INFRARED SPECTROSCOPY OF NEW OXO-CENTRED TRINUCLEAR CARBOXYLATO MIXED-METAL COMPLEXES CONTAINING $Cr^{III}_2Mn^{III}O$ AND $Mn^{III}_2Fe^{III}O$ CLUSTERS

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Abstract

New mixed-metal complexes $Cr^{III}_2Mn^{III}O$ and $Mn^{III}_2Fe^{III}O$ have been prepared and characterized by infrared spectroscopy. The effects of symmetry lowering were observed in the splitting of the $\nu_{as}(M_3O)$ into two components, A_1 and B_2 modes under C_{2v}. The separation between these modes is rather small in comparison to those of the mixed-metals $Fe_2^{III}OM^{11}$ (M^{11} = Fe, Ni, Co and Mn), but similar to those of $Fe_2^{III}Mn^{III}O$, $Fe_2^{III}Co^{III}O$ already reported (Saad, 1990) Vibrational studies in the far I.R would be of interest. Attempts to study the Raman spectra were not possible as the complexes decomposed on exposure to the laser beam.

Keywords: Symmetry, lowering of A_1 and B_2 modes in C_{2v}., spectroscopy

Introduction

In Part I we reported (Karu and Cannon, 2012) the synthesis and characterization of new oxo-centred trinuclear carboxylato mixed-metal complexes containing $Cr^{III}_2Mn^{III}O$ and $Mn^{III}_2Fe^{III}O$ clusters. We now report the infra red spectroscopy of these complexes.

Methodology

A few grams of the sample was ground in a small agate mortar until sample formed a tiny film over the surface of the mortar. To about 5 mg of sample, approximately 250 mg of dry spectroscopic KBr (dried in oven) were added to form a fine powder. The powder was stirred with a spatula and finely ground with a pestle (fine grinding of the sample is essential so as to avoid distorted spectra due to the Christiansen filter effect). The powder was transferred to a disk press and pressed with a 'specac' press to approximately 10 tons pressure. A good transparent disc was always obtained when pressed for longer periods of 5 – 10 minutes. Infrared spectra in the region 4000 – 200cm^{-1} were recorded with the Perkin – Elmer 684 spectrophotometer.

Results and Discussion

In order to assign the infrared bands for $[Cr_2MnO(OOCCH_3)_6(NC_5H_5)_5]^+$ and $[Mn_2FeO(OOCCH_3)_6(NC_5H_5)_3]^+$, the spectra were compared with those of the symmetrical homonuclear complexes already reported in literature (Johnson *et al*, 1981). In interpreting the vibrational spectra of oxo-centred trinuclear carboxylates it is convenient to divide the vibrations into the following categories as was done by previous workers (Saad, 1990 and Johnson, 1985).
The aim of this study was to investigate vibrations associated with compounds and the objectives were to determine the following:

1. Vibrations associated with the acetate groups.
2. Vibrations associated with pyridine.
3. Vibrations of metal frame work.
4. Vibrations of the MO_4 groups.

Vibrations associated with the acetate groups

Assignment of the vibrational modes due to the bridging acetate in trinuclear complexes led to the identification of similar modes in the complexes. These are generally observed in the 1600-600cm^{-1} region. Assignment of the infrared frequencies involving the bridging acetate ligands for some selected homonuclear symmetrical, mixed-metal complexes and the complexes under study are presented in Table 1. The infrared spectra for the mixed-metal $Cr_2^{III}Mn^{III}$ are given under Figures 1 and 2; that of $Mn_2^{III}Fe^{III}$ are given under figures 3 and 4. The infrared spectra of the homonuclear symmetrical complexes M_3O $(OOCCR_3)_6L_3$ (R = H, L = pyridine and M = Cr, Mn and Fe) and a series of oxo-centred carboxylates Fe_2M' (M' = Fe^{II}, Mn Co, Ni) have been reported (Johson *et al*, 1981, and Montri *et al* 1987). Also Saad (1990) reported that the synthesis and vibrational spectroscopy of some mixed-metal complexes. On going from the homonuclear complexes M_3O (M = Cr, Mn and Fe) to the mixed-metal complexes, $Cr_2^{III}Mn^{III}$ and $Mn^{III}Fe^{III}$, the bands expected in theory to be most sensitive to changes of the metal ions, are the asymmetric and symmetric CO_2 stretches. But the changes in frequency and band shape are too small to clearly distinguish the mixed-metal $Cr_2^{III}Mn^{III}$ and $Mn_2^{111}Fe^{111}$ complexes. Thus the asymmetric and symmetric CO_2 stretches are observed at almost invariable frequencies of ca. 1620cm^{-1} and 1450cm^{-1} respectively.

