

Magnetic and Spectroscopic Properties of Some Heterotrinnuclear Basic Acetates of Chromium(III), Iron(III), and Divalent Metal Ions†

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Reaction of Fe^{3+} , M^{2+} , and acetate ions in aqueous solution gives $[\text{Fe}^{\text{III}}_2\text{M}^{\text{II}}\text{O}(\text{MeCO}_2)_6(\text{H}_2\text{O})_3] \cdot 3\text{H}_2\text{O}$ ($\text{M} = \text{Mg, Mn, Co, Ni, or Zn}$), which on crystallisation from pyridine (py) is converted into $[\text{Fe}^{\text{III}}_2\text{M}^{\text{II}}\text{O}(\text{MeCO}_2)_6(\text{py})_3]$. Reaction of chromium(III) acetate with metal(II) acetate in pyridine in the presence of air gives $[\text{Cr}^{\text{III}}_2\text{M}^{\text{II}}\text{O}(\text{MeCO}_2)_6(\text{py})_3]$ ($\text{M} = \text{Mg, Co, or Ni}$), and with $[\text{Fe}^{\text{III}}_2\text{M}^{\text{II}}\text{O}(\text{MeCO}_2)_6(\text{py})_3]$ in pyridine in the absence of air gives $[\text{Cr}^{\text{III}}\text{Fe}^{\text{III}}\text{M}^{\text{II}}\text{O}(\text{MeCO}_2)_6(\text{py})_3]$ ($\text{M} = \text{Mn or Fe}$) and $[\text{Cr}^{\text{III}}_2\text{Fe}^{\text{II}}\text{O}(\text{MeCO}_2)_6(\text{py})_3]$. The compounds with co-ordinated pyridine have been examined crystallographically and magnetically. The Cr_2Mg , Cr_2Ni , Fe_2Ni , and CrFeNi compounds crystallise in the monoclinic system, space group Cc or $C2/c$, $Z = 4$, but the other seven compounds are rhombohedral and isomorphous with $[\text{M}_3\text{O}(\text{MeCO}_2)_6(\text{py})_3] \cdot \text{py}$ ($\text{M} = \text{Mn or Fe}$), indicating that the three metal atoms are crystallographically equivalent as a result of disorder in the molecular orientation. Powder magnetic susceptibilities for the Cr_2Co and Cr_2Ni compounds (4.2–60 K), for the Fe_2Mn and Fe_2Ni compounds (4.2–295 K), and for the $\text{Fe}_2\text{Ni}(\text{aq})$ and Fe_2Mg compounds (80–295 K) have been fitted by use of an exchange Hamiltonian to yield values of the exchange parameters J for the Cr–Cr, Fe–Fe, Cr–Ni, Fe–Ni, and Fe–Mn interactions, which are discussed in terms of superexchange mechanisms. The values of J_{FeFe} in the Fe_2Mg , Fe_2Mn , and Fe_2Ni compounds and of J_{CrCr} in the Cr_2Co and Cr_2Ni compounds are approximately twice their values in the cations $[\text{M}^{\text{III}}_3\text{O}(\text{MeCO}_2)_6(\text{H}_2\text{O})_3]^+$ ($\text{M} = \text{Cr or Fe}$), indicating that the $\mu_3\text{-O}$ atom provides the main superexchange pathway. Diffuse-reflectance and solution spectra (6 000–40 000 cm^{-1}) of the compounds have been recorded at room temperature and are discussed in terms of the ligand-field model; a band in the spectra of the $\text{Fe}^{\text{III}}_2\text{Fe}^{\text{II}}$ and $\text{Cr}^{\text{III}}\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}$ compounds at ca. 7 000 cm^{-1} is assigned to intervalence transfer. The room-temperature spectra of $[\text{M}_3\text{O}(\text{MeCO}_2)_6\text{L}_3]\text{Cl}$ ($\text{M}_3 = \text{Cr}^{\text{III}}_3, \text{Cr}^{\text{III}}_2\text{Fe}^{\text{III}}, \text{Cr}^{\text{III}}\text{Fe}^{\text{III}}_2, \text{or Fe}^{\text{III}}_3$; $\text{L} = \text{H}_2\text{O or py}$) have also been obtained, and intense absorption bands at ca. 19 000 and 26 000 cm^{-1} are tentatively assigned to simultaneous ($\text{Cr}^{3+}, \text{Fe}^{3+}$) double excitations.

The trinuclear basic carboxylate complexes $[\text{M}^{\text{III}}_3\text{O}(\text{RCO}_2)_6\text{L}_3]^+$ ($\text{M} = \text{Cr or Fe}$) occupy a special place in magnetochemistry: they were the first polynuclear complexes to be investigated magnetically,¹ and the first in which the existence of exchange interactions was suggested and a Heisenberg spin-coupling Hamiltonian used to interpret the magnetic data;² following X-ray demonstrations that they contain an essentially equilateral triangle of metal ions surrounding a central O atom,³ they have been the object of intensive study by a variety of methods.^{4–8} Analogues with $\text{M} = \text{V, Mn, Ru, Rh, or Os}$ are also known,⁸ and more recently neutral mixed-valence complexes $[\text{M}^{\text{III}}_2\text{M}^{\text{II}}\text{O}(\text{RCO}_2)_6\text{L}_3]$ ($\text{M} = \text{Fe, Mn, Cr, V, or Ru}$) have been prepared and shown to have the same triangular structure.^{8–11} In this paper we describe the preparation, and some magnetic and spectroscopic studies, of a series of mixed-metal basic acetates of the types $\text{Cr}_2\text{M}^{\text{II}}$, $\text{Fe}_2\text{M}^{\text{II}}$, and CrFeM^{II} , where we use the abbreviation $\text{Cr}_2\text{M}^{\text{II}}$ for $[\text{Cr}^{\text{III}}_2\text{M}^{\text{II}}\text{O}(\text{MeCO}_2)_6\text{L}_3]$, with $\text{L} = \text{pyridine (py)}$ unless otherwise stated (Cr^{III}_3 then stands for the corresponding cationic complex).

Heteronuclear complexes involving such a range of metals are of particular interest because they provide an opportunity to investigate many spin-coupling interactions in an approximately

constant geometric framework, and to probe the spectroscopic consequences of electronic communication between different transition-metal ions. In a magnetic and spectroscopic study of the present compounds, one might hope to answer such questions as: is the exchange interaction mediated by the central oxygen atom, the bridging acetate ligands, or both?; which orbitals contribute to it?; is the interaction between one pair of metal ions affected by the third?; can spectroscopic transitions involving more than one metal centre be observed? The results of our attempts to answer these questions are presented here.

It should be mentioned that the $\text{Fe}_2\text{M}^{\text{II}}$ compounds ($\text{L} = \text{H}_2\text{O}$, $\text{M} = \text{Co, Ni, or Zn}$; $\text{L} = \text{py}$, $\text{M} = \text{Co or Ni}$) were originally prepared in 1928 by Weinland and Holtmeier,¹² although at that time they were incorrectly formulated as $\text{M}_4[\text{Fe}_9(\text{OH})_9(\text{MeCO}_2)_{26}] \cdot 23\text{H}_2\text{O}$ and $\text{M}_3[\text{Fe}_6\text{O}_3(\text{OH})(\text{MeCO}_2)_{17}] \cdot 12\text{py}$. In 1980 Yakubov *et al.*¹³ synthesised iodoacetate complexes for which chemical analysis indicated $\text{Fe}_2\text{M}^{\text{II}}$ formulae ($\text{L} = \text{H}_2\text{O}$; $\text{M} = \text{Mn, Fe, Co, Ni, Cu, or Zn}$), and in 1981 a reinvestigation^{14a} of Weinland and Holtmeier's compounds showed them to have $\text{Fe}_2\text{M}^{\text{II}}$ stoichiometry and to be isomorphous with the compounds of $\text{Fe}_2\text{Fe}^{\text{II}}$ and $\text{Mn}_2\text{Mn}^{\text{II}}$. The $\text{Cr}_2\text{M}^{\text{II}}$ and CrFeM^{II} analogues were reported in 1982.^{14b}

During this investigation our interest was aroused by the anomalous colour of compounds containing Cr^{III} and Fe^{III} in the same molecule. This has led us to examine the spectra of the $\text{Cr}^{\text{III}}_2\text{Fe}^{\text{III}}$ and $\text{Cr}^{\text{III}}\text{Fe}^{\text{III}}_2$ compounds,¹⁵ and these results are also reported.

† Supplementary data available (No. SUP 56342, 7 pp.): experimental magnetic susceptibilities. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii–xix.

Non-S.I. unit employed: B.M. $\approx 9.27 \times 10^{-24}$ A m².

Table 1. Formulae, colours, and crystal systems of the compounds $[M^{III}M^{II}M^{III}O(MeCO_2)_6(py)_3]\cdot npy$

MM'M"	n	Colour ^a	Crystal system ^b
Cr ₂ Mg	0.8	Green ^c	Monoclinic
Cr ₂ Fe	1	Tan	Rhombohedral
Cr ₂ Co	1	Green	Rhombohedral
Cr ₂ Ni	1	Green ^c	Monoclinic
Fe ₂ Mg	1	Olive green ^d	Rhombohedral
Fe ₂ Mn	1.0	Dark brown	Rhombohedral
Fe ₂ Fe	0.5	Dark brown	Rhombohedral
Fe ₂ Co	1	Brown	Rhombohedral
Fe ₂ Ni	1	Olive green	Monoclinic
Fe ₂ Zn	1	Olive green ^d	Rhombohedral
CrFeMn	0.7	Purple-brown	Rhombohedral
CrFeFe	1	Purple-brown	Rhombohedral
CrFeCo	1	Purple-brown	Rhombohedral
CrFeNi	1	Purple-brown	Monoclinic

^a Powder streak on paper. ^b Rhombohedral crystals are all isomorphous, space group $R\bar{3}2$, $Z = 1$ in rhombohedral cell (ref. 10a). Monoclinic crystals are all isomorphous, space group Cc or $C2/c$; for Cr₂Ni, $a = 21.99$, $b = 12.48$, $c = 15.97$ (± 0.02) Å, $\beta = 117.2 \pm 0.3^\circ$, $Z = 4$. ^c Dichroic, green/turquoise blue. ^d Dichroic, green/red.

Results and Interpretation

Preparation and Characterisation of Complexes.—The compounds are listed in Table 1. The Fe₂M^{II} complexes (L = H₂O) were prepared directly from aqueous solutions of Fe³⁺ and M²⁺ and converted into the pyridine adducts by crystallisation from pyridine, but the substitution inertness of Cr³⁺ prevented us from using this method to make chromium analogues. We found, however, that when chromium(II) acetate was warmed with pyridine in air a deep green solution was obtained, which in the presence of metal(II) acetate slowly deposited crystals of Cr₂M^{II} (M = Mg, Co, or Ni). The CrFeM^{II} compounds (M = Mn, Fe, Co, or Ni) and Cr₂Fe^{II} were prepared by reaction of chromium(II) acetate with Fe₂M^{II} in pyridine.

As indicated in Table 1, nine of the mixed-metal compounds are isomorphous with Fe₂Fe^{II} and Mn₂Mn^{II}. Since the rhombohedral unit cell of the latter contains a single molecule of symmetry D_3 ,^{10a} it follows that the molecules in these nine complexes must be disordered, with the divalent ion randomly occupying one of the three equivalent metal sites. The other four compounds are also isomorphous, but their crystals are monoclinic, $Z = 4$, space group Cc or $C2/c$, which requires the molecules to possess at most two-fold symmetry.

Magnetic Properties.—The powder magnetic susceptibilities of ten compounds have been measured, and their magnetic moments per molecule are plotted against temperature in Figures 1–4. We have analysed the data for six of the compounds, and these are discussed below. We comment only briefly on the remaining four, for which lower symmetry or an increased number of parameters makes detailed analysis impractical at present.

