of these, 3242 had $F_o^2 > 3\sigma(F_o^2)$, where σ was estimated from counting statistics.[8] Lorentz-polarisation corrections were applied. An empirical absorption correction, based on azimuthal scans of several reflections, was applied. The resulting transmission factors ranged from 0.82 to 1.18. The intensities of three standard reflections measured at 150 reflection intervals showed no greater fluctuations than those expected from Poisson statistics.

Crystal data. $C_{32}H_{38}CrFeN_4NiO_{13}$, $M_r = 853.2$, purple-black crystals from pyridine, monoclinic, $a = 21.951(4)$, $b = 12.466(3)$, $c = 15.923(5)$ Å, $\beta = 117.02(2)°$, $U = 3881(3)$ Å^3, $Z = 4$, $D_c = 1.46$ g cm^{-3}, space group *Cc* or *C*2/*c* from systematic absences. The non-centric space group *Cc* (no. 9) was established from the Patterson synthesis, packing considerations, and intensity statistics, and confirmed by successful refinement. (The extra vectors expected in the Patterson synthesis if the space group was *C*2/*c* rather than *Cc* were absent. Moreover, the automatic structure solution packages we tried failed to find a solution in *C*2/*c*, and we were unable to find a model that would refine in the latter space group.)

Structure solution and refinement. The metal positions were determined from a three-dimensional Patterson synthesis based on all data, and all other atoms from Fourier-difference maps. Full-matrix least-squares refinement, carried out using the TEXRAY program set,[9] converged to give agreement indices $R = 0.037$, $R' = 0.037$ for the enantiomorph shown, where $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{\frac{1}{2}}$. The function minimised was $\Sigma w(|F_o| - |F_c|)^2$, where $w = 4F_o^2/\sigma^2(F_o^2)$ and $\sigma^2(F_o^2) = [S^2(C + R^2B) + (pF_o^2)^2]/L_p^2$, S, C, R, and B are, respectively, the scan rate, total integrated peak count, ratio of scan time to background counting time, and total background count; L_p is the Lorentz-polarisation factor and the factor $p = 0.02$ is introduced to reduce the weighting of the most intense reflections. For the other enantiomorph, agreement was slightly poorer, $R = 0.040$. The standard deviation of an observation of unit weight, $[\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{var})]^{\frac{1}{2}}$, where N_{obs} = number of observations, N_{var} = number of variables, was 1.68. The non-hydrogen atoms were refined anisotropically, and in the absence of information about the distribution of the Cr, Fe, and Ni atoms among the metal sites all three were treated as Fe^{3+}. The N atom of the solvate pyridine molecule was apparently disordered over the six ring positions, and this molecule was modelled as benzene with an occupancy factor of 5/6 for the H atoms. Plots of $\Sigma w(|F_o| - |F_c|)^2$ against $|F_o|$, reflection order in data collection, $(\sin\theta)/\lambda$, and various classes of indices, showed no unusual trends. Neutral atom scattering factors were taken from Cromer and Waber.[10] Anomalous dispersion effects[11] were included in F_c, the values for $\Delta f'$ and $\Delta f''$ being those of Cromer.[12]

CCDC reference number 186/727.

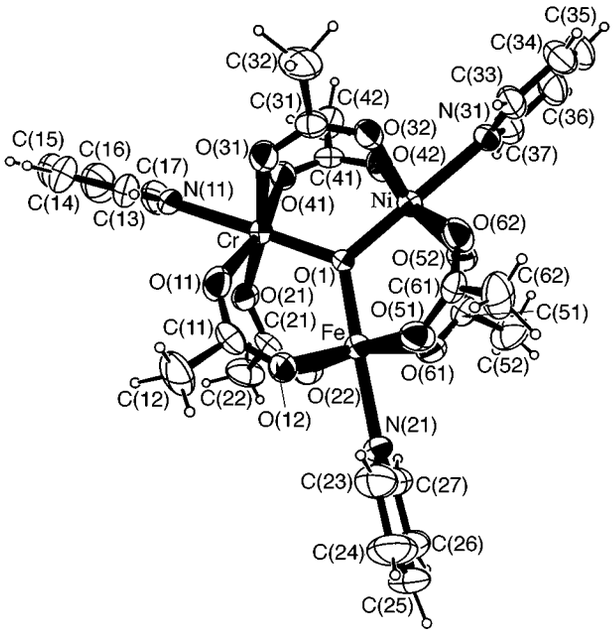

Fig. 1 View of the molecule $[CrFeNiO(O_2CCH_3)_6(py)_3]$ **1**. In practice, the Cr, Fe, and Ni atoms should be regarded as distributed randomly over the positions shown, with disordered Cr_2Ni and Fe_2Ni species also present, as discussed in the text

