Structural and Mechanistic Studies of Co-ordination Compounds. Part XII.[1] Syntheses and Characterization of Some Dianiono(1,4,8,11-tetra-azacyclotetradecane)-manganese(III), -iron(III), and -nickel(III) Salts

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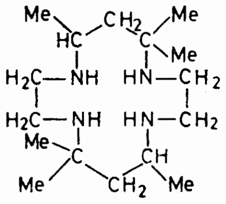
The syntheses and characterization of complexes of the type *cis*-$[\mathrm{FeX_2(L^4)}]^+$ [$\mathrm{L^4}$ = 1,4,8,11-tetra-azacyclotetradecane (cyclam); X = Cl, Br, and NCS] and *trans*-$[\mathrm{MX_2(L^4)}]^+$ (M = Mn, X = Cl, Br, NCS, or $\mathrm{N_3}$; M = Fe, X = Cl, Br, or NCS; and M = Ni, X = Cl or Br) are described. The assignment of geometrical configuration to these complexes is made on the basis of their i.r. spectra in the 790—910 $\mathrm{cm^{-1}}$ region. In some cases, the assignment of a *trans* configuration to the dihalogeno-complexes is confirmed by the presence of only one ν(M–X) stretching frequency in their far-i.r. spectra. Magnetic susceptibilities show that all the d^4 complexes prepared are high spin, whereas d^6 and d^7 complexes are low spin. For the d^5 iron(III) system, all the *cis* complexes prepared are high spin, whereas *trans* complexes are low spin. However, *trans*-$[\mathrm{FeBr_2(L^4)}][\mathrm{ClO_4}]$ with μ_{295} 3.90 B.M. appears to be in a high-spin–low-spin equilibrium at room temperature. The ambidentate thiocyanate ligand is *N*-bonded in each case. The electronic and far-i.r. spectra of these complexes are consistent with the electronic structures based on the magnetic properties.

Mechanisms of octahedral ligand-substitution reactions have been extensively investigated and developed for cobalt(III) [2-7] and, to a lesser extent, for chromium(III) [7-9] amine systems. In order to appreciate the effect of the electronic structure of the central metal ion on the reaction kinetics and mechanisms, it is desirable to extend the investigation to other systems of the first transition series. Recently, manganese(III) complexes of the *meso*- [10] and *rac*-isomer [11] of 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane, ($\mathrm{L^1}$), and iron(III) complexes of 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene, ($\mathrm{L^2}$),[12] and of *meso*-2,12-dimethyl-3,7,11,17-tetra-azabicyclo[11.3.1]heptadeca-1(17),13,15-triene, ($\mathrm{L^3}$),[13] have been described. However, these macrocycles contain excessive methyl substituents and might lead to serious steric effects, as has been observed for the cobalt(III) system of the macrocyclic amine ($\mathrm{L^1}$),[14,15] in the substitution reactions of these complexes. This paper describes the preparation and characterization of *cis*-$[\mathrm{FeX_2(L^4)}]^+$ and *trans*-$[\mathrm{MX_2(L^4)}]^+$ [M = Mn, Fe, and Ni; $\mathrm{L^4}$ = 1,4,8,11-tetra-azacyclotetradecane (cyclam); X = a series of uninegatively charged unidentate ligands]. The corresponding complexes of $\mathrm{Cr^{III}}$ [16] and $\mathrm{Co^{III}}$ [17,18] have been characterized elsewhere.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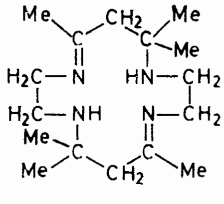
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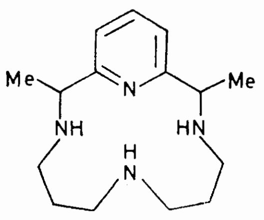
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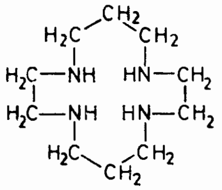
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EXPERIMENTAL

