Oxo-centred Trinuclear Carboxylato Complexes containing Mixed-metal and Mixed-valence Clusters $Cr^{III}_2M^{II}O$ and $Mn^{III}_2M^{II}O$ (M = Co, Ni or Mn)†

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New mixed-metal complexes $[Cr^{III}_2M^{II}O(O_2CCH_3)_6(C_5H_5N)_3]\cdot$solv and $[Mn^{III}_2M^{II}O(O_2CCH_3)_6(C_5H_5N)_3]\cdot$solv (M = Co, Ni or Mn; solv = solvent) have been prepared and characterised by X-ray diffraction and IR spectroscopy. The complex $[Mn^{III}_2Co^{II}O(O_2CCH_3)_6(C_5H_5N)_3]\cdot CH_3CO_2H$ crystallises in the trigonal system, space group *R*32, with *a* = 17.614(18), *b* = 10.470(12) Å and *Z* = 3. In-plane vibrations of the central $M^{III}_2M^{II}O$ unit of each complex are assigned and used to establish the electronic character of the mixed-valence manganese(III,III,II) complex. In contrast to the iron(III,III,II) analogue, this complex shows no tendency towards equalisation of the frequencies of A_1 and B_2 components of $\nu_{asym}(M^{III}_2M^{II}O)$, and it is evidently strongly valence-localised at room temperature.

Trinuclear oxo-centred complexes of the general types $[M^{III}_2M'^{II}O(O_2CR)_6L_3]$ and $[M^{III}_2M'^{III}O(O_2CR)_6L_3]^+$ are of value because of the wide variety of metal-ion combinations which can be incorporated into the same basic structure.[1] The series containing the mixed-metal clusters $Fe^{III}_nCr^{III}_{3-n}$ with n = 0–3 was firmly characterised as early as 1909,[2] and other mixed trivalent-metal combinations have been prepared recently.[3] Some mixed trivalent–divalent metal combinations $Fe^{III}_2M^{II}$ were first prepared in the 1920s[4] but not recognised as such until Blake and co-workers[5] characterised them, and others were prepared by Yakubov *et al.*[6] The first examples of $Cr^{III}_2M^{II}$ clusters were also reported by Blake and co-workers.[5] The main object to date has been to define the magnetic interactions within the trinuclear clusters, and this has been done both by bulk magnetic susceptibility measurements[1,5] and by neutron scattering spectroscopy.[7] The mixed-metal clusters have also been used as control systems against which to compare the electron-transfer behaviour of mixed-valency clusters $M^{III}_2M^{II}$.[8] Interest in the chemical properties of the mixed-metal systems is also growing, but it is still not known how wide a range of transition-metal ions can be incorporated into the trinuclear structure unit. As yet there are only a few complexes with vanadium, and none with titanium.[1,‡] A $Co^{III}_2Co^{II}$ species has been postulated as a catalyst for oxidation of hydrocarbons[10] but is not yet fully characterised.[1] A mixed-metal combination Mn^{III}/Co^{II}, hitherto uncharacterised, is thought to be involved in oxidation of hydrocarbons by dioxygen.[11]

Following the earlier vibrational studies of Cannon, Jayasooriya and co-workers,[8,12] we report here a systematic study of two series of complexes of the mixed-metal clusters $M^{III}_2M'^{II}$, with chromium and manganese as the trivalent ions. A complex of $Cr^{III}_2Mn^{II}$, which previously had been difficult to obtain pure, is fully characterised, and those of $Mn^{III}_2Co^{II}$ and $Mn^{III}_2Ni^{II}$ are reported for the first time. The structure of the Mn_2Co complex is confirmed by X-ray crystallography, and the structural similarity of the whole series is established by infrared spectroscopy.

Experimental

Preparation of Materials.—$[Cr_2CoO(O_2CCH_3)_6(C_5H_5N)_3]\cdot C_5H_5N$. Commercial 'cobaltous acetate', $Co(O_2CCH_3)_2\cdot 2H_2O$ (0.25 g), and hydrated chromium(II) acetate, $Cr_2(O_2CCH_3)_4\cdot 2H_2O$[13] (0.7 g) were heated with pyridine (6.5 g). After stirring for 5 min in the open air, more pyridine was added to dissolve any unreacted chromium(II) acetate. Typically, 3–3.5 cm^3 pyridine were required. The solution was left to cool overnight, and filtered. The green product, a fine powder, was collected and washed with a small amount of pyridine (Found: C, 44.70; H, 4.40; N, 6.40. Requires C, 45.25; H, 4.50; N, 6.60%).