Magnetic measurements on complex 2

The sample was ground in air and placed in a gelatin capsule, and its susceptibility measured between 5 and 300 K in a field of 1 T with a SQUID magnetometer (Quantum Design model MPMS). The data were corrected for sample diamagnetism by use of Pascal constants, and for diamagnetism of the sample container.

Results and Discussion

Crystal structure of $[Cr^{III}_xFe^{III}_{2-x}Ni^{II}O(O_2CCH_3)_6(py)_3]\cdot py$ 1 (*x* = *ca.* 0.7)

The method of preparation of complex **1**, reaction of 1 mol $[Cr^{II}_2(O_2CCH_3)_4(H_2O)_2]$ with 1 mol $[Fe^{III}_2Ni^{II}O(O_2CCH_3)_6(py)_3]$ in pyridine in the presence of air,[1] does not precisely determine the ratio of Cr^{III} to Fe^{III} in the product. It is likely that a continuous range of compositions is possible between the limits $Cr^{III}_2Ni^{II}$ and $Fe^{III}_2Ni^{II}$, and that any intermediate product of composition $Cr^{III}_xFe^{III}_{2-x}Ni^{II}$ will contain proportions of molecules of the limiting types as well as of the mixed type $Cr^{III}Fe^{III}Ni^{II}$. The presence of the latter is manifested unequivocally by the appearance of a purple colour, quite distinct from the green and olive green of the respective limiting forms, as first suggested by Weinland and Gussmann,[13] and discussed more fully elsewhere.[1] Chromium analysis showed that the Cr : Fe ratio was actually 0.7 : 1.3 in the purple-black crystalline product **1**. In a statistical distribution this would correspond to a sample containing the Cr_2Ni, CrFeNi, and Fe_2Ni complexes in the molar proportions 1 : 3.7 : 3.5.

Fig. 1 is an ORTEP[14] diagram of the trinuclear complex with the atom numbering scheme, and Fig. 2 shows the arrangement of the molecules, including the unco-ordinated pyridine, in the unit cell. Selected bond lengths and angles are given in Table 1.

In space group *Cc* the molecule has no crystallographically imposed symmetry. A careful inspection of the electron-density distribution, bond lengths, and atomic vibrational parameters at the three metal sites does not show any definite evidence for

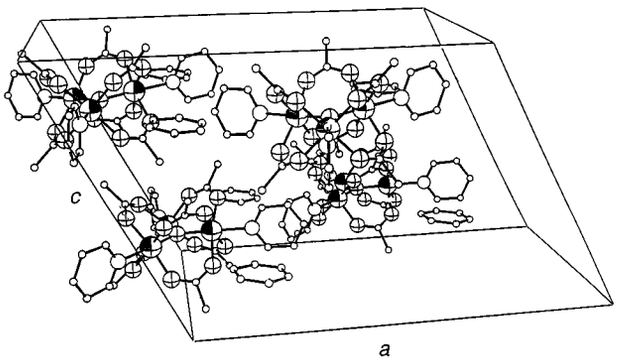

Fig. 2 Unit cell of complex **1**

localisation of the Ni^{2+} ion in a particular metal site. Although atom M(1) has slightly longer M–O bonds (mean 2.008 Å) than those of M(2) and M(3) (means 1.990, 1.993 Å), which may indicate some preference for this site to be occupied by the larger Ni^{2+} ion, the difference of *ca.* 0.017 Å is considerably less than would be expected in a fully ordered structure: Ni^{II}–O bonds are typically *ca.* 0.1 Å longer than Cr^{III}–O or Fe^{III}–O bonds, and in the $Cr^{III}_2Co^{II}$ complex studied by EXAFS a difference of *ca.* 0.1 Å between the Cr^{III}–O and Co^{II}–O distances was found.[5] In the largely valence-localised monoclinic complex $[Fe^{III}_2Fe^{II}O(O_2CCH_3)_6L_3]L$ (L = 4-ethylpyridine) a difference of 0.074 Å between the longer and shorter Fe–μ_3-O bond lengths was found.[6] Moreover, the three M–N bonds in **1** are essentially equal. Differences between the Cr^{3+} and Fe^{3+} ions would be even smaller, and in the absence of any indication to the contrary we assume that these are also distributed randomly. On the balance of evidence, we feel that any metal ion localisation in compound **1** is too small for the observed bond lengths and angles to be used in a meaningful discussion of the individual metal co-ordination geometries.