There were hardly any significant changes in the deformation modes of the methyl groups. This should be expected as their vibrations do not depend on the metal ions. But some differences were observed in the deformation modes of the OCO group. The B_1 ρ_r (COO) observed as a medium band at 520cm^{-1} both in Fe_3O and Mn_3O, splits into two bands in the $[Mn_2^{III}Fe^{III}O(OOCCH_3)_6(NC_5H_5)_3]^+$ complex, at 555cm^{-1} and 519cm^{-1} (Figure 4). This mode was not seen either in the Cr_3O and $Cr_2^{III}Mn^{III}O$ complexes. Generally it was reported as a single peak in the mixed-metal $Fe^{III}{}_2M^{II}$ and the mixed-valence $Fe_2^{III}Fe^{II}O$ complexes. For example in the complexes $Cr_2^{III}Mn^{III}O$ and $Fe_2^{III}Mn^{III}O$, ρ_r (COO) was observed (Saad, A. K 1990) as a weak band at 530cm^{-1} and 525cm^{-1} respectively.

Vibrations associated with pyridine

The observed frequencies for free and co-ordinated pyridine are presented in Table 1. The assignments and the notation for free ligand are known (Karu, E. 1990). The most significant mode expected to show changes, is the metal-nitrogen stretch. The ν(M-N) vibrations have an E symmetry in the trigonal complexes and are expected to split in the mixed-metal and mixed-valence complexes to A_1 and B_2 modes. This was indeed observed[3] in the series Fe_2^{III} M' (M' = Fe^{II}, Co^{II}, Ni^{II}) and also in the $Cr_2^{III}Mn^{II}O$ complexes at around 200cm^{-1}. In the series $Fe_2^{III}M^{III}$ (M = Co, Mn) they were found[3] in the 240cm^{-1} region. This study did not extend into this region. Pyridine modes 4, 6a 6b, 11 and 16b had been assigned to co-ordinated pyridine.

Table 1. Assignments of absorption frequencies (cm^{-1}) for free and coordinated pyridine

	16b	6a	6b	11	4	5	1	12	18a
Pyridine	405m	602m	655sh	703vs	747s	942w	990m	1031s	1069m
$[Cr_3O(OOCCH_3)_6(py)_3]Cl$	432w	652sh	675m	700w	770w	n.o	1015w	1048w	1070
$[Fe_3O(OOCCH_3)_6(py)_3]No_3$	432w 440w		n.o	695m 702m	758m 769m	n.o	1010m 1015m	1040m	1061 1072m
$[Mn_3O(OOCCH_3)_6(py)_3]ClO_4$	444w 438sh	636sh 646m	n.o	694s 710sh	769m 761sh	n.o	1020sh	1044sh	1070m 1064m
$[Cr^{111}_2Mn^{11}O(OOCCH_3)_6(py)_3]$	ob	638m	672sh	690w	755s	n.o	1020w	1045m	1078w
$[Fe_2MnO(OOCCH_3)_6(py)_3$	425sh	630w	n.o	700s	755m	n.o	1010w	1040w	1078w
$[Fe_2MnO(OOCCH_3)_6(py)_3]ClO_4$	430sh	ob	645sh	700s	768s	n.o	1012w	1040m	1075w
$[Cr_2MnO(OOCCH_3)_6(py)_3]Cl$	ob	ob	643s	696vs	769m	ob	1019m	1048m	1069m
$[Cr_2MnO(OOCCH_3)_6(py)_3]NO_3$	ob	ob	642s	698vs	770m	ob	1020m	1049m	1070m
$[Mn_2FeO(OOCCH_3)_6(py)_3]ClO_4$	448w	640m	653vs	696vs	768m	n.o	1019m	1030m	1068vs
$[Mn_2FeO(OOCCH_3)_6(py)_3]NO_3$	450w	640m	650s	698s	770m	n.o	1018m	1030m	1070m

Table 1: (Cont'd) Assignments of absorption frequencies (cm^{-1}) for free and coordinated pyridine