$[Cr_2NiO(O_2CCH_3)_6(C_5H_5N)_3]\cdot C_5H_5N$. This was prepared in the same way using hydrated nickel acetate, $Ni(O_2CCH_3)_2\cdot nH_2O$ (Found: C, 45.00; H, 4.40; N, 6.45. Requires C, 45.25; H, 4.50; N, 6.60%).

$[Cr_2MnO(O_2CCH_3)_6(C_5H_5N)_3]\cdot C_5H_5N$. Manganese(II) acetate, $Mn(O_2CCH_3)_2\cdot 4H_2O$ (0.75 g), and $Cr_2(O_2CCH_3)_4\cdot 2H_2O$ (1.15 g) were heated with pyridine (10 cm^3). After stirring for 5 min more pyridine (5 cm^3) was added to dissolve the remaining chromium(II) acetate. The solution was heated with gentle stirring in the open air until oxidation was complete. The greenish solution was left to cool overnight, and the product, a finely divided green solid, was collected and washed with a small amount of pyridine (Found: C, 44.65; H, 4.50; N, 6.40. Requires C, 45.45; H, 4.50; N, 4.65%). Attempts to prepare this compound starting from 'manganic acetate' (see below) and chromium(II) acetate gave products with a different crystal habit and lower pyridine content.

$[Mn_2CoO(O_2CCH_3)_6(C_5H_5N)_3]\cdot CH_3CO_2H$. Freshly prepared 'manganic acetate'[14] (2.7 g, 0.01 mol) was added to a mixture of ethanol (25 g) and acetic acid (4.2 g) with stirring for 5–10 min and filtered to remove any undissolved solid. Cobalt(II) acetate (2.5 g, 0.01 mol) was added slowly to hot, stirred pyridine (4.0 g), and when all had dissolved the hot purple solution was added to the brown manganese(III) solution. After standing overnight, shiny black crystals were filtered off in the air and washed quickly with ethanol (Found: C, 42.00; H, 4.65; Co, 5.95; Mn^{III}, 13.35; N, 5.10. Requires C,

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

‡ An oxo-centred trigallium(III) carboxylate complex has recently been synthesised.[9]

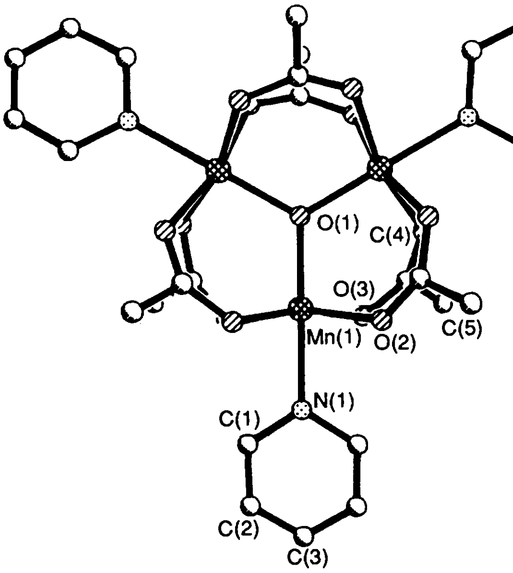

Fig. 1 Numbering scheme for the molecule $[Mn_2CoO(O_2CCH_3)_6(C_5H_5N)_3]$

41.30; H, 4.40; Co, 7.00; Mn^{III}, 13.05; N, 5.00%). To determine manganese(III), aliquots of acidified standard ammonium iron(II) sulfate solution were added to weighed dry portions of the complex. After reaction was complete, the remaining iron(II) was determined by potentiometric titration with cerium(IV) sulfate (bright platinum working electrode, standard calomel electrode with aqueous salt bridge). The total cobalt was determined spectrophotometrically, after first reducing manganese(III) to manganese(II). In a typical experiment, 30 mg of complex (*ca.* 4×10^{-5} mol) were weighed accurately into a small beaker, hydroxylammonium chloride (20 mg) was added, and the two were dissolved in water (10 cm^3). Reduction to pale pink cobalt(II) was complete in *ca.* 2 min. The solution was made up accurately to 100 cm^3 with fresh concentrated hydrochloric acid. Spectra were recorded in the range 560–760 nm, and compared with calibration spectra obtained with standard cobalt(II) nitrate in the same medium.

$[Mn_2NiO(O_2CCH_3)_6(C_5H_5N)_3]\cdot CH_3CO_2H$. This complex was prepared in the same way, using the same molar quantity of nickel(II) acetate in place of cobalt(II) acetate, and using 8 cm^3 pyridine (Found: C, 41.90; H, 4.35; Mn^{III}, 12.45; N, 5.10; Ni, 6.85. Requires C, 41.30; H, 4.40; Mn^{III}, 13.05; N, 5.00; Ni, 6.97%). Manganese(III) was determined as above, and total nickel was determined by atomic absorption spectroscopy.

