

Exchange Interactions in a Series of Novel Heteronuclear Basic Carboxylate Complexes containing Two Iron(III) Ions and a Divalent Metal Ion

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Summary Complexes $[\text{Fe}_2^{\text{III}}\text{M}^{\text{II}}\text{O}(\text{MeCO}_2)_6\text{py}_3]\text{py}$ ($\text{M} = \text{Mg, Mn, Co, Ni, or Zn}$; $\text{py} = \text{pyridine}$), isomorphous (except for $\text{M} = \text{Ni}$) with the mixed-valence compounds $[\text{M}_3\text{O}(\text{MeCO}_2)_6\text{py}_3]\text{py}$ ($\text{M} = \text{Mn or Fe}$), are reported; their magnetic properties provide new information about superexchange pathways in the trinuclear basic carboxylate system.

THE mixed-valence trinuclear complexes $[\text{M}_2^{\text{III}}\text{M}^{\text{II}}\text{O}(\text{MeCO}_2)_6\text{py}_3]\text{py}$ [(**1a**) $\text{M} = \text{Mn}$, (**1b**) $\text{M} = \text{Fe}$; $\text{py} = \text{pyridine}$] have recently been the subject of structural, magnetic, and Mössbauer studies.¹⁻⁴ The two compounds are isomorphous, with a rhombohedral unit cell containing a single molecule in which the three metal atoms are crystallographically equivalent.² We now report the characterisation and preliminary magnetic investigation of a series of analogous mixed-metal trinuclear complexes with the general formulae $[\text{Fe}_2^{\text{III}}\text{M}^{\text{II}}\text{O}(\text{MeCO}_2)_6(\text{H}_2\text{O})_3] \cdot 3\text{H}_2\text{O}$ (**2**) and $[\text{Fe}_2^{\text{III}}\text{M}^{\text{II}}\text{O}(\text{MeCO}_2)_6\text{py}_3]\text{py}$, (**3**) ($\text{M} = \text{Mg, Mn, Co, Ni, or Zn}$).

The compounds (**2**; $\text{M} = \text{Co, Ni, or Zn}$) and (**3**; $\text{M} = \text{Co or Ni}$) were in fact first prepared over 50 years ago by Weinland and Holtmeier,⁵ who assigned to them formulae

such as $\text{M}_4^{\text{II}}[\text{Fe}_6^{\text{III}}(\text{OH})_9(\text{MeCO}_2)_{26}] \cdot 23\text{H}_2\text{O}$ and $\text{M}_3^{\text{II}}[\text{Fe}_6^{\text{III}}\text{O}_3(\text{OH})(\text{MeCO}_2)_{17}] \cdot 12\text{py}$, and believed them to contain Fe_3^{III} units of the type found in basic iron(III) acetate. Following the procedures described,⁵ we have obtained crystalline products for which analytical data are in agreement with formulae (**2**) and (**3**). Moreover, we find that the four compounds (**3**; $\text{M} = \text{Mg, Mn, Co, or Zn}$) are isomorphous with (**1**), and therefore contain trinuclear molecules in which the three metal atoms Fe_2M are crystallographically equivalent.† This equivalence, which implies a threefold disorder of the Fe_2M triangles, is not found in (**3**; $\text{M} = \text{Ni}$), crystals of this compound being monoclinic ($a = 22.14$, $b = 12.52$, $c = 16.03 \text{ \AA}$, $\beta = 117.2^\circ$, $Z = 4$, $D_c = 1.44 \text{ g cm}^{-3}$, space group Cc or $C2/c$).

The diffuse reflectance spectrum of the olive-green compound (**3**; $\text{M} = \text{Mg}$) is similar to that of $[\text{Fe}_3\text{O}(\text{MeCO}_2)_6\text{py}_3]\text{Cl}$, and has absorption bands at 9800, 17,200, and 21,100 cm^{-1} , which we tentatively assign⁶ to the transitions from ${}^6\text{A}_{1g}$ to ${}^4\text{T}_{2g}$, ${}^4\text{T}_{1g}$, and ${}^4\text{A}_{1g} + {}^4\text{E}_g(\text{G})$, respectively, of Fe^{3+} in pseudo-octahedral symmetry (spin-forbidden but enhanced in intensity by the exchange interaction); replacement of py by H_2O shifts the first two bands to higher energies (10,000 and 19,000 cm^{-1}) while the third

† Isomorphism with (**1**) was established in each case by single-crystal precession photographs of several reciprocal-lattice nets. In the Fe_2Co case, the crystal examined was afterwards analysed for iron by atomic absorption spectrometry (Fe found 13.3, calculated 13.0%), in order to eliminate the possibility that the crystal selected was actually of (**1b**) present as an impurity. We thank Dr. J. R. Chipperfield and Mr. S. Clark for this analysis.

is unaffected. The spectrum of the olive-green (**3**; M = Ni) is similar (with an additional band at 12,900 cm⁻¹), but the deep-brown-black (**3**; M = Mn) has strong absorption over the whole region between 9600 and 17,000 cm⁻¹,