Unpublished determinations of the crystal structures of the Cr^{III}_2Mg and $Cr^{III}_2Ni^{II}$ complexes, which have the same crystal structure as that of **1**, indicate that in these also there is extensive disorder in the distribution of the metal atoms over the three sites.[15]

The overall structure of the complex is similar to that in other oxo-centred trinuclear carboxylates, with the μ_3-O atom at the centre of an almost equilateral triangle of metal atoms, and we shall not discuss the details except to note that the M–μ_3-O bond lengths are towards the low end of the range (1.89–1.95 Å) observed in compounds of this general type.[2–6,15–20]

The main feature of the structure that distinguishes the monoclinic compound **1** and the isomorphous Cr_2Mg, Cr_2Ni, and Fe_2Ni complexes from the other complexes concerns the orientation of the pyridine molecules. The planes of the pyridine ligands in **1** are approximately perpendicular to the M_3O plane (dihedral angles 82.0, 83.3 and 90.0°), while the non-co-ordinated pyridine molecule has its plane approximately parallel and nearly coincident with the M_3O plane (dihedral angle 13.6°). The orientations of the ligand and unco-ordinated pyridine molecules in the Cr_2Mg and Cr_2Ni complexes are closely similar to those in **1**.[15] This is in direct contrast with the structure found in all those complexes which crystallise in the trigonal space group *R*32 (mixed-valence $V^{III}_2V^{II}$,[16] $Cr^{III}_2Cr^{II}$,[17] $Mn^{III}_2Mn^{II}$,[2] and $Fe^{III}_2Fe^{II}$ complexes,[2,3a] the $Fe^{III}_2Co^{II}$,[3b] $Ru^{III}_2Co^{II}$,[3c] and $Mn^{III}_2Co^{II}$ complexes,[4] and presumably all the other mixed-metal complexes that are isomorphous with these,[1] including Fe^{III}_2Mg). In those compounds the ligand pyridine rings lie very nearly parallel with the M_3O plane, and the non-co-ordinated pyridine molecule lies with its plane perpendicular to the M_3O plane, along the three-fold axis (and disordered about this axis).

An approximately perpendicular orientation of the terminal ligands with respect to the M_3O plane has also been observed in $[Cr^{III}_3O(O_2CC_6H_5)_6(py)_3]ClO_4$,[18] and in two complexes containing a substituted pyridine ligand, $[Fe^{III}_2Fe^{II}O(O_2CCH_3)_6(NC_5H_4CH_3\text{-}3)_3]\cdot$solv (where solv = 3-methylpyridine or toluene).[6] In the 4-ethylpyridine $Fe^{III}_2Fe^{II}$ complex,[19] and in the valence-localised complex $[Mn^{III}_2Mn^{II}O(O_2CCH_3)_6(NC_5H_4Cl\text{-}3)_3]$,[20] two of the ligands are approximately perpendicular to the M_3O plane and the third is parallel with it.

Apart from the complexes containing a substituted pyridine ligand, where molecular packing effects may be expected to influence the ligand orientations, the tendency for a complex of the type $[M_3O(O_2CCH_3)_6(py)_3]\cdot$py to adopt the rhombohedral (*R*32) or monoclinic (*Cc*) structure, each with a different orientation of the pyridine molecules, must be determined by rather subtle forces arising within the M_3O cluster. Dimorphism has not been observed: it seems that the complex always adopts either the one structure or the other, depending on the nature of the metals. Only the presence of nickel (and, to a lesser extent, magnesium) in the cluster appears to favour the perpendicular orientation of the pyridine ligands, all other metals giving the parallel orientation. The effect may possibly be related to the fact that Ni^{2+} has the smallest radius of the divalent metal ions studied (Mg^{2+} having the second smallest), although all of the divalent ions are, of course, larger than Cr^{3+} or Fe^{3+}.[21]