Infrared spectra were recorded on Perkin Elmer 684 and 577 double-beam grating spectrophotometers and at higher resolution on a Digilab FTS20-V Fourier transform spectrophotometer.

Crystal-structure Determination of $[Mn^{III}_2Co^{II}O(O_2CCH_3)_6(C_5H_5N)_3]\cdot CH_3CO_2H$.—Data collection was carried out using a Siemens R3m/V diffractometer. Crystal data and details of data collection and refinement are given in Table 1. Unit-cell parameters were refined from the setting angles of 22 reflections. All calculations were performed using the SHELXTL PLUS software package. The metal atoms were located in a Patterson map, and Fourier difference syntheses allowed the location of the non-hydrogen atoms of the co-ordinated ligands. The structure was refined with anisotropic thermal parameters for all non-H atoms, to an *R* value of 0.1463 (unit weights). Selected atomic positions, bond lengths and angles are given in Tables 2 and 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Results

Synthesis.—The $Cr^{III}_2Mn^{II}$ complex was first prepared by Blake and Yavari[5a] and the electronic spectrum was reported. However the preparation was found to be difficult, and both of the present groups have found yields and purity to be erratic. The main by-products are homonuclear Cr^{III}_3 complexes, and mixed-metal complexes with low pyridine content, one of which analysed well as $[Cr^{III}_2Mn^{II}O(O_2CCH_3)_6(C_5H_5N)(H_2O)_2]$. The low ligand affinity of manganese compared to chromium(III) was considered to be the problem. All attempts to prepare the complex starting from chromium(III) compounds, such as $CrCl_3\cdot 6H_2O$ or $[Cr^{III}_3O(O_2CCH_3)_6(H_2O)_3]Cl\cdot 5H_2O$, were unsuccessful. Starting from chromium(II) acetate as described above, the best yields were obtained using a considerable excess of manganese(II). The products used in this work analysed correctly for the desired formula, and IR spectra of at least two independently prepared samples agreed well. However the best evidence of the structure is the fact that the same complex was finally prepared by a different route. Controlled-potential electrolytic reduction of the new complex[3a] $[Cr^{III}_2Mn^{III}O(O_2CCH_3)_6(C_5H_5N)_3]NO_3$ gave a green substance with identical electronic and IR spectra. Synthesis of the $Mn^{III}_2Co^{II}$ complex presented a different problem due to the reducibility of manganese(III). Efforts to prepare the adduct $[Mn^{III}_2Co^{II}O(O_2CCH_3)_6(C_5H_5N)_3]\cdot C_5H_5N$ under conditions of high pyridine concentration led to materials low in cobalt, which analysed well as solid solutions $[Mn^{III}_2Co^{II}_xMn^{II}_{1-x}O(O_2CCH_3)_6(C_5H_5N)_3]\cdot C_5H_5N$. In previous work[8d] on the fully oxidised Mn^{III}_3 and mixed-valence $Mn^{III}_2Mn^{II}$ complexes it was found that high acidity and low pyridine concentration were required to avoid reduction of manganese(III). Experiments with varying acetic acid/pyridine and cobalt(II)/manganese(III) ratios suggested the optimum conditions specified above. All well characterised products proved to be acetic acid solvates rather than pyridine solvates, and a small proportion of manganese(II) persisted in every case.

Structure.—The molecular structure of the $Mn^{III}_2Co^{II}$ compound was confirmed as the oxo-centred trinuclear unit shown in Fig. 1. The crystals are isomorphous with those of other mixed-metal and mixed-valence compounds of the type $[M^{III}_2M^{II}O(O_2CCH_3)_6(C_5H_5N)_3]\cdot$solv which have been reported with various combinations of metal ions, and with various non-co-ordinated solvent molecules (solv).[5,15–21] The molecules lie on three-fold axes of symmetry, the Mn and Co atoms being indistinguishable and presumably rotationally disordered, as is assumed in other cases. It is clear from the IR and chemical properties that the molecules are Mn_2Co units, not mixed with any significant proportion of Mn_3, $MnCo_2$ or Co_3 units, though some $Mn^{III}_2Mn^{II}$ is present. (The analogous $Fe^{III}_2Fe^{II}$ and $Fe^{III}_2Co^{II}$ complexes have also been shown to form solid solutions.[15,16])

