

Heterotrinnuclear Basic Acetates containing Chromium(III), Iron(III), and a Divalent Metal: Spectroscopic Consequences of Metal–Metal Interactions

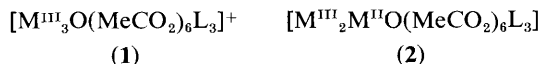
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Complexes $[\text{Cr}^{\text{III}}_2\text{M}^{\text{II}}\text{O}(\text{MeCO}_2)_6\text{py}_3]$ ($\text{M} = \text{Mg, Fe, Co, or Ni}$) and $[\text{Cr}^{\text{III}}\text{Fe}^{\text{III}}\text{M}^{\text{II}}\text{O}(\text{MeCO}_2)_6\text{py}_3]$ ($\text{M} = \text{Mn, Fe, Co, or Ni}$; $\text{py} = \text{pyridine}$) are reported; their absorption spectra, together with those of the analogous $\text{Fe}_2^{\text{III}}\text{M}^{\text{II}}$ complexes, provide new information about electronic properties of the M_3O system.

The series of oxo-centred, trinuclear cationic complexes $[\text{M}^{\text{III}}_3\text{O}(\text{MeCO}_2)_6\text{L}_3]^+$ (**1**) ($\text{M} = \text{V, Cr, Mn, Fe, or Rh}$)[†] has in recent years been extended by the preparation and structural characterisation of a number of mixed-valence and

mixed-metal neutral complexes $[M^{III}_2M^{II}O(MeCO_2)_6L_3]$ (**2a**) ($M^{III} = M^{II} = Mn$)² and (**2b**) ($M^{III} = Fe, M^{II} = Mg, Mn, Fe, Co, Ni, Cu, \text{ or } Zn$)^{3,4}. We now report some new members of the class (**2**), of formulae $[Cr^{III}_2M^{II}O(MeCO_2)_6L_3]$ (**2c**) ($M^{II} = Mg, Fe, Co, \text{ or } Ni$ with $L = py$; $M^{II} = Mn$ or Zn with $L_3 = py + 2H_2O$) and $[Cr^{III}Fe^{II}M^{II}O(MeCO_2)_6py_3]$ (**2d**) ($M^{II} = Mn, Fe, Co, \text{ or } Ni$).[†]



The Cr_2M^{II} complexes (except $M^{II} = Fe$) were obtained by warming the divalent metal acetate, and the Cr_2Fe^{II} and $CrFeM^{II}$ complexes by warming the Fe_2M^{II} complex (**2b**), with chromium(II) acetate in pyridine (under nitrogen in the Fe^{II} cases), and were recrystallised from pyridine. Precession photographs establish that (**2c**; $M^{II} = Fe$ or Co) and (**2d**; $M^{II} = Mn, Fe, \text{ or } Co$), like their Fe_2M^{II} analogues,⁴ have the rhombohedral crystal structure of (**2a**) in which the three metal atoms are crystallographically equivalent,² whereas the complexes with $M^{II} = Mg$ or Ni are monoclinic and isomorphous with the Fe_2Ni analogue.⁴

The compounds (**2**) now constitute by far the largest family of isostructural, heteronuclear complexes known, and offer a rich field for investigation of the magnetic and spectroscopic consequences of electronic communication between different transition-metal ions. Examination of their diffuse reflectance spectra (Figures 1 and 2) leads to several interesting observations.

(a) *d-d spectra*: (i) Replacement of one trivalent ion in (**1**) ($M = Cr$ or Fe) by a divalent ion significantly reduces the

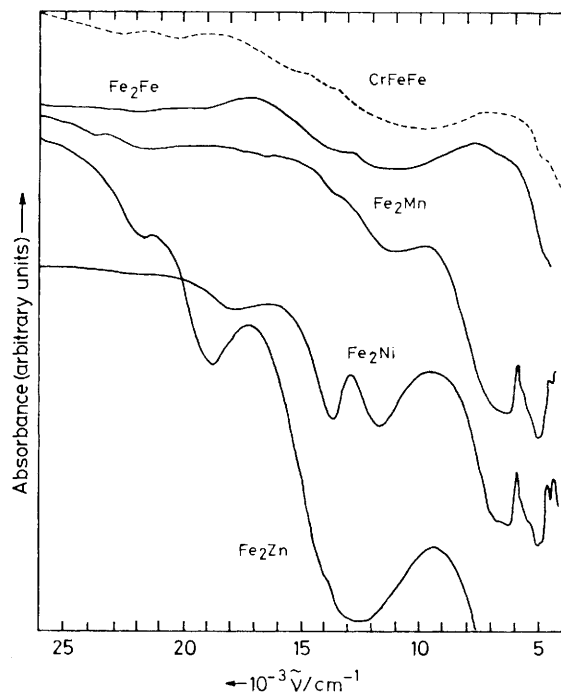


Figure 1. Room-temperature diffuse reflectance spectra of $[Fe^{III}_2M^{II}O(MeCO_2)_6py_3]$ and the $CrFeFe^{II}$ analogue.