Theory. We assume that the interaction of the three magnetic ions in the cluster with each other and with the applied field **H** is given by the isotropic Hamiltonian (1), which with $S_1 = S_2$,

$$\mathcal{H} = -2\Sigma_i J_{ij} S_i \cdot S_j + \mu_B \Sigma_i g_i S_i \cdot \mathbf{H} \quad (1)$$

$g_1 = g_2$, and $J_{13} = J_{23}$ ($\equiv J_3$) takes the form (2), where $S_{12} = S_1 + S_2$ and $S = S_{12} + S_3$. The zero-field energy levels for expression (2) are given by (3).

$$\mathcal{H} = -2J_{12} S_1 \cdot S_2 - 2J_3 S_{12} \cdot S_3 + \mu_B [g_1 S + (g_3 - g_1) S_3] \cdot \mathbf{H} \quad (2)$$

$$E_0(S, S_{12}) = J_{12}[2S_1(S_1 + 1) - S_{12}(S_{12} + 1)] + J_3[S_{12}(S_{12} + 1) + S_3(S_3 + 1) - S(S + 1)] \quad (3)$$

If $S_3 = 0$ (as in Fe₂Mg) or $g_3 = g_1$ (as in Fe₂Mn), expression (2) commutes with S^2 and hence is diagonal in S , so that the susceptibility can be calculated by inserting the Zeeman coefficients $E_1(M) = Mg\mu_B$, $E_2 = 0$ into the Van Vleck equation¹⁶ (we write M for M_S). If $g_3 \neq g_1$ (as in Cr₂Co, Cr₂Ni, and Fe₂Ni), the magnetic part of (2) does not commute with S^2 , and E_1 and E_2 will then depend on S and S_{12} , equations (4) and

$$E_1(S, S_{12}, M) = [Mg_1 + (g_3 - g_1)\langle S, S_{12}, M | S_{3z} | S, S_{12}, M \rangle] \mu_B \quad (4)$$

(5). By tensor-operator methods¹⁷ we obtain the general expression (6) for the matrix of the spherical tensor $S_3^{(1)}$ in the

$$E_2(S, S_{12}, M) = (g_3 - g_1)^2 \mu_B^2 \sum_{S'} \langle S, S_{12}, M | S_{3z} | S', S_{12}, M \rangle^2 / E(S, S') \quad (5)$$

where $E(S, S') = E_0(S, S_{12}) - E_0(S', S_{12})$

$$\begin{aligned} \langle [(S_1, S_2) S_{12}] SM | S_3^{(1)} | [(S_1, S_2) S'_{12}, S_3] S' M' \rangle = \\ (-1)^{S_{12} + S_3 + 2S - M + 1} \\ [(2S + 1)(2S' + 1)S_3(S_3 + 1)(2S_3 + 1)]^{\frac{1}{2}} \times \\ \begin{Bmatrix} S & 1 & S' \\ S_3 & S_{12} & S_3 \end{Bmatrix} \begin{pmatrix} S & 1 & S' \\ -M & q & M' \end{pmatrix} \delta(S_{12}, S'_{12}) \end{aligned} \quad (6)$$

(S, S_{12}) basis, where $q = -1, 0$, or 1 and $S_3^{(1)}$ is related to S_3 by (7). Use of the formulae for the $6j$ and $3jm$ symbols¹⁷ then gives equations (8) and (9) for the diagonal and off-diagonal elements

$$S_z = S_0^{(1)}, S_x = 2^{-\frac{1}{2}}(S_{-1}^{(1)} - S_1^{(1)}), S_y = 2^{-\frac{1}{2}}i(S_{-1}^{(1)} + S_1^{(1)}) \quad (7)$$

$$\begin{aligned} \langle S_{12} SM | S_{3z} | S_{12} SM \rangle = -M\sigma(S) \\ \text{where } \sigma(S) \equiv [S_{12}(S_{12} + 1) - S_3(S_3 + 1) - S(S + 1)]/2S(S + 1) \end{aligned} \quad (8)$$

$$\begin{aligned} \langle S_{12} SM | S_{3z} | S_{12} S' M' \rangle = -\delta(M, M') [\tau(S, S')]^{\frac{1}{2}} \times \\ [(\bar{S} - M)(\bar{S} + M)/\bar{S}(2\bar{S} - 1)(2\bar{S} + 1)]^{\frac{1}{2}} \\ \text{where } \tau(S, S') \equiv (S_{12} + S_3 + 1 + \bar{S})(S_{12} + S_3 + 1 - \bar{S}) \times \\ (\bar{S} + S_{12} - S_3)(\bar{S} - S_{12} + S_3)/4\bar{S} \end{aligned} \quad (9)$$

of S_{3z} , respectively, and after summing over M we obtain expressions (10) and (11). The first-order part of the effective

$$\Sigma_M E_1^2 = (\frac{1}{3})S(S + 1)(2S + 1) \times [g_1 - (g_3 - g_1)\sigma(S)]^2 \mu_B^2 \quad (10)$$

$$\Sigma_M E_2 = (\frac{1}{3})(g_3 - g_1)^2 \mu_B^2 \sum_{S'} \tau(S, S') / E(S, S') \quad (11)$$

g value of the (S, S_{12}) level, $g_1 - (g_3 - g_1)\sigma(S)$, has been derived previously.¹⁸

Results of curve fitting. The J values (Table 2) were determined by least-squares fitting of the calculated susceptibility expression to the unweighted data, using a Simplex algorithm. For Fe³⁺ and Mn²⁺ we assume $S_i = \frac{5}{2}$, $g = 2.00$; for Cr³⁺, $S_i = \frac{3}{2}$, $g = 1.98$. For Co²⁺ and Ni²⁺ we treat g_3 as a fitting parameter.

Fe₂Mg and Fe₂Mn. The data are shown in Figure 1. In the case of Fe₂Mn, the fit at the lowest temperatures was improved

Table 2. Parameters^a derived from least-squares fitting of magnetic data for $[\text{M}^{\text{III}}_3\text{O}(\text{MeCO}_2)_6(\text{H}_2\text{O})_3]^+$ and $[\text{M}^{\text{III}}_2\text{M}^{\text{II}}\text{O}(\text{MeCO}_2)_6\text{L}_3]$

$\text{M}_2\text{M}'$	L	$-J_{12}/\text{cm}^{-1}$	$-J_3/\text{cm}^{-1}$	g_3	$10^2 R^b$
Cr^{III}_3	H_2O	11(1) ^c			
$\text{Cr}^{\text{III}}_2\text{Co}^{\text{II}}$	py	27(2)			4.0
$\text{Cr}^{\text{III}}_2\text{Ni}^{\text{II}}$	py	26(2)	47(2)	2.3(1)	3.3
Fe^{III}_3	H_2O	30(3) ^d			
$\text{Fe}^{\text{III}}_2\text{Mg}^{\text{II}}$	py	62(3)			0.8
$\text{Fe}^{\text{III}}_2\text{Mn}^{\text{II}}$	py	64(3)	21(1)	2.00 ^e	2.6
$\text{Fe}^{\text{III}}_2\text{Ni}^{\text{II}}$	py	73(3)	33(2)	2.29(2)	1.4
$\text{Fe}^{\text{III}}_2\text{Ni}^{\text{II}}$	H_2O	71(3)	31(3)	2.35(5)	0.6

^a Figures in parentheses are estimated uncertainties in units of the least significant digit. ^b $R = [\sum(\chi_{\text{obs.}} - \chi_{\text{calc.}})^2 / \sum \chi_{\text{obs.}}^2]^{1/2}$. ^c Refs. 4, 6b, d, and 19e. ^d Refs. 4, 6a, e, 19e, and f. ^e Assumed.

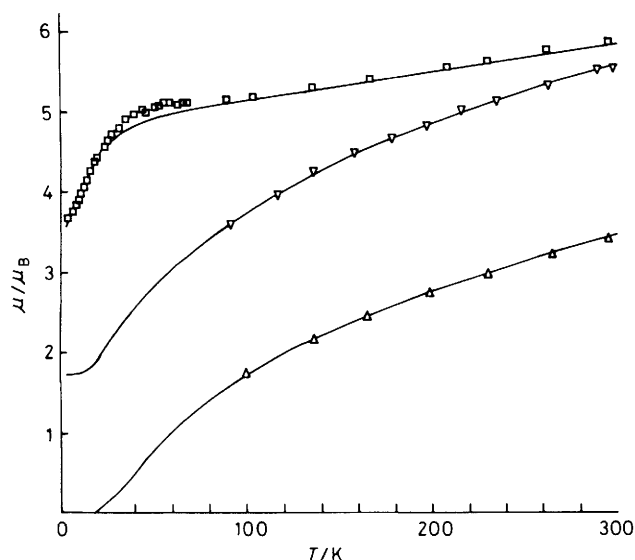


Figure 1. Effective magnetic moment per molecule for $[\text{Fe}^{\text{III}}_3\text{O}(\text{MeCO}_2)_6(\text{H}_2\text{O})_3]\text{Cl}\cdot 2\text{H}_2\text{O}$ (∇) (data from ref. 4) and for $[\text{Fe}^{\text{III}}_2\text{M}^{\text{II}}\text{O}(\text{MeCO}_2)_6(\text{py})_3]\cdot \text{py}$ [$\text{M} = \text{Mg}$ (Δ) or Mn (\square)]. The curves were calculated with the following parameter values: Fe^{III}_3 , $g = 2$, $J_{12} = -38.2$, $J_3 = -28.9 \text{ cm}^{-1}$; Fe_2Mg , $g = 2$, $J_{12} = -62.5 \text{ cm}^{-1}$; Fe_2Mn , $g_1 = g_3 = 2$, $J_{12} = -64.4$, $J_3 = -21.3 \text{ cm}^{-1}$, $\theta = -0.4 \text{ K}$.

by inclusion of a small Weiss constant θ in the fitting model, T being replaced by $T - \theta$ with θ ca. -0.4 K . Since the ground level is magnetic ($S = \frac{3}{2}$), this may reflect weak intermolecular exchange. It is interesting to compare the exchange coupling in these two compounds with that in $[\text{Fe}^{\text{III}}_3\text{O}(\text{MeCO}_2)_6(\text{H}_2\text{O})_3]^+$. (Magnetic data for the corresponding py compound are not available, but as with Fe_2Ni , see below, we believe that its properties would be quite similar to those of the aquo-complex, of which several studies have been made.) For reasons that are still the subject of controversy,^{6,18,19} the magnetic behaviour of this complex deviates somewhat from that predicted for an equilateral triangle with a single J ; in the isosceles triangle model, values found for J_{12} and J_3 are typically -35 and -28 cm^{-1} , while if an equilateral triangle is assumed, a somewhat poorer fit is obtained with J ca. -29 cm^{-1} .^{4,6a,e,19} As a check on our computer program, we first fitted the data of ref. 4 for Fe^{III}_3 and confirmed the above results ($J_{12} = -38$, $J_3 = -29$; single $J = -29 \text{ cm}^{-1}$). Using $J_{12} = J_3 = -30 \text{ cm}^{-1}$ as the initial value in the least-squares iteration, we then fitted the data for Fe_2Mg and Fe_2Mn ; the iterations converged to $J_{\text{FeFe}} = -62$ and -64 cm^{-1} , respectively. Thus, replacement of one Fe^{3+} ion in Fe^{III}_3 by either