A packing diagram for this structure is given in ref. 15. The spacing of the molecules along each three-fold axis is equal to the lattice parameter *b*, and it is apparently determined mainly by the packing of the co-ordinated pyridine molecules. These are almost coplanar with the central metal triangles (dihedral angle 3.0°) and are interleaved in stacks such that the spacing between adjacent, nearly parallel pyridines is $b/3 = 3.49$ Å. This can be compared with the spacing between layers in graphite, typically 3.4 Å.[22] There are large cavities between adjacent complex molecules on each three-fold axis, and the non-co-ordinated solvent molecules are evidently located in these cavities as in other structures of this type. The cavities can be described as trigonal-prismatic holes. One triangular face of each hole is defined by three methyl groups of one complex molecule, and the other by three methyls of the next complex. The radius of a sphere through the carbon atoms of all six methyls is 4.37 Å, and allowing 2.0 Å for the radius of a methyl group the effective radius of the hole is 2.4 Å. In the compound $[V_3O(O_2CCH_3)_6(C_5H_5N)_3]$ this cavity is empty.[17] In $[Fe_3O$-

Table 1 Crystal data and details of data collection and refinement for $[Mn^{III}{}_2Co^{II}O(O_2CCH_3)_6(C_5H_5N)_3]\cdot CH_3CO_2H$

Empirical formula	$C_{29}H_{37}CoMn_2N_3O_{15}$
M	836
Colour habit	Black, cuboid
Crystal size/mm	0.28 × 0.35 × 0.40
Crystal system	Trigonal
Space group	*R*32
Unit-cell dimensions/Å	a = 17.614(18), b = 10.470(12)
U/Å^3	2824(5)
Z	3
D_c/g cm^{-3}	1.475
μ/mm^{-1}	1.122
F(000)	1152
Radiation	Mo-Kα (λ = 0.71073 Å)
T/K	293
Monochromator	Highly oriented graphite crystal
2θ range/°	2.0–50
Scan type	ω
Scan speed	Variable 1.50–14.65° min^{-1} in ω
Scan range (ω)/°	0.60
Background measurement	Stationary crystal and stationary counter at beginning and end of each scan, each for 25% of total scan time
Standard reflections	2 every 48
Index ranges	$-20 < h < 10$, $-10 < k < 20$, $-11 < l < 0$
Reflections collected	1521
Independent reflections	1060 (R_{int} = 0.0585)
Observed reflections	773 [$F > 4.0\,\sigma(F)$]
Absorption correction	None

Table 2 Atomic coordinates (× 10^4) for $[Mn^{III}{}_2Co^{II}O(O_2CCH_3)_6(C_5H_5N)_3]\cdot CH_3CO_2H$

Atom	*x*	*y*	*z*
Mn(1)	6667	4439	8333
O(1)	6667	3333	8333
N(1)	6667	5607	8333
C(1)	7468(14)	6397(12)	8252(30)
C(2)	7534(23)	7267(18)	8287(37)
C(3)	6667	7205	8333
O(2)	5639(11)	4016(12)	9577(31)
O(3)	5817(11)	4096(10)	6959(32)
C(4)	5158(15)	3395(14)	6342(50)
C(5)	4636(21)	3327(25)	5377(39)

Table 3 Selected bond lengths (Å) and angles (°) for $[Mn^{III}{}_2Co^{II}O(O_2CCH_3)_6(C_5H_5N)_3]\cdot CH_3CO_2H$

Mn(1)–O(1)	1.948(2)	C(4)–O(2)	1.412(44)
Mn(1)–O(2)	2.044(25)	Mn(1)–N(1)	2.057(2)
N(1)–C(1)	1.404(16)	Mn(1)–O(3)	1.943(28)
C(1)–C(2)	1.477(43)	C(4)–C(5)	1.330(59)
O(3)–C(4)	1.361(36)		
O(1)–Mn(1)–N(1)	180.0(1)	O(1)–Mn(1)–O(2)	94.5(7)
N(1)–Mn(1)–O(2)	85.5(7)	O(1)–Mn(1)–O(3)	94.3(6)
N(1)–Mn(1)–O(3)	85.7(6)	O(2)–Mn(1)–O(3)	87.4(11)
O(2)–Mn(1)–O(2B)	171.0(8)	N(1)–Mn(1)–O(2B)	85.5(3)
O(2)–Mn(1)–O(3A)	91.9(11)	N(1)–Mn(1)–O(3A)	85.7(3)
Mn(1)–O(1)–Mn(1B)	120.0	O(3)–Mn(1)–O(3A)	171.5(7)
Mn(1)–N(1)–C(1)	119.2(12)	Mn(1)–N(1)–C(1A)	119.2(9)
C(1)–N(1)–C(1A)	121.6(19)	N(1)–C(1)–C(2)	123.0(24)
C(1)–C(2)–C(3)	112.5(19)	C(2)–C(3)–C(2A)	127.3(11)
Mn(1)–O(2)–C(4A)	139.2(21)	Mn(1)–O(3)–C(4)	143.9(23)
O(3)–C(4)–C(5)	132.8(31)	O(3)–C(4)–O(2A)	106.5(35)
C(5)–C(4)–O(2A)	119.7(23)		