	15	9a	14	19b	19a	8b	8a	1+6a	1+6b
Pyridine	1149m	1219m	1375w	1482s	1575sh	1575sh	1581vs	1597s	1069m
$[Cr_3O(OOCCH_3)_6(py)_3]Cl$	1160m	1220m	ob	1420sh	1492s	ob	ob	ob	n.o
$[Fe_3O(OOCCH_3)_6(py)_3]No_3$	1158w	1220m	ob	ob	1490w	ob	ob	ob	ob
$[Mn_3O(OOCCH_3)_6(py)_3]ClO_4$	1152m	1213s	ob	1449m	ob	ob	ob	ob	ob
$[Cr^{111}_2Mn^{11}O\ (OOCCH_3)_6(py)_3]$	1150w	1222s	ob	1420s	1488m	1575sh	1580sh	1610sh	ob
$[Fe_2MnO\ (OOCCH_3)_6(py)_3$	1155w	n.o	ob	1450m	1488m	ob	ob	ob	ob
$[Fe_2MnO\ (OOCCH_3)_6(py)_3]ClO_4$	1160w	1222s	ob	1420sh	1488m	ob	ob	1629sh	ob
$[Cr_2MnO\ (OOCCH_3)_6(py)_3]Cl$	1154w	1219	ob	ob	1480m	1575sh	ob	1740sh	1720m
$[Cr_2MnO\ (OOCCH_3)_6(py)_3]NO_3$	1158w	1220m	ob	ob	1490m	ob	ob	1740sh	1720m
$[Mn_2FeO\ (OOCCH_3)_6(py)_3]ClO_4$	1160m	1222vs	ob	1450vs	1492m	ob	ob	ob	
$[Mn_2FeO\ (OOCCH_3)_6(py)_3]NO_3$	1160m	1220s	ob	1450vs	1491m	ob	ob	1750sh	1730m

Changes in the frequencies of some of these modes were actually observed in the mixed-metal complexes, $Cr_2^{III}Mn^{III}$ and $Mn_2^{III}Fe^{III}$. Band 4 has shifted from 747cm^{-1} to ca 770cm^{-1} in both complexes (Figures 1 and 2). A shift of ca 40cm^{-1} was also observed in pyridine band 6a from 600cm^{-1} to 640cm^{-1} in the $Mn_2^{III}Fe^{III}$ complex but was obscured in $Cr_2^{III}Mn^{III}$. Band 6b which is observed as a shoulder in free pyridine became stronger on co-ordination. A significant change in the spectrum of free pyridine and the complexes is in band 16b at 405cm^{-1}. This peak split on co-ordination and were observed as weak bands at 440cm^{-1} and 432 cm^{-1} in the $Fe_3^{III}O$ complex and also as a weak band at 444cm^{-1} with a shoulder at 438cm^{-1} in $Mn_3^{III}O$. Neither of these splittings were reported for Cr_3O and Fe_2^{III} M' and Fe_2^{III} M^{III} series. This band is obscured by the symmetric metal-oxygen stretches in $Cr_2^{III}Mn^{III}$ but the splitting is observed in the $Mn_2^{III}Fe^{III}O$ complex. These were observed as weak bands at 448cm^{-1} and 438 cm^{-1} in the perchlorate salt and at 440 cm^{-1} and 430 cm^{-1} in the nitrate.