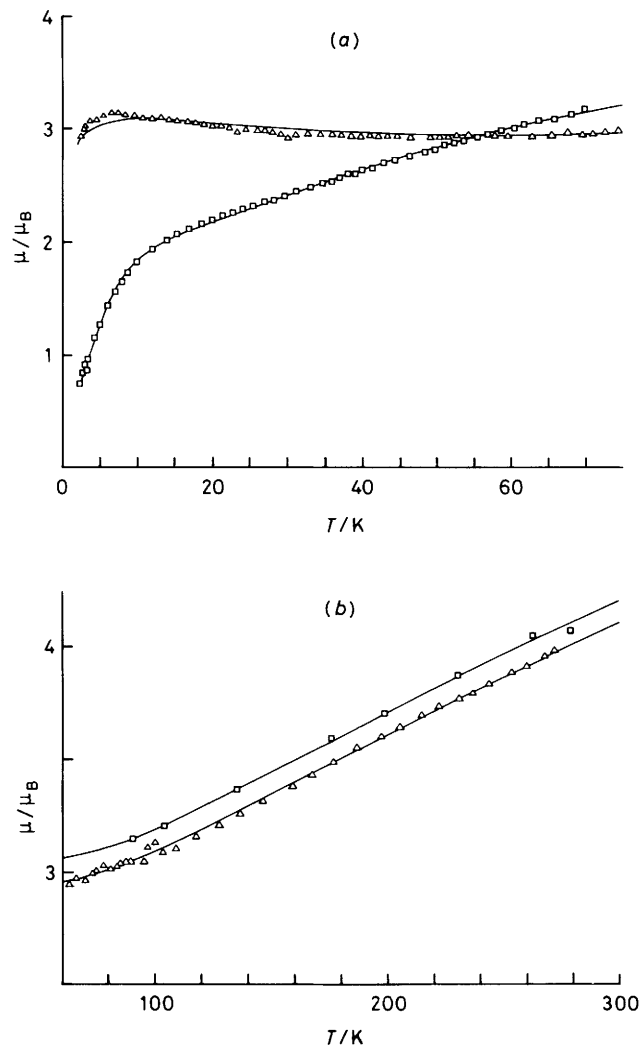


Figure 2. (a) Effective magnetic moment per molecule for $[\text{Cr}^{\text{III}}_2\text{Ni}^{\text{II}}\text{O}(\text{MeCO}_2)_6(\text{py})_3]\cdot \text{py}$ (\square) and $[\text{Fe}^{\text{III}}_2\text{Ni}^{\text{II}}\text{O}(\text{MeCO}_2)_6(\text{py})_3]\cdot \text{py}$ (Δ). The curves were calculated with the following parameter values: Cr_2Ni , $g_1 = 1.98$, $g_3 = 2.38$, $J_{12} = -25.8$, $J_3 = -47.1 \text{ cm}^{-1}$, impurity paramagnetism $860/T \text{ mm}^3 \text{ mol}^{-1}$; Fe_2Ni , $g_1 = 2$, $g_3 = 2.29$, $J_{12} = -72.7$, $J_3 = -32.8 \text{ cm}^{-1}$, $\theta = -0.4 \text{ K}$. (b) Effective magnetic moment per molecule for $[\text{Fe}_2\text{NiO}(\text{MeCO}_2)_6\text{L}_3]\cdot n\text{L}$ [$\text{L} = \text{py}$, $n = 1$ (Δ); $\text{L} = \text{H}_2\text{O}$, $n = 3$ (\square)]. The curves were calculated with the following parameter values: $\text{L} = \text{py}$, as in (a); $\text{L} = \text{H}_2\text{O}$, $g_1 = 2$, $g_3 = 2.35$, $J_{12} = -71.2$, $J_3 = -31.4 \text{ cm}^{-1}$, $\theta = -0.4 \text{ K}$.

Mg^{2+} or Mn^{2+} results in an approximately two-fold increase in the strength of the interaction between the remaining two Fe^{3+} ions.

The value found for J_{FeMn} in the Fe_2Mn complex, ca. -21 cm^{-1} , is significantly smaller in magnitude than J_{FeFe} in the Fe^{III}_3 complex, ca. -29 cm^{-1} . Moreover, from Fe^{III}_3 to Fe_2Mn we go from approximately equal to highly unequal couplings while retaining the $(\frac{5}{2}, \frac{5}{2}, \frac{5}{2})$ spin set. Figure 1 shows one immediate consequence of this: the ground state changes from $S = \frac{1}{2}$ (μ ca. 1.7) to $S = \frac{3}{2}$ (μ ca. 3.9 B.M.). From equation (3), a $S = \frac{3}{2}$ level will lie lowest if J_{12}/J_3 lies between 0.5 and 0.625 or between 1.75 and 3.5. The data indicate that in Fe_2Mn (J_{12}/J_3 3.1) the ground level is (S, S_{12}) = $(\frac{3}{2}, 1)$, with $(\frac{5}{2}, 0)$ ca. 20 cm^{-1} above it and other levels at least 80 cm^{-1} higher. No satisfactory fit could be obtained with $J_{12}/J_3 < 1$, a point of some significance (see below).

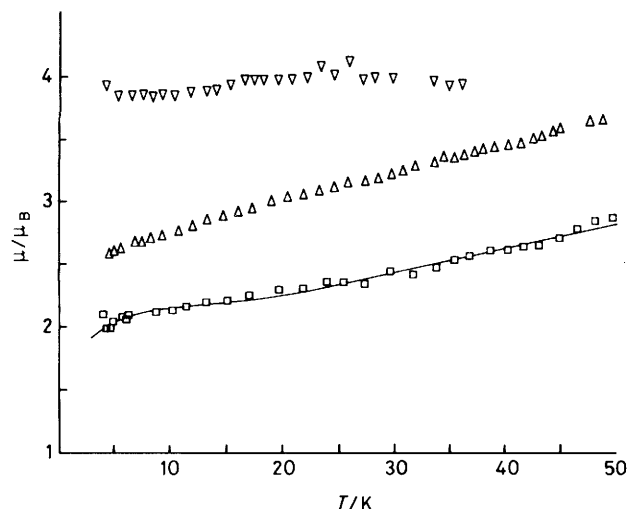


Figure 3. Effective magnetic moment per molecule for $[\text{Cr}^{\text{III}}_2\text{Co}^{\text{II}}\text{O}(\text{MeCO}_2)_6(\text{py})_3]\cdot\text{py}$ (\square), $[\text{Cr}^{\text{III}}\text{Fe}^{\text{III}}\text{Co}^{\text{II}}\text{O}(\text{MeCO}_2)_6(\text{py})_3]\cdot\text{py}$ (Δ), and $[\text{Cr}^{\text{III}}\text{Fe}^{\text{III}}\text{Mn}^{\text{II}}\text{O}(\text{MeCO}_2)_6(\text{py})_3]\cdot 0.7\text{py}$ (∇). The curve was calculated for Cr_2Co with effective spin $S_3' = 0.5$ and the parameter values $g_1 = 1.98$, $g_3 = 2.58$, $J_{12} = -26.4$, $J_3 = -7.4$ ($J_3 = -4.5 \text{ cm}^{-1}$), $\theta = -1.1 \text{ K}$

Fe_2Ni and Cr_2Ni . The data for Fe_2Ni ($L = \text{H}_2\text{O}$) and ($L = \text{py}$) over the range 80–300 K [Figure 2(b)] are rather similar and can be fitted by similar values of the parameters; we use the results for $L = \text{py}$, since these cover a wider temperature range. The ground level of Fe_2Ni appears to be magnetic ($S = 1$), and we again found that the fit at the lowest temperatures was improved by inclusion of a small Weiss constant θ , *ca.* -0.4 K . The low-temperature data for Cr_2Ni (which has a non-magnetic ground state) did not require a Weiss constant but the fit was improved by assuming a small amount of paramagnetic Cr^{3+} (1.8% of total Cr); however, the derived values of J_{12} and J_3 were not significantly affected by this.

Comparing the J_{FeFe} values in $[\text{Fe}^{\text{III}}_3\text{O}(\text{MeCO}_2)_6(\text{H}_2\text{O})_3]^+$ (*ca.* -30) and Fe_2Ni (-73 cm^{-1}), we see an increase by a factor of 2.4 resulting from replacement of one Fe^{3+} by Ni^{2+} . A very similar ratio is found between the J_{CrCr} values of $[\text{Cr}^{\text{III}}_3\text{O}(\text{MeCO}_2)_6(\text{H}_2\text{O})_3]^+$ (-11) and Cr_2Ni (-26 cm^{-1}). The respective J_3 values are such that in Cr_2Ni J_3 is nearly twice J_{12} , whereas in Fe_2Ni J_3 is less than half J_{12} , and in consequence the complexes have different ground states: $S = 0$ and $S = 1$, respectively [Figure 2(a)]. Here, equation (3) implies that, for J_3 and J_{12} both negative, the spin-singlet level (0,1) lies below any triplet level if $0.5 < J_3/J_{12} < 2$, which is the case for Cr_2Ni ($J_3/J_{12} = 1.8$) but not for Fe_2Ni ($J_3/J_{12} = 0.45$). The data indicate that in Cr_2Ni the lowest triplet (1,1) is *ca.* 10 cm^{-1} above the ground singlet (0,1), with (2,3) 62 cm^{-1} higher, whereas in Fe_2Ni the singlet (0,1) is *ca.* 14 cm^{-1} above the ground triplet (1,0), with (1,1) 66 cm^{-1} higher.

Somewhat high values were obtained for g_{Ni} in these compounds. We are inclined not to attach significance to this, since the fitting process is rather insensitive to the value of g_3 , and fixing it at the more reasonable value of 2.25 did not greatly alter the derived J values or the goodness of fit. It may also reflect certain obvious deficiencies of our model, such as the neglect of single-ion anisotropy. Note, however, that zero-field splitting of the Ni^{2+} ground level probably does not affect the results, since inclusion of a term $D(S_{z3}^2 - \frac{3}{2})$ in the Hamiltonian for Cr_2Ni with D/k as large as 10 K had only an insignificant effect on the calculated average susceptibility.

Cr_2Co . The data are shown in Figure 3. Again, the ground

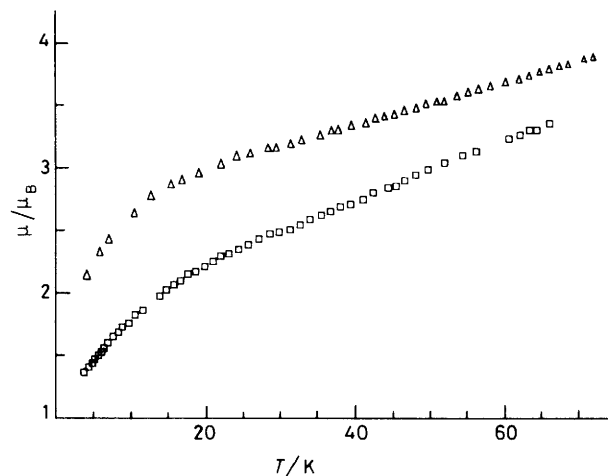


Figure 4. Effective magnetic moment per molecule for $[\text{Cr}^{\text{III}}_2\text{Fe}^{\text{II}}\text{O}(\text{MeCO}_2)_6(\text{py})_3]\cdot\text{py}$ (\square) and $[\text{Cr}^{\text{III}}\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}\text{O}(\text{MeCO}_2)_6(\text{py})_3]\cdot\text{py}$ (Δ)

level appears to be magnetic and a Weiss constant θ was included in the fitting model. The $^4T_{1g}$ ground term of Co^{2+} in octahedral symmetry is split by spin-orbit coupling into three degenerate levels, of which the lowest (by at least 200 cm^{-1}) is normally a Kramers doublet with effective spin $S' = \frac{1}{2}$. Within the $S' = \frac{1}{2}$ subspace the operator S' is equivalent to $\frac{1}{2}S$ and the corresponding g value is $\frac{1}{3}$, though this will be modified by distortion (g becomes highly anisotropic) and by covalency effects.²⁰ Not surprisingly, our attempts to fit the low-temperature magnetic data for this compound by use of equation (2) with $S_3 = \frac{3}{2}$ gave poor fits and rather unlikely J values ($J_{12} - 75$ to -215 , $J_3 - 40$ to -100 cm^{-1}).