average ligand field at the remaining M^{3+} ions. Thus, the bands assigned to ${}^4A_{2g} \rightarrow {}^4T_{2g}$ and ${}^4T_{1g}(F)$ of Cr^{3+} (octahedral) which occur at 17 600 and 23 000 cm^{-1} in (**1**; $M = Cr, L = py$) and at 17 300 and 22 800 cm^{-1} in (**1**; $M = Cr, L = H_2O$) appear at only 16 700 and 21 200 cm^{-1} in (**2c**; $M^{II} = Mg$); while the band assigned to ${}^6A_{1g} \rightarrow {}^4T_{1g}$ of Fe^{3+} which lies at 9150 cm^{-1} in (**1**; $M = Fe, L = py$) is found at 9400 cm^{-1} in (**2b**; $M^{II} = Zn, L = py$). (This transition increases in energy as Dq is reduced.) The reduction in the average ligand field is accompanied by an increase in the strength of $M^{III}-M^{III}$ super-exchange,⁴ suggesting that both effects may be consequences of an increase in $M^{III}-O-M^{III}$ π -bonding. (ii) The spin-forbidden ${}^3A_{2g} \rightarrow {}^1E_g(D)$ transition of Ni^{2+} in the Fe_2Ni complex, which we identify with the prominent band at 12 900 cm^{-1} (Figure 1), is of remarkably high intensity, comparable with that of the first spin-allowed band,[‡] presumably as a result of the $Fe-Ni$ exchange interaction.^{4,5}

(b) *Metal-to-metal electron transfer*: A band at 13 800 cm^{-1} in the spectrum of (**2b**; $M^{II} = Fe, L = H_2O$) has been attributed to $Fe^{2+} \rightarrow Fe^{3+}$ intervalence transfer.⁶ With the availability of $Fe_2Fe, Fe_2Zn, CrFeFe, Cr_2Fe,$ and Cr_2Mg spectra for comparison, a more confident appraisal should be possible. Surprisingly, inspection of Figures 1 and 2 reveals that the $Fe^{III}_2Fe^{II}$ complex ($L = py$) has an additional strong absorption at 6000–7000 cm^{-1} (as does $CrFeFe^{II}$), as well as at *ca.* 13 000 and 17 000 cm^{-1} , the latter being responsible for its dark brown colour, unlike the green of Fe_2Zn . We suggest that the 6000 cm^{-1} band is the primary intervalence transition, the other absorptions perhaps arising from electron transfer coupled with electronic excitation of

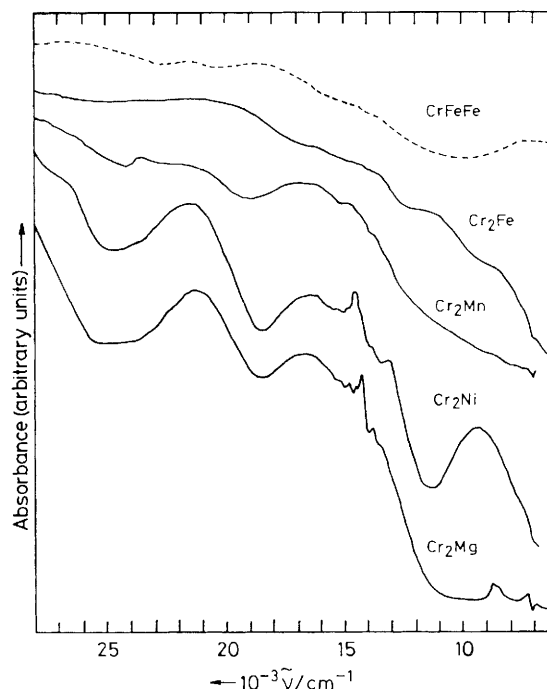


Figure 2. Room-temperature diffuse reflectance spectra of $[Cr^{III}_2M^{II}O(MeCO_2)_6py_3]$ and the $CrFeFe^{II}$ analogue.