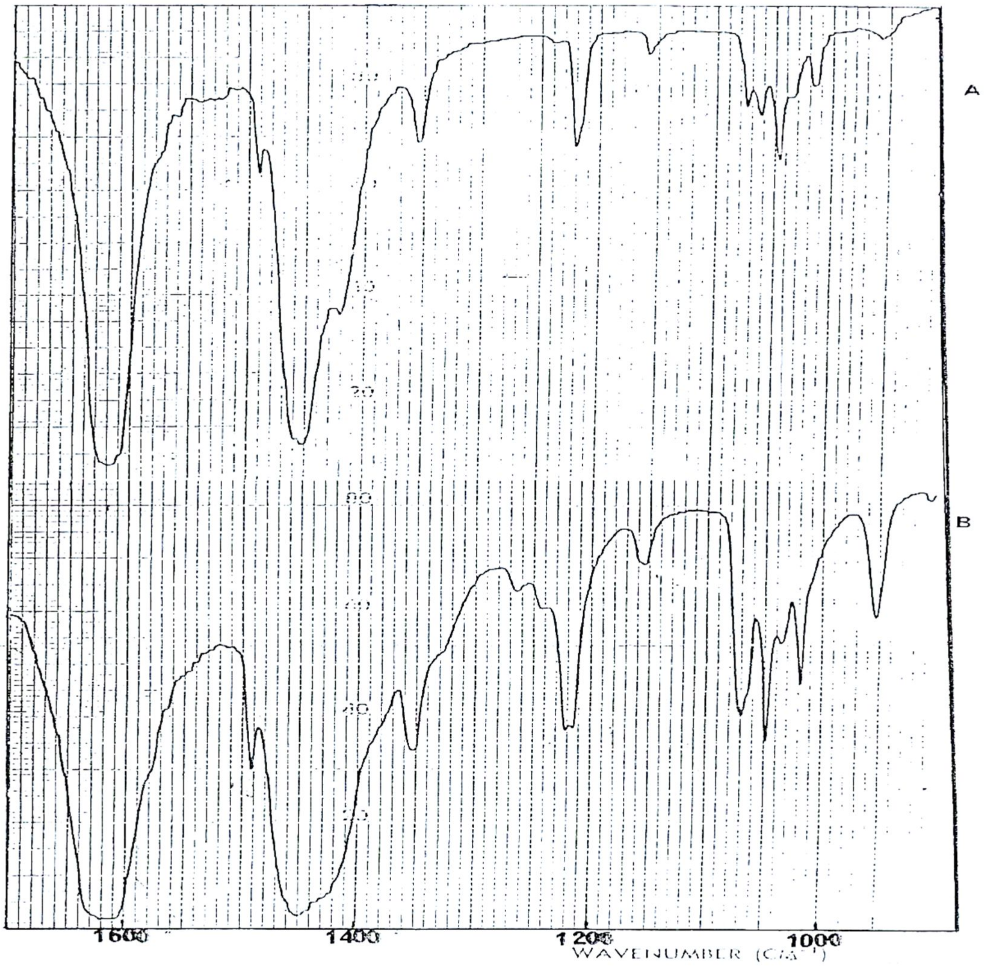

Figure 1 Infrared Spectra of

A = $[Cr_3O\ (OOCCH_3)_6(NC_5H_5)_3]^+$

B = $[Cr_2^{III}Mn^{III}O\ (OOCCH_3)_6(NC_5H_5)_3]^+$

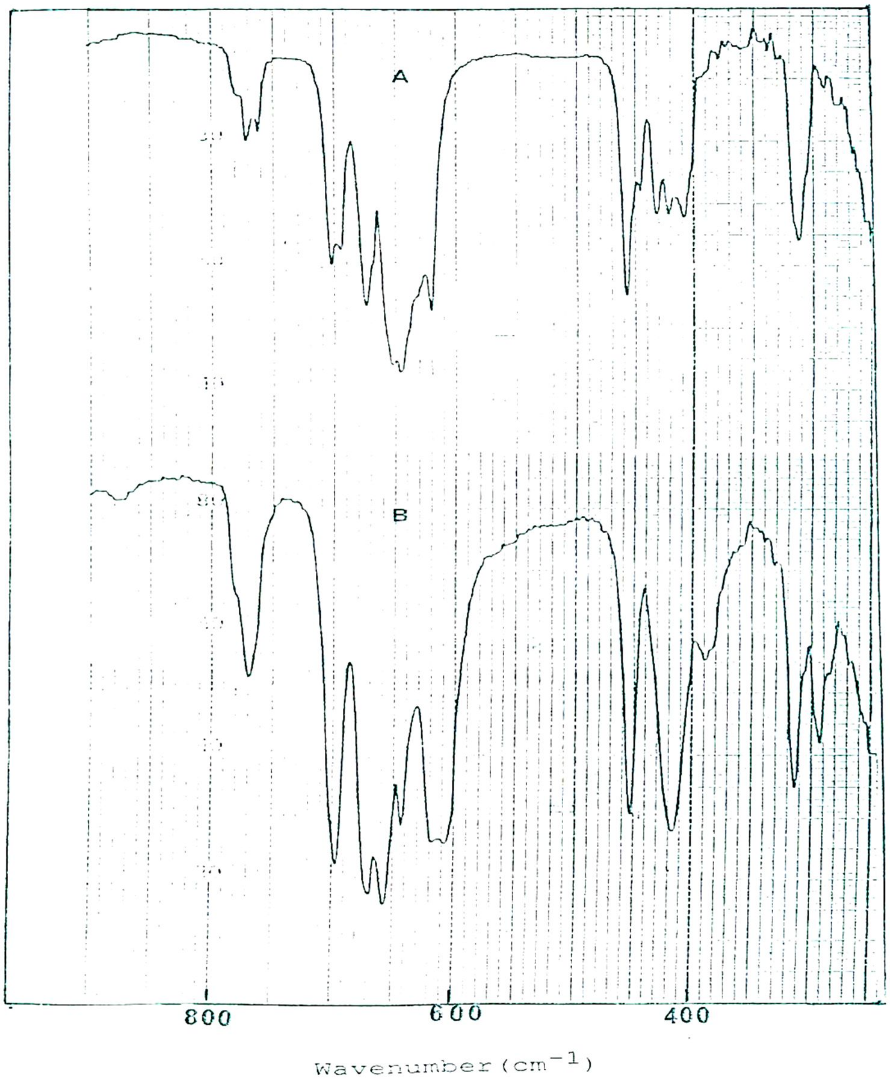

Figure 2. Infrared spectra of

A = $[Cr_3O(OOCCH_3)_6(NC_5H_5)_3]^+$