The fact that the effective moment of Cr_2Co approaches 2.0 at low temperature suggests that the ground level has total spin $S = \frac{1}{2}$ with g *ca.* 2.3. If we neglect distortion and assume that only the lowest Kramers doublet of Co^{2+} is important below 60 K (*i.e.* $S_3 = \frac{1}{2}$, coupled to S_{12} by a term $-2J_3S_{12}\cdot S_3'$ with $J_3 = 5J_3/3$), there will be two $S = \frac{1}{2}$ levels of the complex, corresponding to $S_{12} = 0$ and 1, respectively. Which of them is the ground level depends on the ratio J_{12}/J_3 . If we assume that both J values are negative, equation (3) indicates that with $J_{12}/J_3 > 1$ the lower level is the one with $S_{12} = 0$, for which $g = g_3$; starting from trial J values satisfying this inequality we obtained a reasonable fit (Figure 3) with $J_{12} - 26$, $J_3 - 4.5 \text{ cm}^{-1}$, $\theta - 1.1 \text{ K}$, and $g_3 2.58$. On the other hand, if $J_{12}/J_3 < 1$, the lower level is the one with $S_{12} = 1$, for which $g = (4g_1 - g_3)/3$; from this side of the inequality we obtained a similar fit with $J_{12} - 29$, $J_3 - 31 \text{ cm}^{-1}$, $\theta - 0.9 \text{ K}$, and $g_3 0.37$.

Examination of the energy levels given by these J values shows the reason for the ambiguity: both sets correspond to a sequence of levels of increasing energy in which the first six S values are in the order $\frac{1}{2}, \frac{1}{2}, \frac{3}{2}, \frac{3}{2}, \frac{5}{2}, \frac{5}{2}$, with separations of *ca.* 40, 20, 85, 35, and 125 cm^{-1} (the associated S_{12} values being, of course, different in the two cases). In both fits the value obtained for g_3 is much lower than expected, and it does not seem to be possible to reach any conclusion about the value of J_{CrCo} . However, the data clearly require J_{CrCr} *ca.* -27 cm^{-1} , essentially the same value as in Cr_2Ni .

The remaining compounds. We have been unable to fit the data for $\text{Cr}_2\text{Fe}^{\text{II}}$ satisfactorily with the Hamiltonian (2), presumably because of orbital magnetism and spin-orbit coupling in the ground state of Fe^{2+} . The trend in the magnetic moment (Figure 4), however, strongly suggests a $S = 0$ ground level in this compound.

The CrFeM^{II} compounds have three independent J values, so

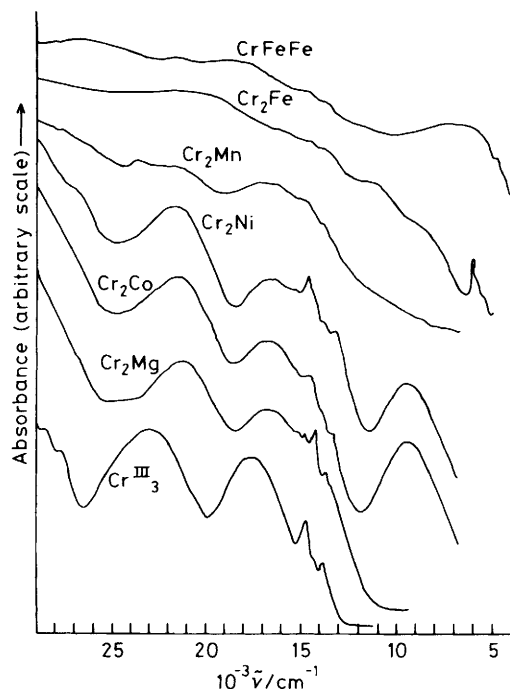


Figure 5. Room-temperature diffuse-reflectance spectra of $[\text{Cr}^{\text{III}}_3\text{O}(\text{MeCO}_2)_6(\text{py})_3]\text{Cl}$, $[\text{Cr}^{\text{III}}_2\text{M}^{\text{II}}\text{O}(\text{MeCO}_2)_6(\text{py})_3]\cdot\text{py}$ ($\text{M} = \text{Mg}, \text{Mn}, \text{Fe}, \text{Co}, \text{or Ni}$), and $[\text{Cr}^{\text{III}}\text{Fe}^{\text{II}}\text{Fe}^{\text{II}}\text{O}(\text{MeCO}_2)_6(\text{py})_3]\cdot\text{py}$. The sharp peak at *ca.* 5 900 cm^{-1} in this and the following Figure is a vibrational overtone of pyridine, as is a very weak shoulder at *ca.* 11 600 cm^{-1} discernible in some spectra

that the exchange Hamiltonian does not commute with S_{12}^2 and we can no longer obtain a simple expression for the energy levels. In view of this theoretical complexity, and the possible presence of $\text{Cr}_2\text{M}^{\text{II}}$ and $\text{Fe}_2\text{M}^{\text{II}}$ as impurities, a detailed analysis of the data for these compounds is not justified at this stage, but we note the following points. (a) CrFeMn (Figure 3) has an approximately constant moment (*ca.* 3.9 B.M.) over the range 4–36 K, suggesting a ground level with $S = \frac{3}{2}$ (like that of Fe_2Mn), which must be separated from the next level by a substantial energy gap. (b) The curves of μ vs. T for $\text{CrFeFe}^{\text{II}}$ (Figure 4) and CrFeCo (Figure 3) are quite similar to those of the corresponding $\text{Cr}_2\text{M}^{\text{II}}$ compounds, with the lowest spin levels probably the same in each case ($S = 0$ and $S = \frac{1}{2}$, respectively), but with the CrFeM^{II} moment consistently higher than that of $\text{Cr}_2\text{M}^{\text{II}}$ over the temperature range.

Optical Electronic Spectra.—Room-temperature diffuse-reflectance spectra between 6 000 and 40 000 cm^{-1} were obtained for all the compounds in this study, together with solution spectra in some cases. Selected spectra are shown in Figures 5 and 6.

Solution and 77-K reflectance spectra of salts containing the ions $[\text{Cr}_3\text{O}(\text{MeCO}_2)_6\text{L}_3]^+$ ($\text{L} = \text{H}_2\text{O}$, py, or other ligands) and $[\text{Fe}_3\text{O}(\text{RCO}_2)_6(\text{H}_2\text{O})_3]^+$,⁵ and a more detailed study of the polarised crystal spectrum of the chromium complex ($\text{L} = \text{H}_2\text{O}$)⁷ at 4.2–300 K, have been reported. The axial and rhombic components of the ligand field appear to be relatively small in all of these cases, and since none of our spectra shows definite evidence of low-symmetry splittings we interpret our results in terms of octahedral symmetry. (The fact that several of the crystals are noticeably dichroic, however, is a reminder that the molecular wavefunctions are of lower symmetry.)

Chromium(III) spectrum. The spectrum of Cr_2Mg , like those of Cr^{III}_3 ($\text{L} = \text{H}_2\text{O}$ or py), shows three broad bands which can be

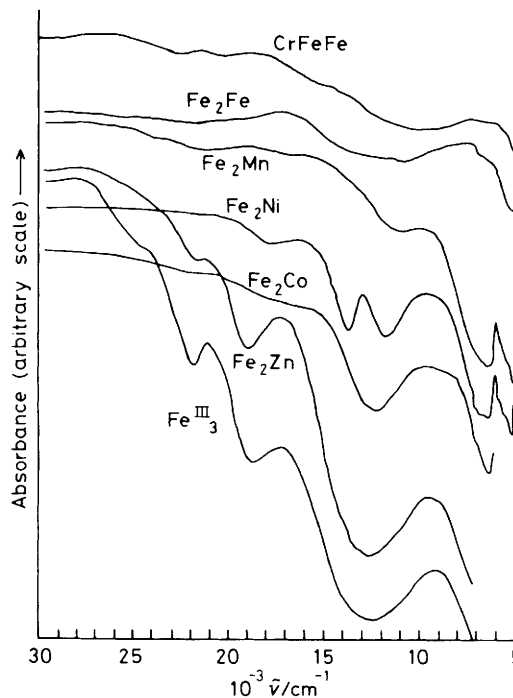


Figure 6. Room-temperature diffuse-reflectance spectra of $[\text{Fe}^{\text{III}}_3\text{O}(\text{MeCO}_2)_6(\text{py})_3]\text{Cl}$, $[\text{Fe}^{\text{III}}_2\text{M}^{\text{II}}\text{O}(\text{MeCO}_2)_6(\text{py})_3]\cdot\text{py}$, and $[\text{Cr}^{\text{III}}\text{Fe}^{\text{II}}\text{Fe}^{\text{II}}\text{O}(\text{MeCO}_2)_6(\text{py})_3]\cdot\text{py}$

Table 3. Spin-allowed absorption bands ($\tilde{\nu}/\text{cm}^{-1}$) in the room-temperature diffuse-reflectance spectra of $[\text{Cr}_3\text{O}(\text{MeCO}_2)_6\text{L}_3]^+$ ($\text{L} = \text{H}_2\text{O}$ or py) and $[\text{Cr}_2\text{MgO}(\text{MeCO}_2)_6(\text{py})_3]$, and derived values of β_{35} for Cr^{3+}

	$\text{Cr}^{\text{III}}_3(\text{H}_2\text{O})$	$\text{Cr}^{\text{III}}_3(\text{py})$	$\text{Cr}_2\text{Mg}(\text{py})$	Uncertainty	Assignment ^a
ν_1^b	17 100	17 700	16 700	± 150	${}^4A_{2g} \rightarrow {}^4T_{2g}$
ν_2	22 600	23 000	21 200	± 150	${}^4T_{1g}(F)$
ν_3^c	(36 500)	(37 500)	(35 100)	± 500	${}^4T_{1g}(P)$
β_{35}^d	0.50	0.48	0.40	± 0.03	

^a In approximate local O_h symmetry. ^b We assume $\Delta = \nu_1$. ^c Calculated value in parentheses, from $\nu_3 = \nu_1(17\nu_1 - 9\nu_2)/(9\nu_1 - 5\nu_2)$. ^d B/B_0 , where $B = (\nu_2 - \nu_1)(2\nu_1 - \nu_2)/3(9\nu_1 - 5\nu_2)$; $B_0 = 1 030 \text{ cm}^{-1}$ from ref. 22, p. 437.

assigned to the transitions ${}^4A_{2g} \rightarrow {}^4T_{2g}$ ($\nu_1 = \Delta$), ${}^4T_{1g}(F)$ (ν_2), and ${}^4T_{1g}(P)$ (ν_3). A set of sharp bands at *ca.* 14 000 cm^{-1} is assigned to ${}^4A_{2g} \rightarrow {}^2T_{1g}$.⁷ The Cr_2Ni spectrum is similar, allowing for the presence of Ni^{2+} . The spectral data are compared in Table 3, which also gives the derived values of the nephelauxetic ratio²¹ β_{35} .