Table 4 Unit-cell parameters for $[M_3O(O_2CCH_3)_6(C_5H_5N)_3]\cdot L$ crystallising in the space group *R*32

M_3	L	*T*/K	*a*/Å	*b*/Å	Ref.
$V^{III}{}_2V^{II}$	—	163	17.582	10.590	17
$Fe^{III}{}_2Fe^{II}$	$CHCl_3$	298	17.819	10.488	18
$Mn^{III}{}_2Co^{II}$	CH_3CO_2H	298	17.61	10.470	This work
$Mn^{III}{}_2Mn^{II}$	C_5H_5N	298 *	17.575	11.077	19
$Mn^{III}{}_2Mn^{II}$	C_5H_5N	223	17.552	10.918	20
$Fe^{III}{}_2Fe^{II}$	C_5H_5N	200	17.563	10.853	21

* Temperature inferred (not specified in ref. 19).

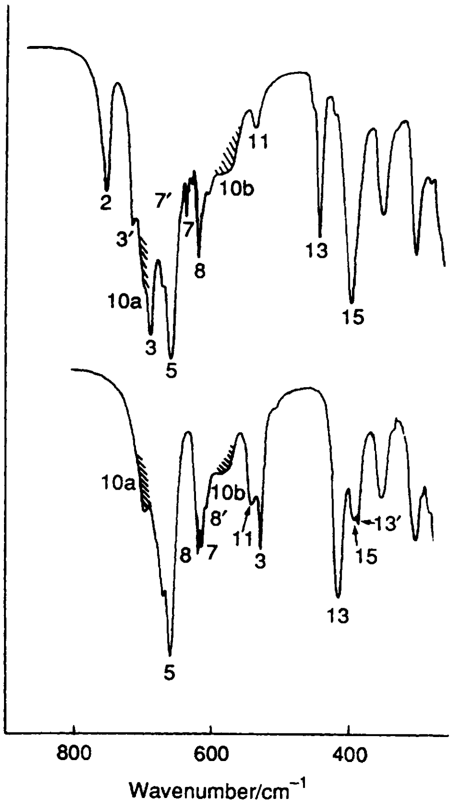

Fig. 2 The IR spectra of $[Cr_2CoO(O_2CCH_3)_6(C_5H_5N)_3]\cdot C_5H_5N$ (upper) and $[Cr_2CoO(O_2CCH_3)_6(C_5D_5N)_3]\cdot C_5D_5N$ (lower) as KBr discs at 300 K

$(O_2CCH_3)_6(C_5H_5N)_3]\cdot CHCl_3$ it contains one chloroform molecule.[18] As shown in Table 4, the lattice parameters *b* for these two and the present compound are very similar (10.5–10.6 Å), but those for three other compounds which contain non-co-ordinated pyridine are significantly greater (10.9–11.1 Å).

All the other complexes reported here clearly have the same molecular structure, from the similarity of IR spectra, and X-ray powder diffraction confirms that the $Cr^{III}{}_2Co^{II}$ and $Cr^{III}{}_2Mn^{II}$ complexes are isomorphous with the $Mn^{III}{}_2Co^{II}$, while the $Cr^{III}{}_2Ni^{II}$ complex is monoclinic, with space group *C*2/*c*.[23,†] We found that samples of the $Mn^{III}{}_2Ni^{II}$ complex were less subject to contamination by Mn^{II} than the $Mn^{III}{}_2Co^{II}$, although prepared under similar conditions, and this also might suggest a different crystal structure.

Infrared Spectra.—Spectra of $[Cr^{III}{}_2Co^{II}O(O_2CCH_3)_6(C_5H_5N)_3]\cdot C_5H_5N$ and of the deuteriopyridine analogue are shown in Fig. 2. Comparison of the two identifies a number of sharp lines as pyridine H- (or D-) wagging and ring-deformation modes. Some of these can be identified with modes

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[†] The main difference in the molecular structure is that in the *R*32 type the co-ordinated pyridine molecules are almost parallel to the trinuclear complex plane, whereas in the *C*2/*c* type they are almost perpendicular.