trans-*Dichloro*(1,4,8,11-*tetra-azacyclotetradecane*)*manganese*(III) *Chloride*.—A methanolic solution of ($\mathrm{L^4}$) [17] (2 g in 100 $\mathrm{cm^3}$) was added to a methanolic solution of $\mathrm{MnCl_2 \cdot 4H_2O}$ (2 g in 200 $\mathrm{cm^3}$). Air was bubbled through the greenish brown solution for 6 h, the colour gradually darkening. Addition of concentrated hydrochloric acid (10 $\mathrm{cm^3}$) gave immediately the desired apple-green solid which was filtered off and recrystallized from warm HCl (1 mol $\mathrm{dm^{-3}}$). The needle-shaped green *crystals* were collected, washed with acetone and diethyl ether, and dried at 100 °C *in vacuo* for 1 h (yield 1.5 g) (Found: C, 33.0; H, 6.4; Cl, 29.4; N, 15.5. Calc. for $\mathrm{C_{10}H_{24}Cl_3MnN_4}$: C, 33.2; H, 6.6; Cl, 29.5; N, 15.5%).

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The *perchlorate* salt was prepared by dropwise addition of a concentrated solution of sodium perchlorate to a solution of the chloride (1.5 g) in HCl (3 mol dm^{-3}, 20 cm^3). The crystals were filtered off, washed successively with ice-cold water, methanol, and diethyl ether, and dried in air (yield 1.2 g) (Found: C, 28.1; H, 5.9; Cl, 25.0; N, 12.6. Calc. for $C_{10}H_{24}Cl_3MnN_4O_4$: C, 28.2; H, 5.7; Cl, 25.4; N, 13.2%).

trans-*Dibromo*(1,4,8,11-*tetra-azacyclotetradecane*)*manganese*(III) *Bromide*.—This complex was prepared by dropwise addition of concentrated hydrobromic acid with stirring to a concentrated aqueous solution of *trans*-[$MnCl_2(L^4)$]Cl (1 g). Yellowish green *crystals* appeared, which were filtered off, washed with acetone and diethyl ether, and dried at 100 °C *in vacuo* for 2 h (yield 0.7 g) (Found: C, 24.6; H, 4.9; Br, 48.1; N, 11.3. Calc. for $C_{10}H_{24}Br_3MnN_4$: C, 24.3; H, 4.9; Br, 48.5; N, 11.3%).

trans-*Di-isothiocyanato*(1,4,8,11-*tetra-azacyclotetradecane*)-*manganese*(III) *Thiocyanate*.—This complex was prepared similarly to the dibromo-analogue by treating a concentrated aqueous solution of *trans*-[$MnCl_2(L^4)$]Cl (1 g) with a clear saturated aqueous solution of [NH_4][NCS]. The yellow *crystals* formed were filtered off, washed with acetone and diethyl ether, and dried in air (yield 0.5 g) (Found: C, 36.3; H, 5.6; N, 23.0; S, 22.1. Calc. for $C_{13}H_{24}MnN_7S_3$: C, 36.4; H, 5.6; N, 22.8; S, 22.4%).

The *perchlorate* salt was prepared by adding perchloric acid (70%) to a saturated solution of the thiocyanate in absolute methanol. The complex was washed with methanol and diethyl ether and dried in air (Found: C, 30.4; H, 5.2; Cl, 7.3; N, 18.0. Calc. for $C_{12}H_{24}ClMnN_6O_4S_2$: C, 30.6; H, 5.1; Cl, 7.5; N, 17.9%).

trans-*Diazido*(1,4,8,11-*tetra-azacyclotetradecane*)*manganese*(III) *Perchlorate*.—This complex was also prepared similarly to the dibromo-analogue by treating a concentrated aqueous solution of *trans*-[$MnCl_2(L^4)$]Cl (1 g) with a clear saturated solution of Na[N_3]. Addition of a strong aqueous solution of Na[ClO_4] precipitated out a yellow crystalline *solid* which was filtered off, washed with ethanol and diethyl ether, and dried in air (yield 0.7 g) (Found: C, 27.5; H, 5.3; Cl, 8.5; N, 32.0. Calc. for $C_{10}H_{24}ClMnN_{10}O_4$: C, 27.4; H, 5.5; Cl, 8.1; N, 31.9%).