Iron(III) spectrum. Unlike Cr^{III}_3 , the Fe^{III}_3 system is not spectroscopically well understood at present. The reflectance spectra of the Fe^{III}_3 , Fe_2Mg , and Fe_2Zn ($\text{L} = \text{H}_2\text{O}$ or py) compounds (Figure 6 and Table 4) show moderately broad bands at *ca.* 10 000, 18 000, and 21 000 cm^{-1} , with further bands around 24 000 and 29 000 cm^{-1} ; in some cases a very weak shoulder around 14 000 cm^{-1} is just barely discernible. The bands at 10 000 and 18 000 cm^{-1} are shifted to lower energy when H_2O is replaced by py (increasing the average ligand field), but that at 21 000 cm^{-1} is relatively little affected, and we therefore assign the latter to the transition ${}^6A_{1g} \rightarrow {}^4A_{1g} +$

Table 4. Absorption bands ($\tilde{\nu}/\text{cm}^{-1}$) in the room-temperature diffuse-reflectance spectra of $[\text{Fe}_3\text{O}(\text{MeCO}_2)_6\text{L}_3]^+$ and $[\text{Fe}_2\text{ZnO}(\text{MeCO}_2)_6\text{L}_3]$ ($\text{L} = \text{H}_2\text{O}$ or py), and derived values of ligand-field and electron-repulsion parameters (cm^{-1}) for Fe^{3+}

	$\text{Fe}^{\text{III}}_3(\text{H}_2\text{O})$	$\text{Fe}^{\text{III}}_3(\text{py})$	$\text{Fe}^{\text{III}}_2\text{Zn}(\text{H}_2\text{O})$	$\text{Fe}^{\text{III}}_2\text{Zn}(\text{py})$	Uncertainty	Assignment ^a ${}^6A_{1g} \rightarrow$
ν_1^b	10 150 (10 150)	9 150 (9 150)	10 400	9 400 (9 430)	± 100	${}^4T_{1g}$
$\nu_2^{b,c}$	14 500 (sh) (14 500)			13 900 (sh) (13 900)	± 200	${}^4T_{2g}$
ν_3	19 400 (sh) 21 350 22 450	17 200 21 050	18 400 21 300 (sh)	17 200 21 200	± 150 ± 200	$({}^4T_{1g}, {}^4T_{1g})$ ${}^4A_{1g} + {}^4E_g$
	24 700	24 100 (sh)		24 000 (sh)	± 400	
	29 000br	28 000br	29 000br	28 000br	± 500	
Δ	13 600	14 000		14 100	± 500	
B	660	760		670	± 100	
C	3 000	2 700		2 900	± 400	

^a In approximate local O_h symmetry. ^b Calculated values in parentheses. ^c A weak shoulder is also visible in the spectra of $\text{Fe}^{\text{III}}_2\text{Mg}(\text{py})$ at 13 600 and $\text{Fe}^{\text{III}}_2\text{Ni}(\text{H}_2\text{O})$ at 14 800 cm^{-1} .

Table 5. Absorption bands ($\tilde{\nu}/\text{cm}^{-1}$) of Ni^{2+} in the room-temperature diffuse-reflectance spectra^a of $[\text{M}^{\text{III}}_2\text{NiO}(\text{MeCO}_2)_6(\text{py})_3]$ ($\text{M} = \text{Cr}$ or Fe), and derived values of parameters B , C (cm^{-1}) and β_{35} for Ni^{2+}

	Cr_2Ni	Fe_2Ni	Uncertainty	Assignment ^b ${}^3A_{2g} \rightarrow$
ν_1^c	9 300(4)		± 100	${}^3T_{2g}$
ν_2^d		15 500 (sh) (15 400)	± 500	${}^3T_{1g}(F)$
ν_3	26 500		± 300	${}^3T_{1g}(P)$
ν_{sf}		12 900 (19)	± 50	${}^1E_g(D)$
B	930 ^e		± 90	
C	4 100 ^f		± 300	
β_{35}	0.86 ^g		± 0.02	

^a Figures in parentheses after $\tilde{\nu}$ are molar absorption coefficients ($\epsilon_{\text{max}}/\text{cm}^2 \text{mmol}^{-1}$) in chloroform. ^b In approximate local O_h symmetry. ^c We assume $\Delta = \nu_1$. ^d Calculated value in parentheses, from $\nu_2 = \nu_1(9\nu_3 - 17\nu_1)/(5\nu_3 - 9\nu_1)$. ^e From $B = (\nu_3 - \nu_1)(\nu_3 - 2\nu_1)/3(5\nu_3 - 9\nu_1)$. ^f From $2\nu_{\text{sf}} = 17B + 4C + \frac{3}{2}\Delta - (49B^2 + 2B\Delta + \Delta^2)^{\frac{1}{2}}$ (sf = spin forbidden). ^g B/B_0 , where $B_0 = 1 084 \text{ cm}^{-1}$ from ref. 22, p. 437.

${}^4E_g(G)$ (ν_3), which corresponds to a 'spin flip' within the ground configuration. If the bands at 10 000 and 14 000 cm^{-1} are then assigned as ${}^6A_{1g} \rightarrow {}^4T_{1g}$ and ${}^4T_{2g}(G)$ (ν_1 and ν_2), and the energies of the latter two terms calculated by means of the electrostatic matrices for d^5 in a cubic ligand field (assuming $\nu_3 = 10B + 5C$),²² fairly good agreement is obtained with reasonable values of Δ , B , and C (Table 4). The quantitative significance of these results is uncertain, however.

Nickel(II) spectrum. The chromium(III) chromophore in these complexes does not absorb below 12 000 cm^{-1} , allowing us to identify the ${}^3A_{2g} \rightarrow {}^3T_{2g}$ ($\nu_1 = \Delta$) transition of Ni^{2+} at 9 300 cm^{-1} in Cr_2Ni (in Fe_2Ni it is hidden by ν_1 of Fe^{3+}). The ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ transition (ν_2) is obscured in both Cr_2Ni and Fe_2Ni (though a careful comparison of the Fe_2Zn and Fe_2Ni spectra suggests the presence of a band at 15 000–16 000 cm^{-1} for the latter). The ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transition (ν_3) is identified with a shoulder at 26 500 cm^{-1} in the Cr_2Ni spectrum which is absent from that of Cr_2Mg . If the spectrum of Ni^{2+} is then assumed to be essentially the same for Cr_2Ni and Fe_2Ni , these values of ν_1 and ν_3 give the values of Δ , B , and β_{35} shown in Table 5, with ν_2 predicted to lie at $15 400 \pm 700 \text{ cm}^{-1}$. The values of the ligand-field parameters are similar to those of nickel(II) complexes with an O_6 donor set.²³

The Fe_2Ni spectrum also contains a rather narrow peak at

Table 6. (a) Irreducible representations of D_{3h} spanned by oxygen orbitals and metal d orbitals of the M_3O system^a

Representation	Oxygen orbitals	Metal d orbitals ^b
A_1'	s	θ, ζ
A_2'		ϕ_+
E'	p_x, p_y	θ, ζ, ϕ_+
A_1''		ε
A_2''	p_z	ϕ_-
E''		ε, ϕ_-

(b) Net effective exchange parameters $\mathcal{J}_{ij} = n_i n_j J_{ij}$, and the contributions from pairs of non-orthogonal magnetic orbitals a_i, b_j

i, j	$-\mathcal{J}_{ij}/\text{cm}^{-1}$	$\Sigma_{a,b} J(a_i b_j)^c$
Cr, Cr	100	$[J(t_2 t_2)]_{\text{CrCr}}$
Fe, Fe	750	$[J(\theta\theta) + \Sigma J(t_2\theta) + \Sigma J(\theta t_2) + \Sigma J(t_2 t_2)]_{\text{FeFe}}$
Cr, Ni	280	$[\Sigma J(t_2\theta)]_{\text{CrNi}}$
Fe, Ni	330	$[J(\theta\theta) + \Sigma J(t_2\theta)]_{\text{FeNi}}$
Fe, Mn	525	$[J(\theta\theta) + \Sigma J(t_2\theta) + \Sigma J(\theta t_2) + \Sigma J(t_2 t_2)]_{\text{FeMn}}$

^a The z axis of O is taken perpendicular to the M_3 plane. The z axis of each M is directed towards the central O, the x and y axes approximately towards acetate oxygen atoms. ^b $\theta = d_{3z}$, $\varepsilon = d_{x^2-y^2}$, $\zeta = d_{xy}$, and $\phi_+ = 2^{-\frac{1}{2}}(d_{xz} \pm d_{yz})$. ^c $\Sigma J(t_2\theta) = \bar{J}(\zeta\theta) + \bar{J}(\phi_+\theta)$; $\Sigma J(t_2 t_2) = J(\zeta\zeta) + J(\zeta\phi_+) + J(\phi_+\zeta) + J(\phi_+\phi_+) + J(\phi_-\phi_-)$.

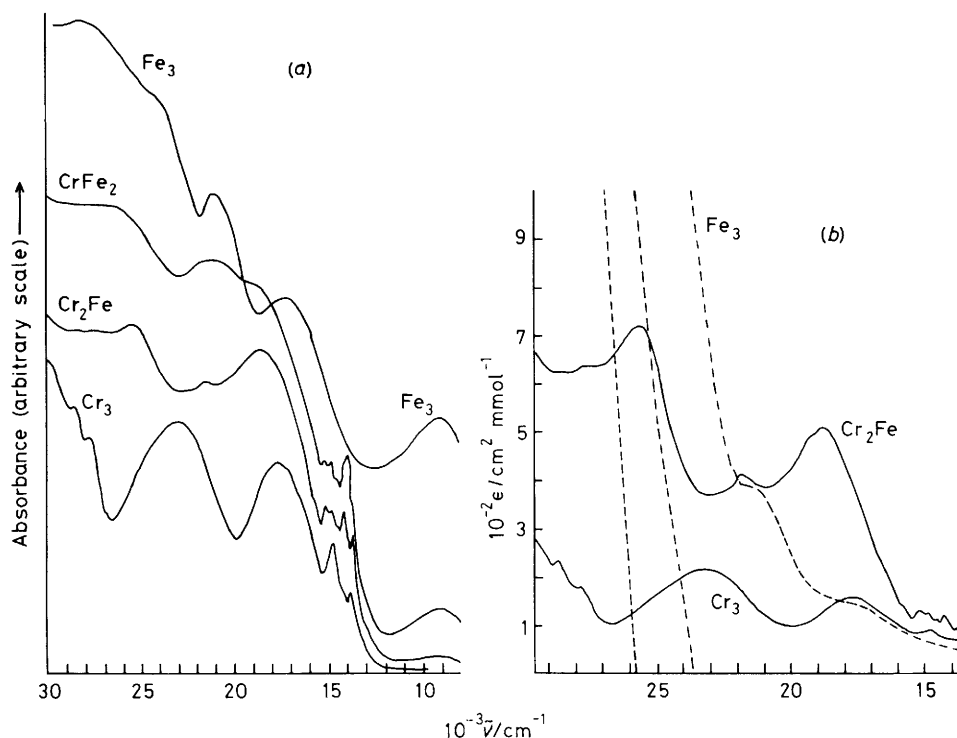
12 900 cm^{-1} , and solution spectra in chloroform (Table 5) show that this band has approximately the same oscillator strength [$f = (4 \pm 1) \times 10^{-5}$] as ν_1 . Although the intensity might suggest a spin-allowed transition, there can be little doubt that it is in fact the ${}^3A_{2g} \rightarrow {}^1E_g(D)$ (ν_{sf}) band of Ni^{2+} , which commonly occurs at ca. 12 000–15 000 cm^{-1} but is normally very weak unless it is close enough to ν_2 to gain significant intensity via spin-orbit coupling.^{23,24} (The alternative assignment of this band as ν_2 would give B the implausibly low value of 360 cm^{-1} .) From the position of this band we calculate²⁵ C .