[†] $py =$ pyridine. Crystals of (**2**) ($L = py$ or H_2O) always contain additional molecules of non-co-ordinated py (0.5–1) or H_2O (2–3), respectively, which we omit from formulae. Satisfactory analyses for C, H, N, and Fe were obtained. In the case of (**2d**), their colours (see below) indicate that they are not merely mixed crystals of the corresponding (**2b**) and (**2c**), although these molecules may also be present in the crystals.

[‡] Assuming that the Ni^{2+} bands occur at the same energies in the Cr_2Ni and Fe_2Ni complexes, we locate the transitions ${}^3A_{2g} \rightarrow {}^3T_{2g}$ at 9300 ($\epsilon_{max} 4 \text{ cm}^2 \text{ mmol}^{-1}$ in $CHCl_3$) and ${}^3T_{1g}(P)$ at 26 600 cm^{-1} . These assignments imply $B \text{ ca. } 940 \text{ cm}^{-1}$ and ${}^3T_{1g}(F)$ at *ca.* 15 500 cm^{-1} . If the 12 900 cm^{-1} band ($\epsilon_{max} 19 \text{ cm}^2 \text{ mmol}^{-1}$) were assigned to ${}^3T_{1g}(F)$, B would have the unreasonably low value of 360 cm^{-1} .

the receptor. (Fe^{2+} d-d bands appear in the $\text{Cr}_2\text{Fe}^{\text{II}}$ spectrum at *ca.* 8500 and 11 000 cm^{-1} .)

(c) Finally, we draw attention to the fact that, in contrast with the green colour of Fe_2Zn and the $\text{Cr}_2\text{M}^{\text{II}}$ complexes, the CrFeM^{II} complexes (**2d**) are purple-brown, with strong absorption at *ca.* 19 000 cm^{-1} . A similar colour due to the simultaneous presence of Cr^{3+} and Fe^{3+} is also very noticeable in the case of (**1**; L = py) (Cr_3 , grey-green; Fe_3 , olive-green; Cr_2Fe , purple-red), where it is associated with quite intense (ϵ_{max} *ca.* 500 $\text{cm}^2 \text{mmol}^{-1}$) absorption bands at 18 600, 21 700, and 25 500 cm^{-1} , which do not coincide with any bands in the spectra of the Cr_3 and Fe_3 compounds, and which shift to higher energy when py is replaced by H_2O .⁷ One possibility is that these are simultaneous (Cr^{3+} , Fe^{3+}) double excitations: pair transitions of the Cr_3 complex are clearly visible at room temperature, and such bands are known to be greatly intensified when the ions are dissimilar.⁸ It would be necessary here to assume coupling of doublet or quartet terms of Cr^{3+} with the lowest spin doublet of Fe^{3+} , which presumably lies below 5000 cm^{-1} .

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References

- 1 J. Catterick and P. Thornton, *Adv. Inorg. Chem. Radiochem.*, 1977, **20**, 291; T. Glowiak, M. Kubiak, and B. Jezowska-Trzebiatowska, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, 1977, **25**, 359; T. Glowiak, M. Kubiak, and T. Szymanska-Buzar, *Acta Crystallogr., Sect. B*, 1977, **33**, 1732.
- 2 A. R. Baikie, M. B. Hursthouse, D. B. New, and P. Thornton, *J. Chem. Soc., Chem. Commun.*, 1978, 62.
- 3 K. M. Yakubov, V. V. Zelentsov, T. A. Zhemchuznikova, S. K. Abdullaev, and V. R. Fisher, *Dokl. Akad. Nauk SSSR*, 1980, **250**, 402.
- 4 A. B. Blake, A. Yavari, and H. Kubicki, *J. Chem. Soc., Chem. Commun.*, 1981, 796.
- 5 J. Ferguson and H. J. Guggenheim, *J. Chem. Phys.*, 1966, **45**, 1134.
- 6 C. T. Dziobkowski, J. T. Wroblewski, and D. B. Brown, *Inorg. Chem.*, 1981, **20**, 679.
- 7 A. B. Blake and J. R. Pitchers, unpublished results. The anomalous colour was first noted (for L = H_2O) by R. Weinfeld and E. Gussmann, *Chem. Ber.*, 1909, **42**, 3881.
- 8 L. Dubicki and P. Day, *Inorg. Chem.*, 1972, **11**, 1868; J. Ferguson, H. J. Guggenheim, and Y. Tanabe, *Phys. Rev.*, 1967, **161**, 207.