cis-*Dichloro*(1,4,8,11-*tetra-azacyclotetradecane*)*iron*(III) *Chloride*.—This complex was prepared by adding a methanolic solution of $FeCl_2$ (1.2 g in 200 cm^3) to a methanolic solution of (L^4) (2 g in 200 cm^3). Air was bubbled through the solution for 5 h and concentrated HCl (10 cm^3) was added with stirring to the final solution. Yellow solids which formed on standing were collected and recrystallized by successively adding ethanol and diethyl ether to a saturated solution of the complex in HCl (1 mol dm^{-3}). The *complex* collected was washed with a small quantity of ice-cold water, then with methanol and diethyl ether, and dried at 80 °C *in vacuo* for 2 h (yield 1.2 g) (Found: C, 33.0; H, 6.5; Cl, 29.6; N, 15.8. Calc. for $C_{10}H_{24}Cl_3FeN_4$: C, 33.1; H, 6.6; Cl, 29.4; N, 15.5%).

cis-*Dibromo*(1,4,8,11-*tetra-azacyclotetradecane*)*iron*(III) *Bromide*.—This complex was prepared by adding hydrobromic acid (48%, 10 cm^3) with stirring to a clear solution of *cis*-[$FeCl_2(L^4)$]Cl (1 g) in cold nitric acid (1 mol dm^{-3}, 20 cm^3). Reddish *crystals* of the desired product gradually appeared, which were collected, washed with ethanol and diethyl ether, and dried in air (yield 0.6 g) (Found: C, 24.3; H, 4.7; Br, 48.0; N, 11.4. Calc. for $C_{10}H_{24}Br_3FeN_4$: C, 24.2; H, 4.9; Br, 48.4; N, 11.3%).

cis-*Di-isothiocyanato*(1,4,8,11-*tetra-azacyclotetradecane*)-*iron*(III) *Thiocyanate*.—This *complex* was similarly prepared with a similar yield to that of the dibromo-analogue by treating *cis*-[$FeCl_2(L^4)$]Cl with [NH_4][NCS] in an acidic medium (Found: C, 36.3; H, 5.5; N, 22.6; S, 22.5. Calc. for $C_{13}H_{24}FeN_7S_3$: C, 36.3; H, 5.6; N, 22.8; S, 22.3%).

The *perchlorate* salt was prepared by dropwise addition of concentrated $HClO_4$ to a saturated ice-cold solution of the thiocyanate in absolute methanol (Found: C, 30.3; H, 5.0; Cl, 7.6; N, 17.9. Calc. for $C_{12}H_{24}ClFeN_6O_4S_2$: C, 30.6; H, 5.1; Cl, 7.5; N, 17.8%).

trans-*Dichloro*(1,4,8,11-*tetra-azacyclotetradecane*)*iron*(III) *Perchlorate*.—An aqueous solution of *cis*-[$FeCl_2(L^4)$]Cl (1 g, 150 cm^3) was warmed on a steam-bath for *ca.* 20 min, during which time the colour became green. Addition of an aqueous solution of Na[ClO_4] slowly precipitated out a light green solid which was recrystallized by adding $HClO_4$ (70%) to a saturated solution of the complex in HCl (1 mol dm^{-3}). The *complex* was collected, washed with ethanol and diethyl ether, and dried in air (yield 0.3 g) (Found: C, 27.9; H, 5.4; Cl, 24.7; N, 13.3. Calc. for $C_{10}H_{24}Cl_3FeN_4O_4$: C, 28.1; H, 5.6; Cl, 25.0; N, 13.1%).

trans-*Dibromo*(1,4,8,11-*tetra-azacyclotetradecane*)*iron*(III) *Perchlorate*.—An aqueous solution (200 cm^3) of Fe[SO_4] (1.5 g) and LiBr (3 g) was added to an ethanolic solution of (L^4) (2 g in 100 cm^3) and air was bubbled through the brown solution for 3 h. Perchloric acid (70%) was added dropwise to the clear filtered solution and the brown complex slowly crystallized out. The complex was recrystallized by dissolving the solid in a minimum amount of HBr (0.5 mol dm^{-3}) and reprecipitating the complex with $HClO_4$ (70%). The *complex* was filtered off, washed with ethanol and diethyl ether, and dried in air (yield 1 g) (Found: C, 23.1; H, 4.6; Br, 30.9; N, 10.7. Calc. for $C_{10}H_{24}Br_2ClFeN_4O_4$: C, 23.3; H, 4.7; Br, 31.0; N, 10.9%).