B = $[Cr_2^{III}Mn^{III}O(OOCCH_3)_6(NC_5H_5)_3]^+$

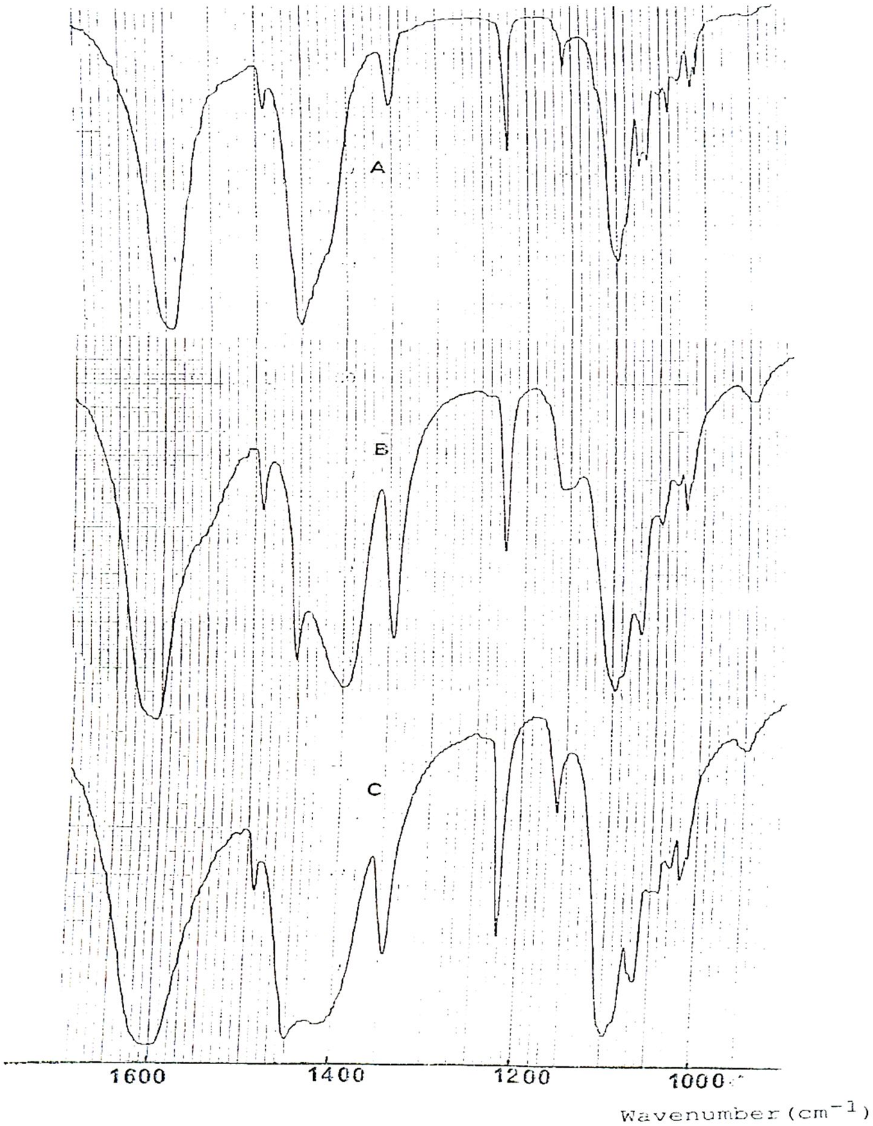

Figure 3. Infrared spectra of

A = $[Fe_3O(OOCCH_3)_6(NC_5H_5)_3]^+$
B = $[Mn_3O(OOCCH_3)_6(NC_5H_5)_3]^+$
C = $[Mn_2^{III}Fe^{III}O(OOCCH_3)_6(NC_5H_5)_3]^+$

