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SYNTHESIS AND PROPERTIES OF TRIS(3-HYDROXY-2-METHYL-4-PYRONATO) COMPLEXES OF CHROMIUM(III), MANGANESE(III) AND IRON(III)

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Tris(3-hydroxy-2-methyl-4-pyronato)complexes of chromium(III), manganese(III) and iron(III) have been prepared. Comparison of their IR spectra suggests that a Jahn-Teller distortion is operative in the Mn(III) complex. The electronic spectrum of this complex is also consistent with a tetragonal structure caused by the Jahn-Teller effect.

It is known that hydroxy-4-pyrones form a five-membered stable chelate ring with various metal ions.[1)] The 5-hydroxy-2-hydroxymethyl-4-pyronato complexes of some bivalent metal ions were prepared and their structures investigated.[2)] On the other hand only the stability constants have been reported for the 3-hydroxy-2-methyl-4-pyronato complexes,[3)] and none of them isolated as yet.

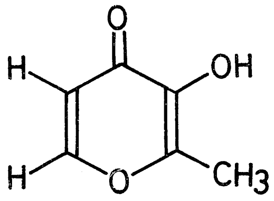

Fig. 1

We have prepared Cr(III), Mn(III) and Fe(III) complexes of 3-hydroxy-2-methyl-4-pyrone(HL, Fig. 1) by the following methods.

$\underline{CrL_3}$; A 15 ml portion of 1N NaOH solution was added to ca. 30 ml of water containing 1.89g of HL and 2.00g of $Cr(NO_3)_3 \cdot 9H_2O$. The mixture was refluxed for about 5hr, and then kept standing overnight in a refrigerator. A green-brown precipitate was recrystallized from hot water. Yield, 1.4g(Found: C,50.64; H,3.55; Cr,11.94%. Calcd for $C_{18}H_{15}O_9Cr$: C,50.60; H,3.51; Cr,12.08%.). $\underline{MnL_3}$; About 0.6 ml of 30% hydrogen peroxide and 15 ml of 1N NaOH solution was added to ca. 30 ml of water containing 1.89g of HL and 0.99g of $MnCl_2 \cdot 4H_2O$. This mixture was left for 10 days in a refrigerator. A brown-black precipitate was filtered and washed with water several times. Yield, 0.8g(Found: C,50.00; H,3.51; Mn,12.33%. Calcd for $C_{18}H_{15}O_9Mn$: C,50.23; H,3.51; Mn, 12.68%.). $\underline{FeL_3}$; A 15 ml portion of 1N NaOH solution was added to ca. 30 ml of water containing 1.89g of HL and 2.01g of $Fe(NO_3)_3 \cdot 9H_2O$. This solution was concentrated on a water bath to about 20 ml, and then kept overnight in a refrigerator. A red precipitate was filtered and recrystallized from hot water. Yield, 1.3g(Found: C,50.10; H, 3.90; Fe,12.47%. Calcd for $C_{18}H_{15}O_9Fe$: C,50.14; H,3.52; Fe,12.95%.).

The observed magnetic moments of the ML_3 complexes coincide very closely with the calculated spin-only values (Table 1), indicating that they are all high-spin complexes.

As shown in Table 2 the frequencies of the C=O and C=C stretching vibrations of these complexes are lower by about 50 cm^{-1} than those of the free ligand, respectively. This fact suggests that the 3-hydroxy-2-methyl-4-pyronate ion is coordinated to the metal atom through both oxygen atoms of the carbonyl and hydroxy groups. The spectral pattern in the ν(C=O) region is complicated in MnL_3. This may suggest that three ligands in MnL_3 are not equivalent.

Van den Bergen et al.[4)] compared the IR spectra of the tris(salisilaldehydato) complexes $M(sal)_3$ of Cr(III), Mn(III) and Fe(III) in the 700—250 cm^{-1} region, and found that the spectrum of the Mn(III) complex is almost an exact superimposition of the spectra of Cr(III) and Fe(III) complexes. Similar finding was also reported by Forman and Orgel[5)] for the IR spectra of tris(acetylacetonato)-chromium(III), -manganese(III) and -iron(III). In both of these series Cr(III), Mn(III) and Fe(III) are of high-spin type having the electron configuration $(t_{2g})^3$, $(t_{2g})^3(e_g)^1$ and $(t_{2g})^3(e_g)^2$, respectively. Mn(III) has only one electron in the two antibonding e_g orbitals. If these orbitals are split by a Jahn-Teller distortion, then four of the bonds will be as strong as in Cr(III) which has no electron in the e_g orbital, and the remaining two will be as weak as in Fe(III) of the $(e_g)^2$ configuration. Thus for a large Jahn-Teller splitting, the IR spectra of the Mn(III) complexes in the metal-sensitive regions could resemble a superimposition of those of the corresponding Cr(III) and Fe(III) complexes. By reference to the literature[4)] the spectra of the present ML_3 complexes (Fig. 2) are tentatively assigned as listed in Table 2. The spectrum of the Mn(III) complex is not an exact superimposition of the spectra of Cr(III) and Fe(III) complexes, but its somewhat intermediate features suggest that the Jahn-Teller effect is operative in the present Mn(III) complex, too.[4,5)]