trans-*Di-isothiocyanato*(1,4,8,11-*tetra-azacyclotetradecane*)-*iron*(III) *Thiocyanate*.—A clear saturated solution of [NH_4]-[NCS] (50 cm^3) was added to a warm aqueous solution of *cis*-[$FeCl_2(L^4)$]Cl (1 g in 150 cm^3). The yellow solution immediately became red and purple *crystals* formed on cooling. They were filtered off, washed with ethanol and diethyl ether, and dried in air (yield 0.8 g) (Found: C, 36.3; H, 5.6; N, 22.9; S, 21.9. Calc. for $C_{13}H_{24}FeN_7S_3$: C, 36.3; H, 5.6; N, 22.8; S, 22.3%). The complex could be recrystallized, if desired, by adding a concentrated solution of [NH_4][NCS] to a saturated aqueous solution of the complex.

The *perchlorate* salt was prepared by adding $HClO_4$ (70%) to a saturated solution of the thiocyanate in absolute methanol (Found: C, 30.8; H, 5.1; Cl, 7.7; N, 17.6. Calc. for $C_{12}H_{24}ClFeN_6O_4S_2$: C, 30.6; H, 5.1; Cl, 7.5; N, 17.8%).

trans-*Dichloro*(1,4,8,11-*tetra-azacyclotetradecane*)*nickel*(III) *Perchlorate*.—This complex was prepared by oxidizing an aqueous solution of [$NiCl_2(L^4)$] [19] (1 g in 70 cm^3) by the slow addition with stirring of an aqueous solution of [NH_4]$_2$[S_2O_8] (0.5 g in 25 cm^3) followed by H_2O_2 (100 vol., 5 cm^3). Dropwise addition of $HClO_4$ (70%) to the clear filtered solution slowly precipitated yellow *crystals* which were collected, washed with methanol and diethyl ether, and dried in air (yield 0.6 g) (Found: C, 27.6; H, 5.6; Cl, 24.8; N, 12.9. Calc. for $C_{10}H_{24}Cl_3N_4NiO_4$: C, 28.0; H, 5.6; Cl, 24.8; N, 12.9%).

[19] B. Bosnich, M. L. Tobe, and G. A. Webb, *Inorg. Chem.*, 1965, **4**, 1109.

trans-*Dibromo*(1,4,8,11-*tetra-azacyclotetradecane*)*nickel*(III) *Perchlorate*.—Hydrobromic acid (48%, 5 cm³) was added dropwise with stirring to an aqueous solution of *trans*-$[NiCl_2(L^4)][ClO_4]$ (0.5 g in 75 cm³) and orange *crystals* slowly separated out. They were filtered off, washed with methanol and diethyl ether, and dried in air (yield 0.4 g) (Found: C, 22.8; H, 4.4; Br, 32.0; N, 10.6. Calc. for $C_{10}H_{24}Br_2ClN_4NiO_4$: C, 23.2; H, 4.6; Br, 31.9; N, 10.8%).

Physical Measurements.—I.r. spectra were measured in Nujol mulls on a Perkin-Elmer 337 spectrophotometer (400—4 000 cm⁻¹) or on a Jesco IR-F far-i.r. spectrophotometer (200—700 cm⁻¹). Electronic solid reflectance spectra were measured with a Unicam SP 700 spectrophotometer. Magnetic susceptibilities of solid samples were measured at room temperature by the standard Gouy method using mercury tetrathiocyanatocobaltate(II) as the calibrant.[20]

RESULTS AND DISCUSSION

All the new complexes are highly coloured and appear to be stable indefinitely in the solid state. The isomeric purity of the complexes was checked by dissolving them in HCl (0.01 mol dm⁻³) and then absorbing them on a Dowex 50W-X8 (20—50 mesh) cation-exchange resin in the acid form. On eluting with HCl of different concentration, in each case only a single band developed on the column, which could then be eluted.