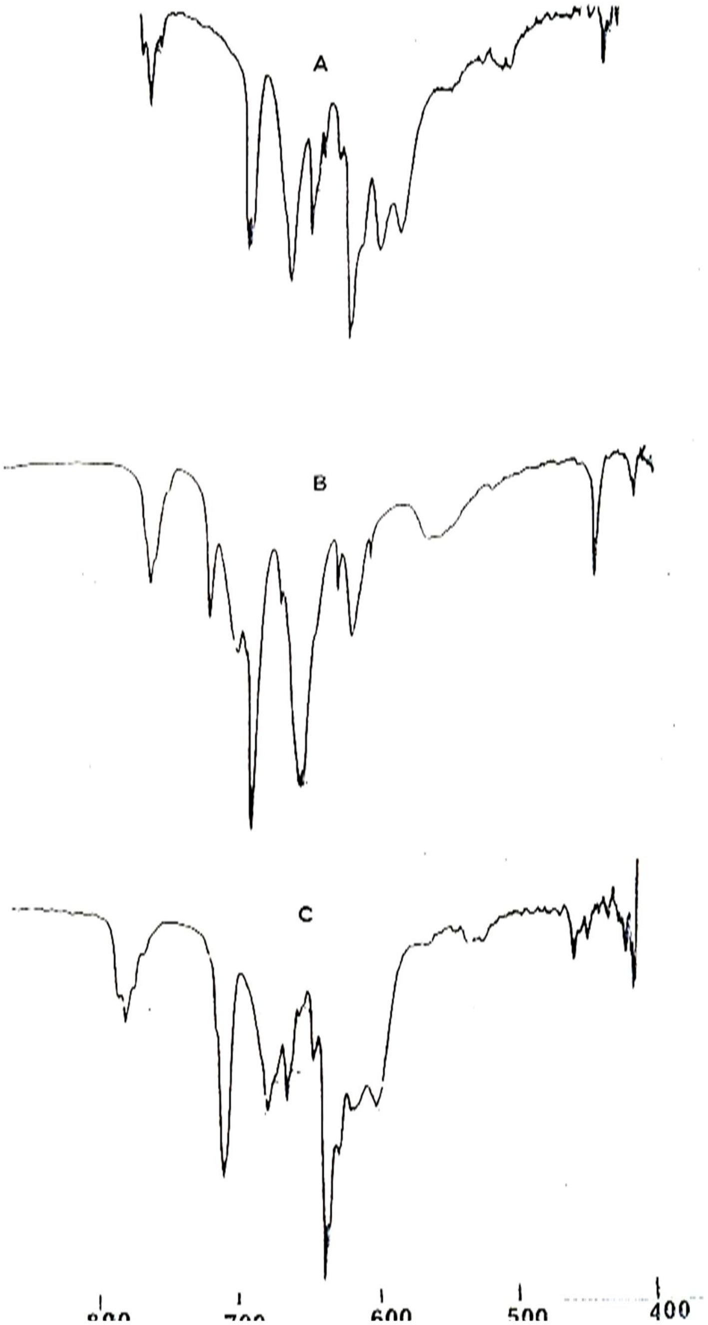

Figure 4. Infrared spectra of

A = $[Mn_2^{III}Fe^{III}O(OOCCH_3)_6(NC_5H_5)_3]^+$
B = $[Mn_2^{III}Mn^{II}O(OOCCH_3)_6(NC_5H_5)_3]$
C = $[Mn_3O(OOCCH_3)_6(NC_5H_5)_3]^+$

Vibrations associated with the metal framework

In assigning the vibrations associated with the metal framework, Johnson, M *et al* (1981), took the vibrations of the planar M_3O group to be separate from the rest of the molecule. This approximation worked successfully. The M_3O unit has four normal modes of vibrations, two of which are doubly degenerate in the symmetrical homonuclear complexes. When the metal ions are identical, the molecule is considered under D_{3h} symmetry group while those with only two identical ions are considered under C_{2V}. We now report our findings with the mixed-metal complexes $Cr_2^{III}Mn^{111}O$ and $Mn_2^{III}Fe^{III}O$.

$Cr_2^{III}Mn^{III}O$

Frequencies associated with this metal framework are given in Table 3 and the spectra under Figure 2. For the homonuclear $Cr_3^{III}O$ and $M_3^{III}O$ clusters, Johnson *et al* (1981) assigned the degenerate E' modes to the strong band at 655cm^{-1} and the shoulder at 604cm^{-1} respectively. In the mixed-valence $Mn_3O(OOCCH_3)_6(py)_3(py)$ complex $\nu_{as}(M_3O)$ is split into two peaks at 603cm^{-1} and 588cm^{-1} which have been assigned to the B_2 and A_1 modes respectively. In addition, the corresponding modes in the spectrum of the mixed-metal $Cr_2^{III}Mn^{11}$ occur as a shoulder at 715cm^{-1} and as a weak band at 570cm^{-1}. In the present compound, they were observed at 658cm^{-1} and 620cm^{-1} and again, the peak at a higher frequency is assigned to the B_2 mode while that of the lower frequency to the A_1 mode.