Table 1 Selected interatomic distances (Å) and angles (°) in compound **1**

M(1)···M(2)	3.274(3)	M(2)–O(22)	2.011(5)
M(2)···M(3)	3.281(3)	M(2)–O(51)	2.026(5)
M(3)···M(1)	3.284(4)	M(2)–O(61)	2.021(5)
M(1)–O(1)	1.908(4)	M(2)–N(21)	2.189(6)
M(1)–O(11)	2.024(5)	M(3)–O(1)	1.893(4)
M(1)–O(21)	2.034(5)	M(3)–O(32)	2.019(5)
M(1)–O(31)	2.040(5)	M(3)–O(42)	2.009(5)
M(1)–O(41)	2.036(5)	M(3)–O(52)	2.027(5)
M(1)–N(11)	2.184(6)	M(3)–O(62)	2.018(5)
M(2)–O(1)	1.880(4)	M(3)–N(31)	2.180(6)
M(2)–O(12)	2.011(5)		
M(1)–O(1)–M(2)	119.7(2)	O(1)–M(2)–O(22)	95.7(2)
M(2)–O(1)–M(3)	120.8(2)	O(1)–M(2)–O(51)	95.8(2)
M(3)–O(1)–M(1)	119.5(2)	O(1)–M(2)–O(61)	94.2(2)
O(1)–M(1)–O(11)	96.8(2)	O(1)–M(2)–N(21)	177.9(2)
O(1)–M(1)–O(21)	92.8(2)	O(1)–M(3)–O(32)	94.7(2)
O(1)–M(1)–O(31)	95.9(2)	O(1)–M(3)–O(42)	95.9(2)
O(1)–M(1)–O(41)	96.2(2)	O(1)–M(3)–O(52)	96.4(2)
O(1)–M(1)–N(11)	177.4(2)	O(1)–M(3)–O(62)	94.8(2)
O(1)–M(2)–O(12)	98.0(2)	O(1)–M(3)–N(31)	178.8(2)

Magnetic properties of $[Cr^{III}_2MgO(O_2CCH_3)_6(py)_3]\cdot$py 2

The molar magnetic susceptibility $\chi_m(Cr_2Mg)$ of the complex was calculated by the matrix method[22] from the Hamiltonian (1), where $S_1 = S_2 = \frac{3}{2}$. Allowance was made in equation (2) for

$$\mathscr{H} = -2J\boldsymbol{S}_1\cdot\boldsymbol{S}_2 + g\mu_B(\boldsymbol{S}_1 + \boldsymbol{S}_2)\cdot\boldsymbol{H} \quad (1)$$

$$\chi_m = (1 - \rho)\chi_m(Cr_2Mg) + \rho(2N_Ag^2\mu_B^2/3kT)(15/4) \quad (2)$$

the presence of a fraction ρ of the Cr^{3+} in monomeric form (assumed to behave as a simple paramagnet). The calculated susceptibility was then fitted by least squares to the experimental data by the Simplex method,[23] minimising the function R^2, equation (3). Fig. 3 shows the agreement between the cal-

$$R^2 = \Sigma[(\chi_m)_{obs} - (\chi_m)_{calc}]^2/\Sigma[(\chi_m)_{obs}]^2 \quad (3)$$

culated and observed values of the molar magnetic susceptibility and the effective magnetic moment per molecule, $\mu/\mu_B = [(3k/N_A\mu_B^2)(\chi_mT)]^{\frac{1}{2}}$.

The magnetic moment of a pair of exchange-coupled Cr^{3+}

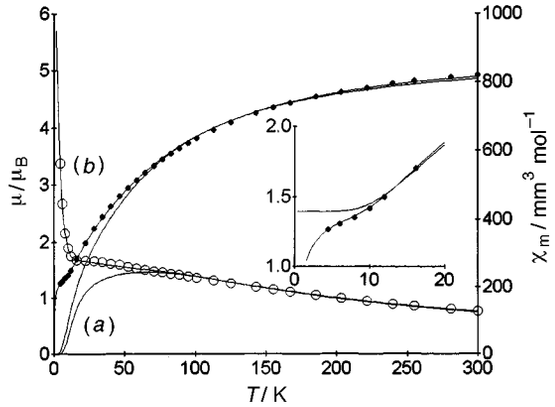

Fig. 3 Magnetic moment (solid circles and left-hand axis) and molar magnetic susceptibility (open circles and right-hand axis) of compound **2**. Curves: (*a*) fitted to data above 50 K with $J = -14$ cm^{-1}, (*b*) fitted to the full data set with $J = -17$ cm^{-1}, $\rho = 0.073$, and $\theta = -1.6$ K, calculated as described in the text. Inset: the effect of including (lower curve) the Weiss constant θ in the paramagnetic impurity correction