Chromium(III)–iron(III) combination spectra. A remarkable feature of the $\text{Cr}^{\text{III}}\text{Fe}^{\text{III}}\text{M}^{\text{III}}$ complexes is their purple colour, which contrasts with the green colour of most of the $\text{Cr}_2\text{M}^{\text{III}}$ and $\text{Fe}_2\text{M}^{\text{III}}$ compounds, and appears to be associated with an intense band at ca. 19 000 cm^{-1} . We have sought to elucidate this problem by looking at the related ionic compounds $[\text{M}_3\text{O}(\text{MeCO}_2)_6\text{L}_3]\text{Cl}$ ($\text{M}_3 = \text{Cr}^{\text{III}}_3$, $\text{Cr}^{\text{III}}_2\text{Fe}^{\text{III}}$, $\text{Cr}^{\text{III}}\text{Fe}^{\text{III}}_2$, or Fe^{III}_3 ; $\text{L} = \text{py}$ or H_2O) (Figure 7 and Table 7). In the pyridine series, the $\text{Cr}^{\text{III}}_2\text{Fe}^{\text{III}}$ complex is purple-red, in striking

Table 7. Absorption bands ($\tilde{\nu}/\text{cm}^{-1} < 35\,000$) in the diffuse-reflectance spectra of $[\text{M}^{\text{III}}_3\text{O}(\text{MeCO}_2)_6\text{L}_3]^+$ ($\text{M}_3 = \text{Cr}_3, \text{Cr}_2\text{Fe}, \text{CrFe}_2$, or Fe_3 ; $\text{L} = \text{py}$ or H_2O) and of $[\text{Cr}_2\text{MgO}(\text{MeCO}_2)_6(\text{py})_3]$

L = py					L = H ₂ O				Assignment
Cr ₂ Mg	Cr ₃	Cr ₂ Fe	CrFe ₂	Fe ₃ ^a	Cr ₃	Cr ₂ Fe	CrFe ₂	Fe ₃ ^a	
		9 200br	9 000br	9 150		10 300	10 000	10 150	Fe ³⁺ : ${}^6A_{1g} \rightarrow {}^4T_{1g}$
13 470 (sh)									Cr ³⁺ : ${}^4A_{2g} \rightarrow {}^2T_{1g}$
13 830	13 820	13 700	13 750		13 950	13 820			
14 280	14 230w	14 200	14 000		14 250w (sh)	14 370	14 100		
14 470		14 450w	14 500			14 600w	14 600w		
14 840	14 740	14 850	14 860		14 900 (sh)	15 000 (sh)	15 060		Cr ³⁺ : ${}^4A_{2g} \rightarrow {}^4T_{2g}$ (Cr ³⁺ , Fe ³⁺): $({}^4A_{2g}, {}^6A_{1g}) \rightarrow ({}^2T_{1g}, {}^2T_{2g})$
15 270 (sh)		15 200	15 200		15 250w (sh)	15 400	15 400w		
16 700	17 700				17 100	17 000 (sh)			
		18 600 ^b	19 000 (sh)			19 400 ^c	19 200 (sh)		
							21 300 (sh)	21 350	Fe ³⁺ : ${}^6A_{1g} \rightarrow {}^4A_{1g} + {}^4E_g$ Cr ³⁺ : ${}^4A_{2g} \rightarrow {}^4T_{1g}(F)$ (Cr ³⁺ , Fe ³⁺): $({}^4A_{2g}, {}^6A_{1g}) \rightarrow ({}^4T_{2g}, {}^4T_{1g})$
21 200	23 000	21 700	21 100	21 050	22 500	22 400	22 350		
		25 500 ^d	26 400 ^e						
	27 700	27 600			26 800 (sh) ^f	26 700 ^g			
	28 530	28 500							(Cr ³⁺ , Cr ³⁺): $({}^4A_{2g}, {}^4A_{2g}) \rightarrow ({}^2T_{1g}, {}^2T_{1g})$
					29 500				
					30 150				

^a Selected bands only; cf. Table 4. ^b $13\,700 + (4\,900) = 18\,600\text{ cm}^{-1}$. ^c $13\,820 + (5\,580) = 19\,400\text{ cm}^{-1}$. ^d $17\,700 + 9\,200 = 26\,900\text{ cm}^{-1}$. ^e $17\,700 + 9\,000 = 26\,700\text{ cm}^{-1}$. ^f $17\,100 + 10\,300 = 27\,400\text{ cm}^{-1}$. ^g $17\,100 + 10\,000 = 27\,100\text{ cm}^{-1}$.

**Figure 7.** (a) Room-temperature diffuse-reflectance spectra of $[\text{M}^{\text{III}}_3\text{O}(\text{MeCO}_2)_6(\text{py})_3]\text{Cl}$ ($\text{M}_3 = \text{Cr}_3, \text{Cr}_2\text{Fe}, \text{CrFe}_2$, or Fe_3). (b) Absorption spectra of $[\text{M}^{\text{III}}_3\text{O}(\text{MeCO}_2)_6(\text{py})_3]\text{Cl}$ ($\text{M}_3 = \text{Cr}_3, \text{Cr}_2\text{Fe}$, or Fe_3) in ethanol-pyridine (4:1) solution

contrast with the grey-green Cr^{III}_3 and olive-green Fe^{III}_3 analogues, and its solution spectrum [Figure 7(b)] has intense bands at $18\,600$ and $25\,500\text{ cm}^{-1}$ which do not appear to correspond with any bands in the spectra of the Cr_3 and Fe_3 compounds. Both bands shift to higher energy ($19\,400$ and $27\,000\text{ cm}^{-1}$) when py is replaced by H_2O . The $\text{Cr}^{\text{III}}\text{Fe}^{\text{III}}_2$ complex is less distinctive in both its colour (red-brown) and absorption spectrum, and indeed, the spectrum somewhat resembles a superposition of the Cr_2Fe and Fe_3 spectra. The intensities

however, are greater than would be expected from a simple mixture.

Iron(II) spectra. Comparison of the spectra of $\text{Fe}^{\text{III}}_2\text{Fe}^{\text{II}}$, Fe_2Zn , $\text{Cr}^{\text{III}}\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}$, $\text{Cr}_2\text{Fe}^{\text{II}}$, and Cr_2Mg (Figures 5 and 6) reveals the following: (a) the $d-d$ transitions of Fe^{2+} appear in the $\text{Cr}_2\text{Fe}^{\text{II}}$ spectrum as two bands at ca. $8\,500$ and $11\,000\text{ cm}^{-1}$ (typical for this ion in octahedral co-ordination);²⁶ (b) the $\text{Fe}_2\text{Fe}^{\text{II}}$ and $\text{CrFeFe}^{\text{II}}$ spectra are unique in having intense absorption at ca. $7\,000\text{ cm}^{-1}$.

Discussion

Structures.—The question of valence trapping *versus* delocalisation in mixed-valence compounds is a matter of current interest. Trinuclear basic carboxylates of the mixed valence ($M^{III}M^II$) type are now known for V, Cr, Mn, Fe, and Ru, and with only one exception^{10b} the evidence points to a considerable degree of delocalisation (Robin and Day²⁷ Class IIIA). The crystal structures of $[Mn^{III}_2Mn^{II}O(MeCO_2)_6(py)_3] \cdot py^{10a}$ and $[Cr^{III}_2Cr^{II}O(CHF_2CO_2)_6(py)_3] \cdot Et_2O^{11a}$ for example, have been refined in space group $R32$ to R 0.043 and 0.069, respectively, and the X-ray data give no suggestion that disorder is present. However, the observation that at least nine mixed-metal complexes of this type are isomorphous with the above manganese complex is a warning of the readiness with which crystallographic disorder can give rise to the apparent equivalence of chemically distinct metal atoms in this system. It is clear that, in general, valence delocalisation should not be assumed solely on the basis of space-group symmetry unless accurate structural data (including vibrational tensors) or other evidence (e.g. the Mössbauer²⁸ and i.r.²⁹ data for $Fe^{III}_2Fe^{II}$) are available.

The $M-\mu_3-O$ distances in $[M^{III}_3O(RCO_2)_6]^+$, which lie within a fairly narrow range (1.91 ± 0.01 Å for V and Fe, 1.90 ± 0.01 Å for Cr and Mn),^{3,11b,30} increase on average by ca. 0.03 Å when one M^{3+} is replaced by the corresponding M^{2+} .^{10,11a,b} In the only case where the crystal structure clearly indicates trapped valences, $[Mn^{III}_2Mn^{II}O(MeCO_2)_6(3Cl-py)_3]$ ($3Cl-py$ = 3-chloropyridine), the bond lengths are characteristic of the oxidation states, with $M-\mu_3-O$ distances of 1.86, 1.86, and 2.03 Å.^{10b} It thus seems possible that replacement of one Fe^{3+} in Fe^{III}_2 by a divalent ion (e.g. Mn^{2+}) would result in a slightly decreased Fe–O bond length and a slightly increased Fe–O–Fe angle. With smaller divalent ions (Mg^{2+} , Ni^{2+}) the effect would presumably be less pronounced.

Exchange Pathways.—There are two possible superexchange pathways in the $[M_3O(RCO_2)_6]^+$ system: the central O atom and the carboxylate groups. (The metal–metal distance, ca. 3.3 Å, is too great for significant direct overlap.) Although at least 50 papers have been published in which various properties of trinuclear basic carboxylates have been interpreted in terms of exchange, the question of which pathway predominates has received very little discussion, presumably because there seemed no experimental way to answer it. Recently, however, it has been concluded, from the similarity of the exchange parameters in $[Fe_3O(RCO_2)_6]^+$ and $[Fe_3O(SO_4)_6]^{5-}$, that the antiferromagnetic interaction in these complexes arises primarily within the Fe_3O unit.³¹ The approximate doubling of the value of J_{12} which results when one of the M^{3+} ions in $[M^{III}_3O(MeCO_2)_6]^+$ is replaced by a divalent ion (Table 2) provides strong support for this conclusion: although the electron distribution (and possibly the location) of the central oxygen atom could well be altered by such replacement, thereby influencing its effectiveness as an exchange pathway, it is hard to see how changing the charge or radius of the third metal ion could drastically alter the interaction between the first two if this were transmitted largely through their bridging carboxylate groups. Since a similar effect is found in both the chromium(III) (t_{2g}^3) and iron(III) ($t_{2g}^3e_g^2$) cases, it seems clear that the central O atom provides the main pathway for all the important contributions to J . In the following discussion we shall therefore consider only interactions involving the $2s$ and $2p$ orbitals of this atom.

It may be noted that the increase in J_{FeFe} produced by the Mn^{2+} ion is not significantly greater than that produced by the smaller Mg^{2+} and Ni^{2+} ions, suggesting that the effect may be related more to a polarisation of the electron distribution on the O atom than to a change in its location.

The Cr^{III}_3 , Fe^{III}_3 , Cr_2Ni , Fe_2Ni , and Fe_2Mn complexes allow

comparisons of exchange interactions involving different spin configurations. To make these comparisons, we note that in the absence of orbital degeneracy the exchange parameter J_{ij} connecting two ions can be expressed in terms of the individual orbital contributions $J(a_i, b_j)$ by equation (12), where n_i , n_j are

$$J_{ij} = (n_i n_j)^{-1} \sum_{a,b} J(a_i, b_j) \quad (12)$$

the respective numbers of unpaired electrons and a_i , b_j are spin-containing orbitals of the ions i , j .³² For convenience we shall denote $n_i n_j J_{ij} = \sum J(a_i, b_j)$ (previously called the 'net effective exchange integral'^{32c}) by \mathcal{J} . We assume that the negative (antiferromagnetic) terms in \mathcal{J} arise from pairs of metal orbitals which have non-zero overlap with orbitals of the central O atom, and that these terms dominate the overall effect.³³ The positive (ferromagnetic) contributions, arising from orthogonal pairs of magnetic orbitals, are expected to be smaller, though they may be quite numerous.