The magnetic properties of the new complexes are collected in Table 1. Since there is no real difference between the high- or low-spin states of chromium(III) complexes (d^3) and all cobalt(III) complexes (d^6) of (L^4) are low spin,[17,18] it is clear from Table 1 that as the central metal ion changes from Cr through Mn, Fe, Co, to Ni, the spin state of the (L^4) complexes changes gradually from high to low spin and the change-over point occurs at Fe^{III}. This variation in magnetic properties seems to be related to the increasing effective nuclear charge and hence the increasing combined ligand-field-splitting effect of (L^4) and any given axial ligand on these metal ions. The magnetic moment of *trans*-$[FeBr_2(L^4)][ClO_4]$ (μ_{295} 3.90 B.M.) * is obviously far in excess of the value expected for low-spin Fe^{III}, but is much smaller than that for a high-spin system. The reliability of this experimental value of μ_{295} has been carefully checked by two independent preparations, recrystallizations, and measurements of the magnetic susceptibility of the complex. There are at least two possible explanations for this extraordinary value, both of which assume a tetragonal-splitting pattern of the valence *d* orbitals (Figure 1) based on a D_{4h} microsymmetry of the complex with the *z* axis lying along the X–M–X axis. The observed moment could be taken as an indication that the complex is in equilibrium between low-spin $^2B_{2g}$[core $(e_g)^4(b_{2g})^1$] and high-spin $^6A_{1g}$[core $(e_g)^2(b_{2g})^1(a_{1g})^1(b_{1g})^1$]. However, the observed moment is also consistent with the complex being in an ' intermediate spin ' ^4E_g state [core $(e_g)^3(b_{2g})^1(a_{1g})^1$]. The latter explanation is rather unlikely in the light of the far-i.r. spectrum of the complex, which will be discussed later. The former explanation, on the other hand, can only be taken as tentative until some further information, such as the temperature variation of the magnetic susceptibility of the complex, becomes available.

TABLE 1

Magnetic moments (μ_{eff}) at 295 K of some complexes of the type $[MX_2(L^4)]Y$

Configuration	M	X	Y	μ_{eff} (B.M.)	Spin state
trans	Mn	Br	Br	4.85	High
trans	Mn	Cl	ClO_4	5.03	High
trans	Mn	NCS	NCS	4.79	High
trans	Mn	N_3	ClO_4	4.95	High
cis	Fe	Br	Br	6.13	High
cis	Fe	Cl	Cl	6.03	High
cis	Fe	NCS	NCS	5.14	High
trans	Fe	Br	ClO_4	3.90	High–low equilibrium
trans	Fe	Cl	ClO_4	2.71	Low
trans	Fe	NCS	NCS	2.35	Low
trans	Ni	Br	ClO_4	2.30	Low
trans	Ni	Cl	ClO_4	2.20	Low

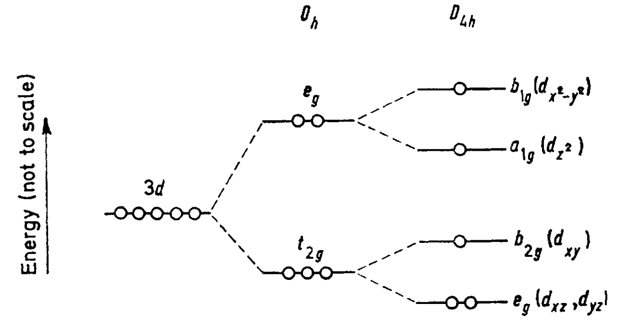

FIGURE 1 Assumed ordering of valence *d* orbitals of a complex of D_{4h} symmetry containing a relatively weak axial ligand

Such spin-state equilibria have been reported for a phenanthroline complex of Fe^{II} with the macrocyclic amine (L^2).[12] In terms of Figure 1, the ground states of the other systems are: Cr^{III}, $^4B_{1g}$[core $(e_g)^2(b_{2g})^1$]; Mn^{III}, $^5B_{1g}$[core $(e_g)^2(b_{2g})^1(a_{1g})^1$]; Co^{III}, $^1A_{1g}$[core $(e_g)^4(b_{2g})^2$]; and Ni^{III}, $^2A_{1g}$[core $(e_g)^4(b_{2g})^2(a_{1g})^1$]. *cis*-Iron(III) complexes, with a microsymmetry of C_{2v}, have a $^6A_1$ ground state since each of the five *d* orbitals is singly occupied. It should, however, be noted that the relative ordering of e_g and b_{2g} in Figure 1 may not be correct. For these *trans*-$[MX_2(L^4)]^+$ complexes, the d_{xy} orbital is essentially non-bonding and may be more stable than the d_{xz},d_{yz} pair which is usually π antibonding in character. This possible reversed ordering of e_g and b_{2g} only alters the ground-state designation of one of the systems discussed above. In this reversed ordering scheme, the ground electronic configuration of low-spin Fe^{III} becomes [core $(b_{2g})^2(e_g)^3$] with a ^2E_g ground state. Unfortunately, we cannot yet assign with confidence, in the absence of sufficient experimental information, the proper ground state of these low-spin iron(III) complexes.