Table 2 Values of the exchange parameter $J(M^{III}–M^{III})$ in trinuclear oxoacetate complexes $[M^{III}_3O(O_2CCH_3)_6(H_2O)_3]^+$ and $[M^{III}_2M^{II}O(O_2CCH_3)_6(py)_3]$

Exchange cluster	$-J$/cm^{-1}	Ref.
$Fe^{III}_2O–Fe^{III}$	30 ± 3	24, 25
$Fe^{III}_2O–Mn^{II}$	64 ± 3	1
$Fe^{III}_2O–Ni^{II}$	73 ± 3	1
$Fe^{III}_2O–Mg^{II}$	62 ± 3	1
$Cr^{III}_2O–Cr^{III}$	11 ± 1.5	24, 26
$Cr^{III}_2O–Co^{II}$	27 ± 2	1
$Cr^{III}_2O–Ni^{II}$	26 ± 1	1
$Cr^{III}_2O–Mg^{II}$	17 ± 1	This work

ions with negative J would be expected to vanish as the temperature approached zero. Fitting only the data above 50 K and making no allowance for paramagnetic impurity, we obtained a calculated curve of the expected type, with $g = 1.94$ and $J = -14$ cm^{-1} (-15 cm^{-1} if the value of g is fixed at 1.98). However, it is evident that the experimental susceptibility below about 20 K is dominated by the impurity contribution, and use of the whole data set with allowance for this factor gave a greatly improved fit, with $g = 2.00$, $J = -17$ cm^{-1}, and $\rho = 0.06$. As shown in Fig. 3 (inset), when the impurity is assumed to be paramagnetic the calculated moment levels off to a value of $1.4\mu_B$ at low temperature. An improved fit to the data below 10 K can be obtained by introducing a small Weiss constant (*i.e.* replacing T by $T - \theta$) in the impurity contribution to equation (2), suggesting that the impurity is weakly antiferromagnetic. The best fit had $g = 1.988$, $J = -17.1$ cm^{-1}, $\rho = 0.073$, and $\theta = -1.6$ K, with $R = 0.011$.

The rather large value of ρ is somewhat perplexing, since the sample was of good crystallinity and gave satisfactory chemical analysis. It is conceivable that the impurity might be the $Cr^{III}_2Cr^{II}$ analogue, which could have a ground-state spin of either 2 or 5, depending on the exchange parameters, and would be scarcely detectable by chemical analysis. Whatever the significance of ρ might be, however, it does not greatly affect the estimation of J.

In previous work we have drawn attention to the increase in magnitude of the coupling constants J_{FeFe} and J_{CrCr} in the Fe^{III}_3 and Cr^{III}_3 oxoacetate complexes by a factor of *ca.* 2.3 when one of the trivalent ions is replaced by a divalent ion, as in the Fe_2Mn, Fe_2Ni, Fe_2Mg, Cr_2Co, and Cr_2Ni, complexes, Table 2.[1] We regard the magnitude of this effect as evidence that the central O atom provides the main pathway for superexchange, and have argued that the increase in J must be due at least partly to polarisation of the electron cloud at the central O atom due to the asymmetric charge distribution in the trinuclear cluster.[1,5] The value of -17 cm^{-1} for J in the Cr_2Mg complex is, however, much lower than that of *ca.* -26 cm^{-1} that would be expected by comparison with the other compounds, if the main factor at work is simply the charge on the Mg^{2+} ion. It is possible that differences in bond lengths or angles play a particularly important role in determining the value of J in this case, but we can at present see no reason why the Cr–O bond lengths and angles in the Cr_2Mg complex should be significantly different from those in the Cr_2Co and Cr_2Ni complexes (bearing in mind that the radius[21] of Mg^{2+} is considered to lie between those of Co^{2+} and Ni^{2+}), especially in view of the similarity in J values shown by the Fe_2Mg and Fe_2Ni complexes. Further investigation, perhaps by EXAFS measurements, may be necessary to resolve this question.

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