The separation of A_1 mode from the B_2 mode in the $Cr_2^{III}Mn^{11}$ complex, is very large (145cm^{-1}) while in $Cr_2^{III}Mn^{111}$, it is comparatively very small (39cm^{-1}). The frequency difference between Cr^{III}-O and Mn^{II}-O stretch is expected to be considerably greater than that between Cr^{III}-O and Mn^{III}-O (Table 2). On the other hand, no effects of symmetry lowering were seen in the $Cr_2^{III}Fe^{111}$complex (Johnson, M. 1977) though the relevant frequencies were intermediate between those of the homonuclear complexes.

Table 2: I.R Frequency assignments of the $M_2M'O$ framework in some trinuclear complexes

Complex	$\nu(M_3O)$	$\nu_{as}(M_2M'O)$	$\nu_s(M_2M'O)$	$\nu(MO)$
	E'(cm^{-1})	B_2(cm^{-1})	A_1(cm^{-1})	E_u(cm^{-1})
$[Cr_3O(OOCCH_3)_6(py)_3]Cl$	655s			453s 414s
$[Fe_3O(OOCCH_3)_6(py)_3]No_3$	590b			365s
$[Mn_3O(OOCCH_3)_6(py)_3]ClO_4$	604sh			389m 380sh
$[Cr^{111}_2Mn^{11}O\ (OOCCH_3)_6(py)_3]$		715w	570w	
$[Fe_2MnO(OOCCH_3)_6(py)_3$		712w	535w	
$[Fe_2MnO(OOCCH_3)_6(py)_3]ClO_4$		625sh	582m	
$[Cr_2MnO(OOCCH_3)_6(py)_3]Cl$		658s	620s	453s 419s 390sh
$[Cr_2MnO(OOCCH_3)_6(py)_3]NO_3$		659s	620s	454s 420s 390sh
$[Mn_2FeO(OOCCH_3)_6(py)_3]ClO_4$		607ms	586msh	
$[Mn_2FeO(OOCCH_3)_6(py)_3]NO_3$		616m	590msh	

N.B. vs = very strong, a = strong, m = medium, mw = medium weak, w = weak, sh = shoulder, ob = obscured, n.o = not observed, py = pyridine

Table 3: Vibrational frequencies (cm^{-1}) of acetate ligand in some oxo-centred trinuclear complexes

Complex	$\delta(CH_3)$	$\rho(CH_3)$	$\rho(COO)$	$\nu(CH)$	$\delta(CH_3)$	$\rho(CH_3)$	$\pi(COO)$
	B_1	B_1	B_1	B_2	B_2	B_2	B_2
$[Cr_3O(OOCCH_3)_6(py)_3]Cl$	1413s	1036sh	-	-	1427s	1047s	623m
$[Fe_3O(OOCCH_3)_6(py)_3]No_3$	1420sh	1030m	520mw	2975w	1420sh	1049ob	614sh
$[Mn_3O(OOCCH_3)_6(py)_3]ClO_4$	ob	ob	520m	2975sh	ob	ob	620m
$[Cr^{111}_2Mn^{11}O(OOCCH_3)_6(py)_3]$	1445sh	1040w	530w	3010w	1450w	1040w	620w
$[Fe_2MnO(OOCCH_3)_6(py)_3]ClO_4$	1450m	1040w	525w	2985w	1450s	1040w	615m
$[Cr_2MnO(OOCCH_3)_6(py)_3]Cl$	1420sh	1035sh	n.o	3080w	1430sh	1049m	608m
$[Cr_2MnO(OOCCH_3)_6(py)_3]NO_3$	1420sh	1035sh	n.o	3080w	ob	1049m	620m
$[Mn_2FeO(OOCCH_3)_6(py)_3]ClO_4$	1418s	1040sh	555m 519w	3120w	1418s	1040m	618m 615s
$[Mn_2FeO(OOCCH_3)_6(py)_3]NO_4$	1420s	1034w	525w	3115w	ob	1045m	616s

Table 3: (Cont'd) Vibrational frequencies (cm^{-1}) of acetate ligand in some oxo-centred trinuclear complexes