To determine which overlaps are non-zero we assume approximate D_{3h} symmetry for the M_3O unit. Table 6(a) shows the irreducible representations of this group spanned by the s and p orbitals of the O atom and the d orbitals of the metal atoms. The $d_{x^2-y^2}$ orbitals are orthogonal to all oxygen orbitals, and overlaps involving the d_{xy} orbitals are probably also small. (The $d_{x^2-y^2}$ orbitals overlap with σ orbitals, and the d_{xy} with π orbitals, of the six bridging acetates, but on the experimental grounds discussed above we believe that this pathway is unimportant.) Note that only one term, $J(\varphi_-, \varphi_-)$, involves the oxygen p_z (out-of-plane π) orbital; this term is absent in the Cr–Ni and Fe–Ni cases.

Table 6(b) then lists the main antiferromagnetic contributions to the Cr–Cr, Fe–Fe, Cr–Ni, Fe–Ni, and Fe–Mn exchange interactions, together with the experimentally determined values of \mathcal{J} . (The values selected are such that in each case the third ion is trivalent.) We wish to use these data to infer something about the relative magnitudes of the $J(a,b)$ values, but in doing so we must bear in mind that the ferromagnetic terms have been deliberately omitted, and that each $J(a,b)$ will vary somewhat from one pair of ions to another. This variation is rather difficult to assess, since J depends on both the covalency parameters and electron-transfer energies. Anderson^{32a} suggested an increase of ca. 60% from MnO to NiO, while a calculation by de Jongh and Block³⁴ of superexchange in the linear $M^{2+}-F^- - M^{2+}$ system yields a somewhat smaller increase. The assumption we shall make, which is admittedly arbitrary but we believe reasonably conservative, is that there may be an increase from Cr to Fe and from Mn to Ni, but by a factor not greater than 2 in each case.

We note first that from Cr^{III}_3 to Fe^{III}_3 , $|\mathcal{J}|$ increases from ca. 100 to 750 cm^{-1} , in spite of the greater number of ferromagnetic terms in the latter case. This clearly implies that the additional $\theta\theta$, θt_2 , and $t_2\theta$ terms in \mathcal{J}_{FeFe} are together considerably bigger than the $t_2 t_2$ terms. It would appear that π superexchange, which has been suggested⁷ as the principal cause of antiferromagnetism in $[Cr_3O(MeCO_2)_6(H_2O)_3]^+$, is not a very effective mechanism in the M_3O unit. Next, comparing $|\mathcal{J}_{CrNi}|$ with $|\mathcal{J}_{FeNi}|$, we find a much smaller increase, from ca. 280 to 330 cm^{-1} . This strongly suggests that the $\theta\theta$ term (present in \mathcal{J}_{FeNi} but not in \mathcal{J}_{CrNi}) is smaller than the $t_2\theta$ terms. Finally, comparing $|\mathcal{J}_{FeMn}|$ with $|\mathcal{J}_{FeNi}|$, we can reasonably account for the decrease from ca. 525 to 330 cm^{-1} (in spite of a smaller ferromagnetic contribution) by the presence of θt_2 terms in the former but not in the latter, supporting our previous conclusion that θt_2 overlaps provide the most effective superexchange pathway.

The overall conclusion is that overlaps between d_{x^2} and d_{xz} , d_{yz} orbitals of the metal ions *via* in-plane p orbitals of the central

oxygen atom are the most effective mechanism of superexchange in the M_3O system.

The isoelectronic Fe^{III}_3 and Fe_2Mn complexes provide an opportunity to examine the effect on exchange of removing a unit of nuclear charge from one atom. Comparing J_{FeFe} in Fe^{III}_3 with J_{FeMn} in Fe_2Mn (where in both cases the third ion is Fe^{3+}), we see a reduction of about 30% in the value of J for the d^5-d^5 interaction. This is somewhat surprising, in view of recent evidence that replacement of both Cr^{3+} ions in $[Cr_2Cl_6]^{3-}$ by the isoelectronic V^{2+} results in an increase in the strength of the d^3-d^3 interaction by an order of magnitude,^{35,36} which was attributed to expansion of the magnetic orbitals resulting from the decrease in nuclear charge. The opposite behaviour in the Fe^{III}_3 vs. Fe_2Mn^{II} comparison may be due to a greater $Mn^{II}-O$ bond length compared with $Fe^{III}-O$. It may, however, be a consequence of the fact that only one nuclear charge has been reduced in this case; the resulting mismatch between the energies of the magnetic orbitals on the interacting ions is expected to reduce all the antiferromagnetic interactions considerably without directly affecting the ferromagnetic terms.^{32d}

Spectra.—Generally speaking, all the electronic spectra can be interpreted in terms of transitions of the individual metal ions in the appropriate ligand environment. However, distinctive and significant effects do arise from interactions among the three ions in the complex.

From Figure 5 and Table 3 it can be seen that replacement of one Cr^{3+} in Cr^{III}_3 by a divalent ion (Mg^{2+} or Ni^{2+}) reduces the average ligand field at the chromium(III) sites by ca. 6% (twice the reduction produced by replacement of the pyridine by a water molecule), and reduces β_{35} substantially (from an already rather low value). This is not what would have been expected from a decrease in the $Cr-O$ distance, but might be accounted for by the lower effective electronegativity of the bridging $O-M^{II}$ 'ligand,' together with a polarisation of its electron density away from M^{2+} and towards the region between the two Cr^{3+} ions, leading to a general increase in covalency and a particular increase in the overlap between the oxygen $2p$ and chromium d_{xz}, d_{yz} orbitals. The accompanying increase in the exchange parameter J_{CrCr} can also be understood on this basis.

One well recognised consequence of exchange in a condensed system is a marked increase in the intensities of transitions which are spin forbidden for the single ions. An example is the band of Fe_2Ni at $12\,900\text{ cm}^{-1}$ which we identify as a transition of the type $(^6A_{1g}, ^6A_{1g}, ^3A_{2g}) \rightarrow (^6A_{1g}, ^6A_{1g}, ^1E_g)$ (using approximate local O_h symmetry). The ground manifold is split by exchange into levels (S, S_{12}) with $S = 1-6$, the magnetic data indicating that the (1,0) level lies lowest, and the excited manifold will be split into spin levels with $S = S_{12} = 1-5$, presumably with J_{12} not very different from its ground-state value. The observed band must then correspond to one or more transitions satisfying the selection rule $\Delta S = 0$.³⁷ Its intensity is similar to that of the spin-allowed $^3A_{2g} \rightarrow ^3T_{2g}$ transition, whereas in Cr^{III}_3 the $(^4A_{2g}, ^4A_{2g}, ^4A_{2g}) \rightarrow (^4A_{2g}, ^4A_{2g}, ^2T_{1g})$ transition, though greatly enhanced, is an order of magnitude less intense than the spin-allowed bands.⁷ However, it has been shown that intensity enhancement of such excitations in pair spectra is much more pronounced in the case of unlike ions than like ions.^{37b} Note that in the Fe_2Ni case we also expect the selection rule $\Delta S_{12} = 0$ to operate. This would allow only the transition from the (1,1) level, which, according to magnetic evidence, lies ca. 80 cm^{-1} above the ground level. We have not been able to measure the spectrum at a sufficiently low temperature to test this hypothesis.

In the iron(III) spectra all $d-d$ transitions are spin forbidden for the single ions, and the considerable intensities observed probably involve an exchange mechanism. Our assignment

(Table 4) differs from that of Dubicki and Martin⁵ (who assigned the band at $18\,000\text{ cm}^{-1}$ as the 'spin flip' v_3), but agrees with that of Ferguson and Fielding³⁸ for iron(III) pairs in sapphire, in that we assign the band at $18\,000\text{ cm}^{-1}$ as a simultaneous pair excitation (s.p.e.) of two Fe^{3+} ions to the $^4T_{1g}$ (G) level. Although its energy is less than $2v_1$ by some 10^3 cm^{-1} , the difference could be accounted for by strongly antiferromagnetic coupling in the $(^6A_{1g}, ^4T_{1g}, ^4T_{1g})$ state.³⁸ Some of the higher-energy bands may also involve s.p.e.

The anomalous colour of complexes containing both Cr^{III} and Fe^{III} was first noticed in the series $[M^{III}_3O(MeCO_2)_6(H_2O)_3]^+$ by Weinland and Gussmann,¹⁵ who recognised it as evidence that these products contain mixed-metal complex cations. It is difficult to account for the intense bands which dominate these spectra. We have considered the possibility of electron transfer from Cr^{3+} to Fe^{3+} , but even allowing for the electrostatic stabilisation we believe this would occur at much too high an energy (ca. 10^5 cm^{-1}). The only explanation we can think of is that these bands are due to simultaneous (Cr^{3+}, Fe^{3+}) double excitations. Pair transitions in the Cr^{III}_3 complexes are clearly visible at room temperature, with intensities ca. 5–10% of those of the spin-allowed bands,⁷ and it is known that the oscillator strengths for such double excitations increase with the strength of the exchange³⁵ and are greatly increased (up to 100-fold) when the two ions are dissimilar,^{37c} so this hypothesis is not automatically ruled out by the observed intensities. A difficulty is presented by the low energy of the band of $Cr^{III}_2Fe^{III}$ at $19\,000\text{ cm}^{-1}$: assuming that the latter involved a chromium(III) $^4A_{2g} \rightarrow ^2T_{1g}$ excitation, the associated iron(III) excitation would have to have an energy of ca. $4\,900$ ($L = \text{py}$) or $5\,600\text{ cm}^{-1}$ ($L = H_2O$). A possible assignment is $(^4A_{2g}, ^4A_{2g}, ^6A_{1g}) \rightarrow (^4A_{2g}, ^2T_{1g}, ^2T_{2g})$: the $^2T_{2g}(t_{2g}^5)$ term of Fe^{3+} may well be in this region, and its energy would be expected to increase sharply as Dq decreased. In any case, it is clear that this interesting spectrum merits a more detailed experimental and theoretical investigation.

We turn now to the two mixed-valence complexes, $Fe^{III}_2Fe^{II}$ and $CrFe^{III}Fe^{II}$. The iron compounds ($L = H_2O$ or py) have been the subject of several studies,^{28,29} the balance of evidence indicating behaviour intermediate between Classes II and III,²⁷ with trapped valences but shallow energy minima, so that at room temperature thermal electron transfer causes the oxidation states to be equivalent on the Mössbauer²⁸ but not on the i.r. time-scale.²⁹ Dziobkowski *et al.*^{28b} reported the diffuse-reflectance spectrum of the Fe_2Fe^{II} aqua-complex, and assigned an absorption maximum at $13\,800\text{ cm}^{-1}$ to intervalence transfer. Our comparison of spectra in the pyridine series leads us to assign the band at $7\,000\text{ cm}^{-1}$ as the primary $Fe^{2+} \rightarrow Fe^{3+}$ intervalence transition. The splitting of ca. $1\,500\text{ cm}^{-1}$ observed in this band may be related to the expected splitting of the $^5T_{2g}$ term of Fe^{2+} into 5B_2 and 5E in C_{4v} symmetry, corresponding to electron transfer into the d_{xy} and d_{xz}, d_{yz} orbitals, respectively. A similar interpretation has been made of the spectra of mixed-valence dimeric ferrocene cations, which show a band at $5\,000-7\,000\text{ cm}^{-1}$, slightly split in some cases.³⁹

Conclusions

Complexes of the types $[Cr^{III}_3M^{II}O(MeCO_2)_6L_3]$, $[Fe^{III}_2M^{II}O(MeCO_2)_6L_3]$, and $[Cr^{III}Fe^{III}M^{II}O(MeCO_2)_6L_3]$ exhibit antiferromagnetic exchange interactions, the magnitudes of which have been estimated for the $Cr^{III}-Cr^{III}$, $Cr^{III}-Ni^{II}$, $Fe^{III}-Fe^{III}$, $Fe^{III}-Mn^{II}$, and $Fe^{III}-Ni^{II}$ pairs. The strength of the $M^{III}-M^{III}$ interaction is approximately independent of the nature of M^{II} , but is increased by a factor of about 2 compared with its value in the M^{III}_3 analogues, strong evidence that the central O atom provides the main superexchange pathway. The values of the exchange parameters suggest that the in-plane p orbitals of this