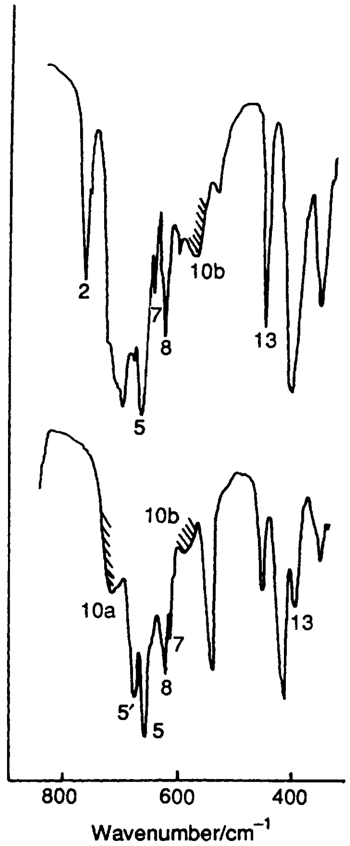

Fig. 3 The IR spectra of $[Cr_2MnO(O_2CCH_3)_6(C_5H_5N)_3]\cdot C_5H_5N$ (upper) and $[Cr_2MnO(O_2CCH_3)_6(C_5D_5N)_3]\cdot C_5D_5N$ (lower) as KBr discs at 300 K

already reported for oxo-centred trinuclear complexes, notably bands 2 and 3 (wag, shifted from 755 to *ca.* 590 and 690 to 530 cm^{-1} on deuteriation), 7 (ring deformation, 638 shifted to 615 cm^{-1}) and 13 (ring deformation, 445 shifted to 390 cm^{-1}). However, there are more bands than previously found in, for example, the triiron(III) complexes,[12] presumably because of splittings due to the two different metals. The extra bands, numbered 3', 7' and 13' in Fig. 2, are provisionally regarded as being associated with bands 3, 7 and 13. Among the bands not appreciably shifted on deuteriation, we recognise easily the very sharp $\pi(CO_2)$, band 8, and the strong $\delta(CO_2)$, band 5. In both spectra the latter appears to have a small satellite band, again a splitting due to the two metals. Band 11, the so-called 'mystery band',[1] which we still provisionally assign to $\rho_r(CO_2)$, is also unshifted with deuteriation. The remaining bands are a small sharp band at 605 cm^{-1}, which is provisionally assumed to be a split component of $\pi(CO_2)$, and which is therefore numbered 8', and two much broader bands, not totally resolved, which we consider to be components of the in-plane oxygen vibration $\nu_{asym}(Cr_2CoO)$. The higher-frequency component 10a appears as a shoulder at *ca* 700 cm^{-1} in the spectrum of the undeuteriated form of the complex, and as the well defined peak 10a at 698 cm^{-1} in the spectrum of the deuteriated form. The resolution in the latter case may be partly spurious however, since a pyridine H wag, shifted by deuteriation, is also expected at about this wavenumber [*cf.* ref. 11(*c*), band 1]. The lower-frequency component of $\nu_{asym}(Cr_2CoO)$ appears in the spectrum of the undeuteriated form as a broad shoulder 10b, at about 580 cm^{-1}, and again as a shoulder 10b at *ca.* 575 cm^{-1} for the deuteriated form.

Spectra of the corresponding pair of Cr_2Mn complexes are compared in Fig. 3. The pyridine modes 2, 7 and 13 are clear, as are $\delta(CO_2)$ and $\pi(CO_2)$, bands 5 and 8. In the region 670–720 cm^{-1} the spectrum of the undeuteriated form contains a complicated pattern of bands, but these must include the pyridine modes 3 and 3', since for the deuteriopyridine adduct the pattern is simplified to reveal clearly band 5' at 675 cm^{-1}, about half the intensity of band 5, and the broad band 10a at *ca.* 710 cm^{-1} which we assign as a component of $\nu_{asym}(Cr_2MnO)$.

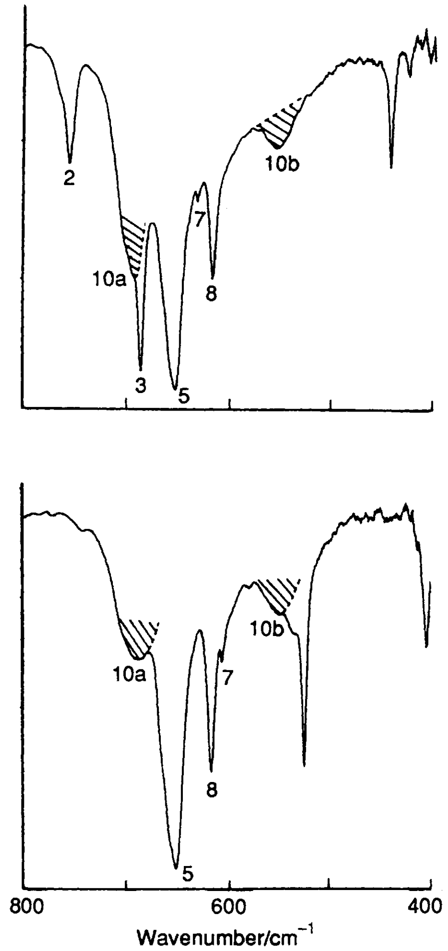

Fig. 4 The Fourier-transform IR spectra $[Mn_2CoO(O_2CCH_3)_6(C_5H_5N)_3]\cdot CH_3CO_2H$ (upper) and $[Mn_2CoO(O_2CCH_3)_6(C_5D_5N)_3]\cdot CH_3CO_2H$ (lower) as KBr discs at 300 K