The i.r. spectra of these complexes in the 790—910 cm⁻¹ region, together with those of some relevant cobalt(III) complexes of (L^4) are collected in Table 2.

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* 1 B.M. ≈ 9.27×10^{-24} A m².

[20] B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 1958, 4190.

The spectra are clearly divided into two sets, each being very similar to those of either the *cis* or *trans* isomers of the well characterized cobalt(III) complexes.[21] Since these vibrations are almost exclusively associated with the macrocyclic amine ligand, it is expected that they should be dependent on the geometrical configuration of the macrocycle about the central metal ion, but would not be much affected, as observed,[21] by the nature of the other ligands and counter ions present. It is also expected that the i.r. spectra would be independent of the nature of the central metal ion. This is now observed and hence the assignment of the geometrical configuration to the new complexes has been made on the basis of the i.r. spectra in this 790—910 cm^{-1} region where a consistent variation between the *cis* and *trans* isomers of cobalt(III) complexes of (L^4) has been observed.[21] Those complexes assigned a *trans* configuration showed two groups of bands separated by $\geqslant$70 cm^{-1}. The group at a lower frequency, which arises essentially from the methylene vibration,[21] consisted of one sharp band, while the group at a higher frequency, which is due predominantly to the secondary amine vibration,[21] mainly consisted of two bands, although in some cases one relatively broad band or three closely packed bands were also observed. For the less symmetrical *cis* isomers the methylene vibration invariably showed two bands in the 790—830 cm^{-1} region, while the amine vibration showed at least three bands in a lower frequency range (840—890 cm^{-1}) and hence closer to the methylene bands than those of the *trans* isomers. The i.r. spectra of the [M(NCS)$_2$(L^4)]-[ClO$_4$] complexes clearly indicate that the ambidentate thiocyanate ligand is *N*-bonded since all the ν(C–S) vibrations occurred above 780 cm^{-1} [22] [*trans*-Mn, 800w; *trans*-Fe, 860m; and *cis*-Fe, 812m(sh) cm^{-1}] and, less critically, all the strong ν(N–C) vibrations occurred below 2 100 cm^{-1} [22] (*trans*-Mn, 2 060; *trans*-Fe, 2 080; and *cis*-Fe, 2 100, 2 060, and 2 020 cm^{-1}). It is of interest that the ν(C–S) vibrations of *trans*-Mn and *cis*-Fe are distinctly lower than those of *trans*-Fe and *trans*-Co (852 cm^{-1}), indicating that the corresponding M–NCS bond strength is weaker, as suggested by the presence of an electron in the σ-antibonding d_{γ^*} orbital in the former two complexes.

TABLE 2

Infrared spectra in the 790—910 cm^{-1} region of some *cis* and *trans* complexes of the type [MX$_2$(L^4)]Y [a]