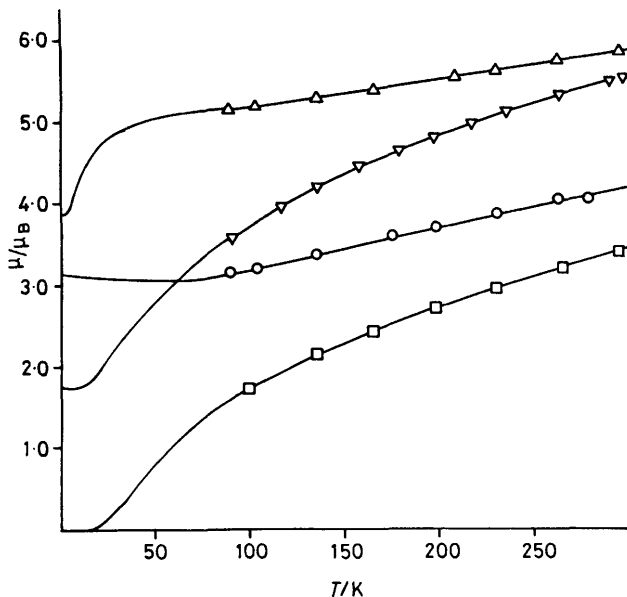


FIGURE. Effective magnetic moment per trinuclear molecule, with calculated^{†§} curves: □ (**3**; M = Mg) ($g = 2$, $J = -62.5$ cm⁻¹); △ (**3**; M = Mn) ($g = 2$, $J = -64.8$, $J' = -20.6$ cm⁻¹); ▽ [$\text{Fe}_3\text{O}(\text{O}_2\text{CMe})_6(\text{H}_2\text{O})_3\text{Cl}\cdot 2\text{H}_2\text{O}$] ($g = 2$, $J = -38.2$, $J' = -28.9$ cm⁻¹); ○ (**2**; M = Ni) ($g = 2$, $g' = 2.2$, $J = -71.7$, $J' = -21.0$ cm⁻¹).

† The Hamiltonian used was $\mathcal{H} = -2J\mathbf{S}_1 \cdot \mathbf{S}_2 - 2J'\mathbf{S}_3 \cdot (\mathbf{S}_1 + \mathbf{S}_2) + [g(S_{z1} + S_{z2}) + g'S_{z3}]\mu_B H$ with zero-field energy levels given by $E_0(S, S_{12}) = J[17.5 - S_{12}(S_{12} + 1)] + J'[S_3(S_3 + 1) + S_{12}(S_{12} + 1) - S(S + 1)]$, where $\mathbf{S}_{12} = \mathbf{S}_1 + \mathbf{S}_2$, $\mathbf{S} = \mathbf{S}_{12} + \mathbf{S}_3$, and $S_3 = 5/2, 1$, and 0 for $M = \text{Mn}, \text{Ni}$, and Mg , respectively. If $g = g'$, \mathcal{H} commutes with S^2 , S_z , and S_{12}^2 , and the susceptibility can be calculated from the first-order Zeeman coefficients $E_1(S, M_s) = M_s g \mu_B$. For $M = \text{Mg}$ or Mn , we assumed $g = 2.00$, and started least-squares fitting with trial values $J = J' = -30$ cm⁻¹, the value found (refs. 7–9) in $[\text{Fe}_3^{\text{III}}\text{O}(\text{O}_2\text{CMe})_6(\text{H}_2\text{O})_3]^+$.

For $M = \text{Ni}$, g' is likely to differ significantly from g , and the Zeeman part of \mathcal{H} then does not commute with S^2 . This part was therefore treated as a perturbation, *i.e.* its matrix elements in the zero-field basis (S, S_{12}, M_s) were used in the Van Vleck equation, with the assumptions $g = 2$, $g' = 2.2$, temperature-independent paramagnetism = 180×10^{-6} cm³ mol⁻¹. Some 15% of the susceptibility is contributed by terms involving $g - g'$.

§ In order to confirm the rather unexpected difference between the J values of (**3**) and that of $[\text{Fe}_3\text{O}(\text{O}_2\text{CMe})_6(\text{H}_2\text{O})_3]^+$, we fitted published data (ref. 7) for the latter, using the same computer program and susceptibility expression as for (**3**; M = Mn). The result agreed with the values found in a 20–300 K study (ref. 8). The best fit to a single- J expression was given by $J = -29.2$ cm⁻¹, in agreement with ref. 7 and a recent re-evaluation (ref. 9).

which we attribute to optical electron transfer from Mn²⁺ to Fe³⁺.

Preliminary magnetic susceptibility measurements (90–300 K) on those compounds where the interpretation is not complicated by orbital magnetism have yielded interesting information on superexchange in the trinuclear basic carboxylate system. The Figure shows observed magnetic moments and calculated curves, from which the following conclusions can be drawn.† (a) The exchange parameter J for spin coupling between the Fe³⁺ ions is almost independent of the divalent ion M [$J = -63$ cm⁻¹ for (**3**; M = Mg); -65 cm⁻¹ for (**3**; M = Mn); -72 cm⁻¹ for (**2**; M = Ni)] but is approximately twice as great as that in the cation $[\text{Fe}_3^{\text{III}}\text{O}(\text{MeCO}_2)_6(\text{H}_2\text{O})_3]^+$ (*ca.* -30 cm⁻¹).§ Since the third metal ion is unlikely to have much influence on the acetate ligands bridging the first two, this remarkable difference strongly suggests that the central O atom provides the main superexchange pathway. (b) The Fe³⁺–Mn²⁺ interaction in (**3**; M = Mn) is much weaker ($J = -20$ cm⁻¹) than the Fe³⁺–Fe³⁺ interaction, a difference which, since the electron configurations are the same, evidently reflects the quantitative influence of effective nuclear charge in the superexchange mechanism. (c) The J values for the Fe³⁺–M²⁺ interaction in (**3**; M = Mn) ($t_{2g}^3 e_g^2$), and (**2**; M = Ni) ($t_{2g}^6 e_g^2$), are similar (*ca.* -20 cm⁻¹). We infer that both σ - and π -overlaps with the central O atom play a part in the superexchange.

We are grateful to Dr. L. F. Larkworthy for the use of magnetic susceptibility equipment at the University of Surrey, and to the S.R.C. for financial support.

(Received, 16th April 1981; Com. 454.)

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