Spectra of the Mn_2Co complexes, with co-ordinated C_5H_5N and C_5D_5N, are compared in Fig. 4. These were recorded with improved resolution, but they are nevertheless simpler in appearance than the previous spectra, suggesting that splittings due to the different metals Mn^{III} and Co^{II} are less pronounced. In the range considered, pyridine modes 2 and 3, and probably 7, are seen. The two broad components of $\nu_{asym}(Mn_2CoO)$ are clear in both spectra, bands 10a and 10b.

Spectra of the Cr_2Ni and Mn_2Ni complexes are shown in Figs. 5 and 6. Comparisons with the other spectra establish the main features, as indicated by the common numbering scheme. For the Cr_2Ni complex, band 10a occurs at *ca.* 725 cm^{-1}, though it may be artificially sharpened by overlap with band 3', which otherwise is not detected, while band 10b is a clear and fairly strong shoulder at 595 cm^{-1}. For the Cr_2Mn complex, the lower-frequency component of $\nu_{asym}(Cr_2MnO)$ seems unambiguous, band 10b at 575 cm^{-1}, though its breadth suggests that overlap with some other unidentified band should not be ruled out.

Discussion

The IR data leave no doubt that all six compounds have the same oxo-centred triangular molecular unit, and that any structural differences are slight. Splittings of modes such as $\delta(CO_2)$ and $\pi(CO_2)$ are expected for mixed-metal complexes,

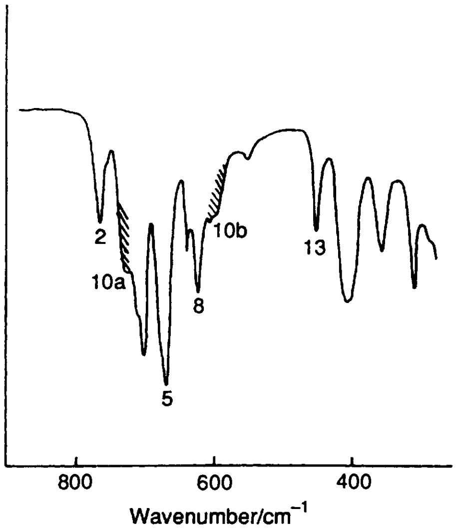

Fig. 5 The IR spectrum of $[Cr_2NiO(O_2CCH_3)_6(C_5H_5N)_3]{\cdot}C_5H_5N$ as a KBr disc at 300 K

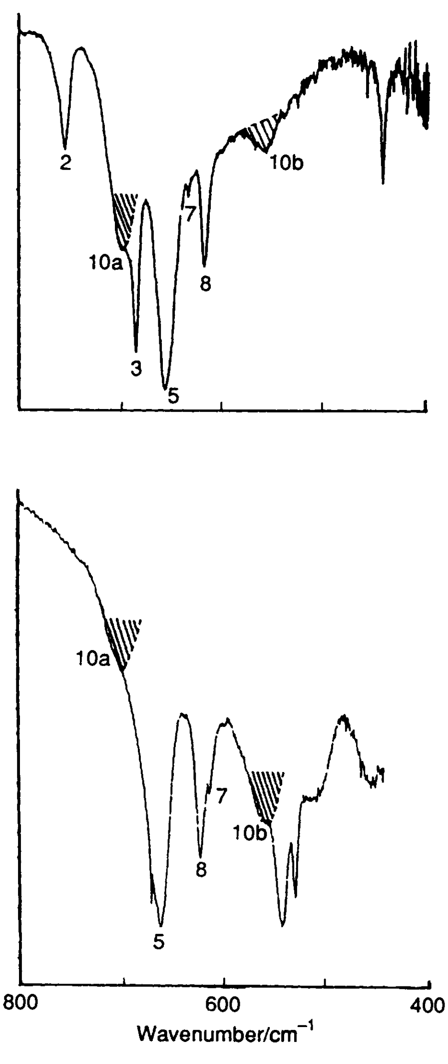

Fig. 6 The Fourier-transform IR spectra of $[Mn_2NiO(O_2CCH_3)_6(C_5H_5N)_3]{\cdot}CH_3CO_2H$ and $[Mn_2NiO(O_2CCH_3)_6(C_5D_5N)_3]{\cdot}CH_3CO_2H$ (lower) as KBr discs at 300 K