Configuration	M	X	Y	Frequencies of absorption bands (cm^{-1}) [b]					
				N–H vibration				CH$_2$ vibration	
cis	Co	Cl	Cl	890 (w)	872 (s)	859 (s)	841 (w)	824 (w)	808 (s)
cis	Co	N$_3$	NO$_3$	888 (w)	874 (m)	859 (m)	840 (w)	825 (m)	808 (m)
cis	Co	NCS	½(PtCl$_6$)	890 (w, sh)	876 (m)	860 (m)	846 (m)	822 (w, sh)	807 (m)
cis	Co	NO$_2$	NO$_3$		874 (m)	860 (m)	840 (w)	828 (m)	802 (w)
cis	Fe	Cl	Cl		866 (s)	858 (m)	850 (s)	808 (m)	794 (s)
cis	Fe	Br	Br		866 (s)	860 (m)	850 (s)	808 (m)	795 (s)
cis	Fe	NCS	ClO$_4$	892 (w)	872 (m)	860 (m)	850 (m)	808 (m)	798 (m)
trans	Co	Cl	Cl	906 (s)	888 (s)			818 (s)	
trans	Co	Br	Br	900 (m)	888 (m)			812 (m)	
trans	Co	N$_3$	NO$_3$	900 (m)	890 (m)			812 (m)	
trans	Co	NCS	NCS	902 (m)	890 (m)			822 (w)	
trans	Co	NO$_2$	½(PtCl$_6$)	892 (m, sh)	887 (m)			820 (m, sh)	
trans	Co	CN	Cl	903 (m)	893 (m)			822 (m)	
trans	Fe	Cl	ClO$_4$	890 (s)	888 (s, sh)			810 (m)	
trans	Fe	Br	ClO$_4$	888 (s)	882 (s)			810 (m)	
trans	Fe	NCS	ClO$_4$	898 (s)	890 (s)			815 (m)	
trans	Mn	Cl	Cl	798 (s)				805 (m)	
trans	Mn	Br	Br	880 (s)				798 (m)	
trans	Mn	NCS	ClO$_4$	882 (s)				808 (m)	
trans	Mn	N$_3$	ClO$_4$	882 (s)				808 (m)	
trans	Ni	Cl	ClO$_4$	908 (s)	890 (s)	884 (s)		820 (s)	
trans	Ni	Br	ClO$_4$	905 (s)	888 (s)	882 (s)		820 (s)	
trans	Ru	Cl	Cl	898 (s)	888 (s)			805 (m)	

[a] Data for cobalt(III) complexes are quoted from ref. 21 and those for the ruthenium(III) complex from P. K. Chan, D. A. Isabirye, and C. K, Poon, *Inorg. Chem.*, 1975, **14**, 2579. [b] Absorptions due to axial ligand vibrations in this region are not included, abbreviations: s. strong; m, medium; w, weak; sh, shoulder.

A comparison of the far-i.r. spectra (200—700 cm^{-1}) of *trans*-[MCl$_2$(L^4)]Y and those of the corresponding dibromo-complexes, as typified in Figure 2 for the iron(III) system, enabled the ν(M–X) stretching frequencies to be determined. For all the *trans* complexes, only one band was observed (M = Mn, X = Cl, Y = ClO$_4$, 212; M = Fe, X = Cl and Br, Y = ClO$_4$, 335 and 230 respectively; M = Co, X = Y = Cl and Br, 338 and 235 respectively; and M = Ni, X = Cl, Y = ClO$_4$, 220 cm^{-1}). The ν(M–Br) stretching frequencies of the dibromo-complexes of Mn$^{\text{III}}$ and Ni$^{\text{III}}$ occurred well below our instrumental limit of 200 cm^{-1} and hence could not be determined. The far-i.r. spectra of *cis*-dihalogeno-complexes are rather complex and no unambiguous assignment of ν(M–X) bands can yet be made. The present observation is important in two aspects. First, the presence of only one ν(M–X) band confirms the previous assignment of a *trans* configuration to these dihalogeno-complexes. Secondly, the much

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[21] C. K. Poon, *Inorg. Chim. Acta*, 1970, **5**, 322.

[22] K. Nakamoto, 'Infrared Spectra of Inorganic and Coordination Compounds,' 2nd edn., Wiley, New York, 1970, p. 187.

lower ν(M–X) stretching frequencies in the manganese(III) and nickel(III) systems relative to those of Fe^{III} and Co^{III} is fully consistent with the presence of an electron in the σ-antibonding d_{z^2} orbital in the former two systems. Similarly, it can be argued that the relatively high ν(Fe–Br) vibration for *trans*-$[FeBr_2(L^4)][ClO_4]$ indicates that the 'intermediate-spin' ground-state designation (^4E_g), which has an electron in the d_{z^2} orbital, is very unlikely.