Complex	$\nu(CH)$	$\delta(CH_3)$	$\nu(COO)$	$\nu(CC)$	$\delta(OCO)$	$\nu(CH)$	$\nu(COO)$
	A_1	A_1	A_1	A_1	A_1	A_1	B_1
$[Cr_3O(OOCCH_3)_6(py)_3]Cl$	2930w	1348m	1454vs	958m	673s	-	1610vs
$[Fe_3O(OOCCH_3)_6(py)_3]No_3$	2930w	1350m	1440vs	950mw	658sh 669s	2975w	1590vs
$[Mn_3O(OOCCH_3)_6(py)_3]ClO_4$	2932m	1348m	1410vs	948mw	670m	2975sh	1609vs
$[Cr^{111}_2Mn^{11}O(OOCCH_3)_6(py)_3]$	2940w	1340m	1410vs	940w	655m	2985w	1630vs
$[Fe_2MnO(OOCCH_3)_6(py)_3]ClO_4$	2880w	1350s	1410vs	955w	660m	2920w	1605vs
$[Cr_2MnO(OOCCH_3)_6(py)_3]Cl$	2930w	1350m	1450vs	950m	670s	3080w	1620vs
$[Cr_2MnO(OOCCH_3)_6(py)_3]NO_3$	2930w	1350m	1450vs	952w	670s	3080w	1620vs
$[Mn_2FeO(OOCCH_3)_6(py)_3]ClO_4$	2930w	1348m	1450vs	950w	660vs 663s	2990w	1600vs
$[Mn_2FeO(OOCCH_3)_6(py)_3]NO_4$	2940w	1345m	1450s	950vw	660s	3115w	1605vs

$Mn^{III}Fe^{III}O$

The I.R spectrum of $[Mn_2FeO(OOCCH_3)_6(NC_5H_5)_3]^+$ together with those of their symmetrical analogues in the 700-400cm^{-1} region, are shown under Figure 2. The infrared spectrum for the symmetrical homonuclear complexes have been reported by Johnson *et al.* (1981) and that of the mixed-valence $Mn_2^{III}Mn^{II}$ is known. Saad (1990) reported that of the analogous complex $Fe_2^{III}Mn^{II}O$. The $\nu_{as}(Fe_3O)$ has been assigned to the broad band at 590cm^{-1} and $\nu_{as}(Me_3O)$ to a shoulder at 604cm^{-1}. The $\nu_{as}(Me_3O)$ split into A_1 and B_2 modes and were observed at about 586cm^{-1} and 607cm^{-1} respectively. The separation between the B_2 and A_1 modes is of the order of 25cm^{-1} in both the nitrate and the perchlorate salts, but it is 43cm^{-1} in the $Fe_2^{III}Mn^{II}O$ complex.

Vibrations of the MO_4 groups

This unit in an isolated system, the $\nu_d(MO_4)$ is doubly degenerate (symmetry E_u) but under D_{3h} symmetry, three such units couple to give four components, A_2', A_2", E' and E". Only the A_2' and E' modes are IR active (Table 3). The strongest I.R band is the E_u $\nu_d(MO_4)$ and was assigned to a strong band at ca. 360cm^{-1} in Fe_3O complex. In the symmetrical complexes Cr_3O and Mn_3O, the two (E_u' + A_2") modes are separated. These are observed at 453cm^{-1} and 391cm^{-1} in the Cr_3O and as a shoulder at 380cm^{-1} and medium band at 389cm^{-1} in Mn_3O. The frequency separation is expected to increase in the mixed-metal complexes but this study did not extend below 400cm^{-1}. However a shoulder of a weaker intensity appeared at 390cm^{-1} in addition to two strong bands at 453cm^{-1} and 419cm^{-1} in the $[Cr_2MnO(OOCCH_3)_6(NC_5H_5)_3]^+$ complex. The additional splitting may be attributed to the splitting of the E_u' mode under C_{2V} symmetry. Between 400-360cm^{-1} the spectrum of $[Mn_2FeO(OOCCH_3)_6(NC_5H_5)_3]^+$ is dominated by a broad peak.

Comparison of the IR spectrum of the complex with that of symmetrical complexes Fe_3O, Mn_3O and the mixed valence $Mn_2^{III}Mn^{II}O$ in the 700-600cm^{-1} region, give strong evidence of existence of the $Mn_2^{III}Fe^{III}O$ complexes. A band at 718cm^{-1} in the spectrum of the mixed-valence $Mn^{III}{}_2Mn^{II}$ totally absent from that of the complex, ruled out the presence of the mixed-valence $Mn_2^{III}Mn^{II}$ but the presence of some other impurity may not be ruled out.

Conclusions

By means of vibrational studies, we have been able to confirm the existence of two complexes by detecting effects of symmetry lowering in the new mixed-metal complexes, $Cr_2^{III}Mn^{III}$ and $Mn_2^{III}Fe^{III}$. The effects were observed in the splittings of the $\nu_{as}(M_3O$ in to two components A_1 and A_2 modes under C_{2v}. The separation between these modes is rather small in comparison to those of the mixed-metals $Fe_2^{III}M'O$, (M = Fe, Ni, Co and Mn) but similar to those of $Fe_2^{III}Mn^{III}O$, $Fe_2^{III}Co^{III}O$ and $Cr_2^{III}Co^{III}O$.. The consistency of the assignments provides additional justification for the existence of these complexes. It is hoped that they will provide further basis for electron transfer and magnetic studies.

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