Table 5 Band wavenumbers (cm^{-1}) and assignments for complexes $[M^{III}{}_2M'^{II}O(O_2CCH_3)_6(C_5H_5N)_3]{\cdot}C_5H_5N$ (T = 300 k)

$M^{III}{}_2M'^{II}$	5 δ(OCO)	8 π(CO_2)	10a ν_{asym},B_2	10b ν_{asym},A_1	$\Delta\nu_{asym}$[a]
Cr_2Mn[b]	655	620	≈705	575	130
Cr_2Co[b]	662	620	≈700	580	120
Cr_2Ni[b]	670	625	≈725	595	130
Mn_2Mn[c]	648	614	696[d]	545	151
Mn_2Co[c,e]	654	617	693[d]	553	140
Mn_2Ni[c,e]	656	616	≈700	559	141

[a] $\Delta\nu_{asym} = \nu_{asym}(B_2) - \nu_{asym}(A_1)$. [b] Resolution *ca.* 5 cm^{-1}. [c] Resolution *ca.* 2 cm^{-1}.

regardless of the space group. In each molecule, four carboxylate ions form bridges between different metal atoms, M^{III}–O(CR)O–M'^{II}, and two form bridges between like atoms, M^{III}–O(CR)O–M^{III}. Probable examples of doublets arising in this way are bands 5 and 5′ and 8 and 8′, in Figs. 2 and 3. In most cases it is difficult to tell the relative intensities of the two components of the doublet, owing to unsymmetrical background absorption, but an exception is the pair 5, 5′ in Fig. 3. Here it is reasonably clear that the higher-frequency component is the less intense of the two, which is expected if it represents the two Cr^{III}–O(CR)O–Cr^{III} groups rather than the four Cr^{III}–O(CR)O–Mn^{II} groups.

Selected wavenumbers are listed in Table 5. For a number of vibrational modes, frequencies vary with changes in the divalent metal, in the order $M^{III}{}_2Ni^{II}$ > $M^{III}{}_2Co^{II}$ > $M^{III}{}_2Mn^{II}$, for each of the two series with M^{III} = Cr^{III} or Mn^{III}, as for the series M^{III} = Fe^{III} reported previously.[8b] This applies to the MO_4 stretch modes (not shown), and to δ(CO_2), band 8, which is also expected to have some metal–oxygen stretch character. In contrast, π(CO_2), band 5, is relatively constant for all complexes. The same trend is seen in the low-frequency component of $\nu_{asym}(M^{III}{}_2M^{II}O)$, band 10b, again for all three series, but not in the high-frequency component, band 10a. This supports an earlier proposal that band 10b is the A_1 component of ν_{asym}, having significant M^{II}–O stretch character, while 10a is the B_2 component, essentially an asymmetric $M^{III}{}_2O$ stretch.

In the $Fe^{III}{}_2M^{II}$ series of complexes reported previously the mixed-valence $Fe^{III}{}_2Fe^{II}$ complex was characterised as valence-localised,[8] but from an anomaly in the frequencies of ν_{asym} it was concluded that valence localisation was not complete (on the vibrational time-scale, at room temperature.)[8b] The low-frequency component of ν_{asym} was significantly higher, and the high-frequency component was significantly lower, than the values interpolated from the mixed-metal series M^{II} = Mn^{II}, Co^{II}, or Ni^{II}. The new data presented here make it possible to say that no such anomaly is apparent for the mixed-valence $Mn^{III}{}_2Mn^{II}$ complex. One indication is the trend of values of ν_{asym} just noted for the series $M^{III}{}_2Ni^{II}$, $M^{III}{}_2Co^{II}$, $M^{III}{}_2Mn^{II}$. Here the mixed-valence complex is the end member of a series and cannot be bracketed with mixed-metal complexes on either side. However it is now possible to bracket the mixed-valence manganese complex within a series by varying the trivalent metal. For the complexes $Cr^{III}{}_2Mn^{II}$, $Mn^{III}{}_2Mn^{II}$, $Fe^{III}{}_2Mn^{II}$,[8b] the frequency difference between A_1 and B_2 components varies monotonically: $\Delta\nu$ = 130, 151, 177 cm^{-1}. There is no indication that $\Delta\nu$ for the mixed-valence complex is particularly low, especially when we compare the corresponding figures for the series of isomorphous mixed-metal complexes $Cr^{III}{}_2Co^{II}$, $Mn^{III}{}_2Co^{II}$ and $Fe^{III}{}_2Co^{II}$,[8b] for which $\Delta\nu$ = 120, 140 and 167 cm^{-1}. For the iron(III,III,II) complex, $\Delta\nu$ was found to be out of line by some 45–50 cm^{-1}. The indication, from these data at least, is that the mixed-valence manganese cluster is close to the valence-localised limit.

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