Table 8. Results of chemical analysis, with calculated values in parentheses

	M ^{II}	n	C	H	N	Fe	M
[Fe₂MO(MeCO₂)₆(H₂O)₃].nH₂O							
	Mg	2	24.0 (24.2)	4.8 (4.7)		18.7 (18.7)	
	Mn	3	22.3 (22.3)	4.4 (4.7)		17.7 (17.3)	
	Co	3	22.7 (22.2)	4.6 (4.7)		17.4 (17.2)	8.75 (9.1)
	Ni	3	22.3 (22.2)	4.4 (4.7)		17.1 (17.2)	9.3 (9.05)
	Zn	3	21.9 (22.0)	4.3 (4.6)		17.6 (17.0)	
[Fe₂MO(MeCO₂)₆(py)₃].npy							
	Mg	1	46.6 (46.7)	4.7 (4.6)	6.8 (6.8)	13.7 (13.6)	2.7 (3.0)
	Mn	1	44.6 (45.0)	4.45 (4.5)	6.6 (6.6)	13.0 (13.1)	6.4 (6.4)
	Mn	0	41.45 (41.9)	4.3 (4.3)	5.85 (5.4)		
	Fe	0.5	43.9 (43.5)	4.4 (4.4)	6.3 (6.0)	20.35 (20.6)	
	Co	1	44.5 (44.8)	4.5 (4.5)	6.4 (6.5)	13.3 (13.0)	6.7 (6.9)
	Ni	1	44.75 (44.8)	4.4 (4.5)	6.45 (6.5)	13.3 (13.0)	6.65 (6.85)
	Zn	1	44.0 (44.5)	4.4 (4.4)	6.5 (6.5)	13.1 (12.9)	
[Cr₂MO(MeCO₂)₆(py)₃].npy							
	Mg	0.8	46.7 (46.6)	4.8 (4.7)	6.7 (6.7)		
	Fe	1	45.35 (45.4)	4.4 (4.5)	6.5 (6.6)	6.7 (6.6)	
	Co	1	44.9 (45.2)	4.4 (4.5)	6.6 (6.6)		
	Ni	1	45.0 (45.3)	4.5 (4.5)	6.95 (6.6)		
[CrFeMO(MeCO₂)₆(py)₃].npy							
	Mn	0.7	44.1 (44.2)	4.4 (4.45)	6.2 (6.2)		
	Fe	1	45.2 (45.2)	4.5 (4.5)	6.6 (6.6)	13.3 (13.15)	
	Co	1	44.25 (44.8)	4.4 (4.5)	6.7 (6.5)		
	Ni	1	45.2 (45.0)	4.4 (4.5)	6.5 (6.55)	6.9 (6.9)	

atom are especially effective in this respect. Electronic interactions between the ions also manifest themselves in the absorption spectra, in particular in the $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ intervalence transition, identified at $7\,000\text{ cm}^{-1}$, and in intense bands in the visible region attributed to simultaneous excitation of Cr^{3+} , Fe^{3+} pairs.

Experimental

Preparation of Compounds.—All materials were reagent grade, except for chromium metal (Koch-Light 99.9%). The compound $[\text{Fe}^{\text{III}}_2\text{Fe}^{\text{II}}\text{O}(\text{MeCO}_2)_6(\text{H}_2\text{O})_3]\cdot 2\text{H}_2\text{O}$ was prepared by the method of Chrétien and Lous.⁹ Chromium(II) acetate monohydrate was prepared by addition of an excess of sodium acetate dissolved in oxygen-free water to a solution of chromium(II) chloride (obtained by reaction of pure chromium flake with dilute hydrochloric acid at 65°C and removal of excess of metal); the precipitate was filtered off, washed with water and acetone, and dried, all in an atmosphere of nitrogen, and stored under nitrogen until required.

$[\text{Fe}_2\text{M}^{\text{II}}\text{O}(\text{MeCO}_2)_6(\text{H}_2\text{O})_3]\cdot n\text{H}_2\text{O}$ ($\text{M} = \text{Mn, Co, Ni, or Zn; } n = 3$). These compounds were prepared by the method of Weinland and Holtmeier.¹² A solution of sodium acetate trihydrate (42 g, 0.31 mol) in water (70 cm^3) was added to a filtered, stirred solution of iron(III) nitrate nonahydrate (8 g, 0.02 mol) and the metal(II) nitrate (0.1 mol) in water (70 cm^3), and the brown precipitate was filtered off, washed with water and with ethanol, and dried in air. (For $\text{M} = \text{Zn}$, the total volume of water used in the preparation was restricted to 70 cm^3 .) For $\text{M} = \text{Mg}$ ($n = 2$), sodium acetate trihydrate (11 g, 0.076 mol) in water (8 cm^3) was added to a solution of magnesium chloride hexahydrate (2 g, 0.01 mol) in water (9 cm^3); a red-brown precipitate appeared overnight.

$[\text{Fe}_2\text{M}^{\text{II}}\text{O}(\text{MeCO}_2)_6(\text{py})_3]\cdot n\text{py}$ ($\text{M} = \text{Mn, } n = 0 \text{ or } 1$; $\text{M} = \text{Fe, } n = 0.5$; $\text{M} = \text{Mg, Co, or Ni, } n = 1$). These were

obtained¹² by dissolving the aqua-complex (2 g) in hot pyridine (25 cm^3); well formed shiny black *crystals* appeared after 2–4 d at room temperature, and were removed, washed with pyridine, and dried in air. For $\text{M} = \text{Zn}$ ($n = 1$), zinc acetate dihydrate (0.6 g) and $[\text{Fe}_2\text{ZnO}(\text{MeCO}_2)_6(\text{H}_2\text{O})_3]\cdot 3\text{H}_2\text{O}$ (2.0 g) were dissolved in pyridine (25 cm^3) by heating, and the solution filtered. Black *crystals* separated after 12 d.

$[\text{Cr}_2\text{M}^{\text{II}}\text{O}(\text{MeCO}_2)_6(\text{py})_3]\cdot n\text{py}$. For $\text{M} = \text{Mg}$ ($n = 0.8$), chromium(II) acetate monohydrate (1.3 g, 7 mmol) was dissolved in pyridine (20 cm^3) by heating in air. Magnesium acetate tetrahydrate (0.85 g, 4 mmol) dissolved in water (2 cm^3) was added, and the deep green solution was heated for 5 min and cooled. Green *crystals* separated after 2 weeks, and were filtered off, washed with pyridine, and dried in air. The filtrate was evaporated to dryness at room temperature, the solid redissolved in hot pyridine (15 cm^3), and the solution filtered. More large green crystals appeared after 2 weeks. For $\text{M} = \text{Fe}$ ($n = 1$), chromium(II) acetate monohydrate (1.5 g, 8 mmol) was added under nitrogen to a solution of $[\text{Fe}^{\text{III}}_2\text{Fe}^{\text{II}}\text{O}(\text{MeCO}_2)_6(\text{py})_3]\cdot 0.5\text{py}$ (2.3 g, 2.8 mmol) in pyridine (30 cm^3). The mixture was refluxed for 1 h, filtered, and allowed to stand for 1 week. Shiny black *crystals* were filtered off, washed with pyridine, and dried *in vacuo*. Qualitative tests confirmed the presence of Cr^{III} and Fe^{II} and the absence of Fe^{III} . For $\text{M} = \text{Co or Ni}$ ($n = 1$), chromium(II) acetate monohydrate (1.5 g, 8 mmol) was dissolved in pyridine (25 cm^3) by heating in air. Cobalt(II) or nickel(II) acetate tetrahydrate (0.7 g, 2.8 mmol) dissolved in water (3 cm^3) was added, and the solution was evaporated to dryness. The solid was redissolved in hot pyridine (15 cm^3), and the solution filtered and allowed to stand. Dark green *crystals* separated after 3–7 d.

$[\text{CrFeM}^{\text{II}}\text{O}(\text{MeCO}_2)_6(\text{py})_3]\cdot n\text{py}$. For $\text{M} = \text{Mn}$ ($n = 0.7$), chromium(II) acetate monohydrate (0.6 g, 3.2 mmol) was added in small portions to a solution of $[\text{Fe}_2\text{MnO}(\text{MeCO}_2)_6(\text{H}_2\text{O})_3]\cdot 3\text{H}_2\text{O}$ (2.0 g, 3.1 mmol) in pyridine (30 cm^3), and the solution

was heated for 15 min then filtered. After 5 d the dark purple precipitate was filtered off, washed with pyridine, redissolved in warm pyridine (20 cm³), and the solution filtered and set aside. Black crystals separated after 4 weeks. For M = Fe (*n* = 1), [Fe^{III}₂Fe^{II}O(MeCO₂)₆(py)₃].0.5py (3.1 g, 3.8 mmol), dissolved in pyridine (60 cm³) by heating, was added to chromium(II) acetate monohydrate (0.72 g, 3.8 mmol) under nitrogen, and the resulting brown solution was heated for 1 h with reflux under nitrogen and allowed to stand overnight. A small quantity of green crystals was redissolved by heating, and the solution was left for a further 2 d. Black crystals were filtered off, washed several times with pyridine to remove a few remaining small green crystals, and dried in a stream of nitrogen. Qualitative tests confirmed the presence of Cr^{III}, Fe^{III}, and Fe^{II}. For M = Co (*n* = 1), chromium(II) acetate monohydrate (0.54 g, 2.9 mmol) was added to a solution of [Fe₃CoO(OH)₃(MeCO₂)₆].7H₂O¹² (1.3 g, 1.7 mmol) and cobalt(II) acetate tetrahydrate (0.2 g, 0.8 mmol) in pyridine (30 cm³), and after heating to 120 °C for 10 min the solution was filtered and set aside. Large black crystals appeared after 10 d. For M = Ni (*n* = 1), the preparation was as for the manganese compound, but pyridine (35 cm³) was used for the recrystallisation. Large black crystals were removed after 4 d, and on concentration to 15 cm³ the filtrate yielded further crystals after 3 d.

Chemical Analysis.—Determination of C, H, and N was by the microanalytical service of the London School of Pharmacy. Fe, Mg, Mn, Co, and Ni were determined by titration with ethylenediaminetetra-acetate or by atomic absorption spectrophotometry. All compounds gave satisfactory analytical results (Table 8).

Magnetic Measurements.—Magnetic susceptibilities of finely powdered samples were measured between 4.2 and 90 K at 1.00 T by means of a Princeton Applied Research model 155 vibrating-sample magnetometer as previously described,⁴⁰ and between 80 and 300 K by the Faraday method (Fe₂Ni) or the Gouy method (Fe₂Ni, L = H₂O; Fe₂Mg, Fe₂Mn). Corrections were applied for diamagnetism, 5.0 (L = py) or 3.3 mm³ (L = H₂O) per mol of complex, calculated from Pascal constants, and for temperature-independent paramagnetism, 1.6 (Cr³⁺), 1.3 (Co²⁺), and 2.5 mm³ (Ni²⁺) per mol of metal ion, calculated from $\chi_{\text{tip}} = 8N_A\mu_0\mu_B^2/\Delta$. The corrected data are listed in SUP 56342.

X-Ray Crystallography.—To establish isomorphism and determine unit cells and space groups, crystals were sealed in Lindemann glass capillaries and precession photographs of several reciprocal-lattice nets were taken with Mo-K_α radiation.

Spectroscopy.—Spectra were recorded on a Unicam SP700 instrument equipped with a SP735 diffuse-reflectance attachment. Magnesium oxide was used as reference, and the wave-number scale was calibrated against standard rare-earth-metal oxide glass filters.

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