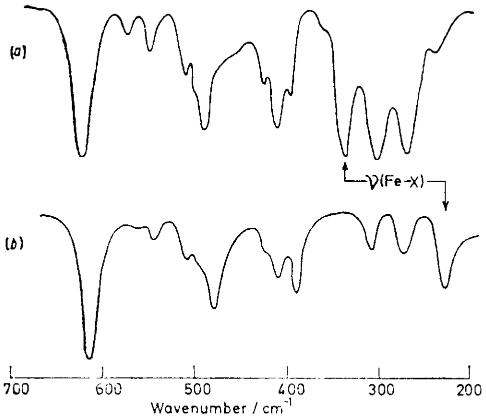

FIGURE 2 Far-i.r. spectra (700—200 cm^{-1}) of *trans*-$[FeX_2(L^4)][ClO_4]$ [X = Cl (*a*) and Br (*b*)]

The electronic spectra of these complexes are also consistent with previous discussion of their electronic structures. Since most of the complexes are either only sparingly soluble in most common solvents or their spectra are solvent dependent in some cases, only the solid reflectance spectra are recorded in Table 3. The spectra of the complexes of Mn^{III} and Ni^{III} were characterized by the presence of a relatively weak ligand-field band in the near-i.r. region (9 000—13 000 cm^{-1}). This is consistent with the presence of an electron in the d_{z^2} orbital such that the transition from this orbital to the $d_{x^2-y^2}$ orbital (*i.e.* Mn, $^5B_{1g}\rightarrow{}^5A_{1g}$; Ni, $^2A_{1g}\rightarrow{}^2B_{1g}$) will occur at a much lower energy than the transitional energy originating from either the d_{xy} or d_{xz},d_{yz} orbitals in low-spin complexes of Fe^{III}, Cr^{III},[16] and Co^{III},[17,18] the ligand-field bands of which usually occur in the visible region. As expected, no spin-allowed ligand-field band exists in high-spin *cis*-iron(III) complexes. In the case of *cis*-$[Fe(NCS)_2(L^4)][NCS]$, the visible band at 18 600 cm^{-1} is probably charge transfer in nature because its intensity is nearly matching those of other charge-transfer bands in the u.v. region and it is too intense to be assigned as a spin-forbidden ligand-field band.

TABLE 3

Solid reflectance spectra of some complexes of the type $[MX_2(L^4)]Y$

Configuration	M	X	Y	Bands (cm^{-1}) [a]
cis	Fe	Cl	Cl	~25 200 (s, b, sh), 29 200 (s), ~35 000 (s, b, sh), 37 500 (s), 44 400 (s)
cis	Fe	Br	Br [b]	~25 000 (s, b), ~30 000 (s, b, sh), ~35 600 (s, b)
cis	Fe	NCS	NCS	18 600 (m), ~22 000 (m, sh), ~36 400 (s, b, sh), 39 200 (s), 44 400 (s)
trans	Fe	Cl	ClO_4	17 200 (m), 21 200 (m), 27 600 (s), ~33 000 (s, b, sh), ~39 000 (s, b)
trans	Fe	NCS	NCS	18 400 (s), 28 800 (s), 33 300 (s, b), 38 100 (s), 44 500 (s)
trans	Mn	Cl	Cl	12 800 (w), ~27 500 (s, sh), 32 800 (s), 37 300 (s), 42 600 (s)
trans	Mn	Br	Br	12 100 (w), ~27 600 (s, sh), 32 400 (s), 37 400 (s), 43 000 (s)
trans	Mn	NCS	NCS	10 900 (w), ~25 600 (s, sh), ~27 600 (s, sh), 29 700 (s), 37 300 (s), 42 900 (s)
trans	Mn	N_3	ClO_4	9 200 (w), ~24 600 (s, sh), 28 500 (s), 37 500 (s), 42 600 (s)
trans	Ni	Cl	ClO_4	12 300 (w), ~26 000 (s, sh), 34 000 (s, b), ~36 000 (s, sh), ~42 800 (s, sh)
trans	Ni	Br	ClO_4 [c]	~25 600 (s, b), ~32 000 (s, b), ~40 200 (s, b)

[a] Abbreviations: w = weak, m = medium, s = strong, b = broad, and sh = shoulder. [b] Energy cut off above 44 000 cm^{-1}. [c] Energy cut off below 15 000 cm^{-1}.

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