The electronic spectra of high-spin manganese(III) compounds are of special interest

Table 1 Magnetic Moments(B.M.) of ML_3 Complexes

Complex	μ_{eff} (K)	Calcd
CrL_3	3.91(303.6)	3.87
MnL_3	4.87(303.6)	4.90
FeL_3	5.91(303.2)	5.92

Table 2 Characteristic Infrared Spectra(cm^{-1}) of ML_3 Complexes

HL	CrL_3	MnL_3	FeL_3	Assignment
1650s		1611s		ν(C=O)
	1601s	1597s	1602s	
1620s	1564s	1583s	1568s	ν(C=C)
1560s	1547s	1567s		
	1493s	1520s	1499s	
		640s		ν(M-O)*
	632s	630sh		
		610m	607m	
	553s	563s		ν(M-O)
		536s	540s.br	
563m	540sh			ligand vibration
537m	529sh	528sh		
510s.br	480s	492m		
		468s	473s	
	413s			ν(M-O)
	402s	397s		
	388s	378s	364s.br	
	356w			ligand vibration
322s	337w	339w	340w.sh	
305sh	313w	308w	320sh	

*ν(M-O) likely to be coupled with ring deformation modes.

because the ground state anticipated in the octahedral complex, ^5E_g(in O_h symmetry) is subject to strong Jahn-Teller forces. Davis et al. assumed a tetragonally elongated structure for the manganese(III) complex, and convincingly showed that the low-energy band (~10,000 cm^{-1}) can be assigned to the $^5B_{1g} \rightarrow {}^5A_{1g}$ transition in D_{4h} symmetry.[6] The absorption spectrum of the present MnL_3 complex shows bands at about 10.0(ε=51), 16.0(ε=150) and 23.6(ε=690) kK in dichloromethane which may be assigned to the $^5B_{1g} \rightarrow$

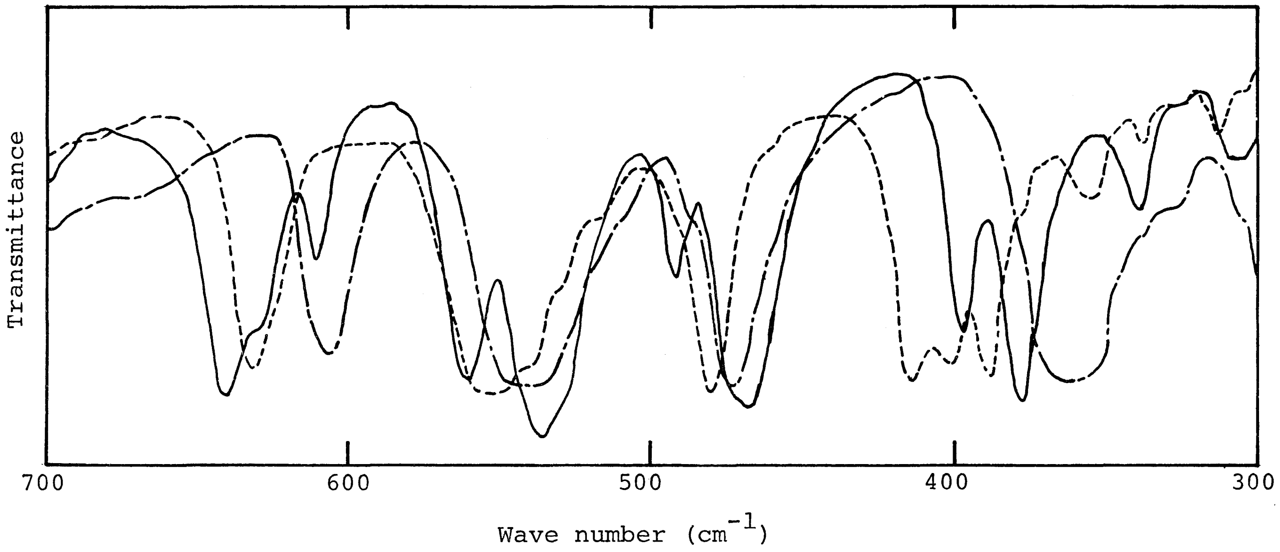

Fig. 2 Infrared Spectra of ML_3 Complexes

a) ------- CrL_3, b) ——— MnL_3, c) —·—·—FeL_3

$^5A_{1g}$, $^5B_{1g}\rightarrow{}^5B_{2g}$ and $^5B_{1g}\rightarrow{}^5E_g$ transitions in D_{4h} symmetry, respectively.

The absorption spectrum of CrL_3 shows bands at 16.8(ε=69.7), 21.1(ε=273) and 28.4 (ε=13,700) kK in dichloromethane, revealing that the complex has the octahedral structure. The bands at 16.8 and 21.6 kK may be assigned to the transitions $^4A_{2g}\rightarrow{}^4T_{2g}$ and $^4A_{2g}\rightarrow{}^4T_{1g}$, respectively. On the basis of the magnitude of the molar extinction coefficient, the band at 28.4 kK may be assigned to the charge transfer transition between the metal and ligand orbitals. The absorption spectrum of FeL_3 shows bands at about 24.3(ε=4,610) and 21.3(ε=3,800) kK in ethanol, which are also attributable to the charge transfer absorption.

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