Magnetic Circular Dichroism and Absorption Spectra of Some d^5 Hexahalides

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We have measured the m.c.d. and absorption spectra of $RuCl_6^{3-}$, $RuBr_6^{3-}$, and $Ru(NH_3)_6Cl_3$ in solution at room temperature and $IrCl_6^{2-}$ in a rigid polymer matrix at room temperature and 10 K. The results are analysed in terms of the well-established charge-transfer interpretation. The splittings observed in the $^2T_{2u}$ band at room temperature and that found in $^2T_{1u}(\pi)$ at low temperature are attributed to the combined effects of a low symmetry distortion and spin–orbit coupling. The m.c.d. of the first band in $Ru(NH_3)_6^{3+}$ suggests that this is a transition to the $^2T_{1u}(\sigma)$ state.

In a recent paper on bonding studies from charge transfer spectra [1-3] we have emphasised the importance of a reliable interpretation of the spectrum of the parent hexacyanide or hexahalide species before approaching the substituted series $IrCl_4L_2$, $Fe(CN)_5L^{n-}$, and $RuCl_3L_3$. We have shown however that when the spectra of the latter compounds can be interpreted important information concerning metal–ligand bonding is obtained.

In this work we report a further investigation of some low-spin d^5 hexahalides including m.c.d. and absorption spectra of $IrCl_6^{2-}$ in an isotropic host at 10 K; $RuCl_6^{3-}$ for the first time and a confirmation of previous work [4] on $RuBr_6^{3-}$. In addition we report the m.c.d. spectrum of $Ru(NH_3)_6^{3-}$ for the first time. This is of interest since the filled π orbitals found in cyanide and halide complexes are absent and the first parity allowed L $\longrightarrow$ M charge transfer is $t_{1u}(\sigma) \longrightarrow t_{2g}$.

EXPERIMENTAL

In this study we are concerned with $K_2IrCl_6,6H_2O$, $(PhNH_3)_3RuCl_6$, $(PhNH_3)_3RuBr_6$, and $Ru(NH_3)_6Cl_3$.

The m.c.d. of $IrCl_6^{2-}$ has been previously published together with a well developed theory.[4,5] These references report the m.c.d. and absorption spectra of $(Bu^n_4N)_2IrCl_6$ in dichloromethane solution and doped into crystals of $(MeNH_3)_2SnCl_6$ where the $IrCl_6^{2-}$ ion was thought to experience a trigonal distortion. Here, $K_2IrCl_6,6H_2O$ has been examined in a polymethacrylic acid (PMA) film at room and liquid helium temperature. The room-temperature spectrum and m.c.d. (Figure 1) is identical to that of $K_2IrCl_6,6H_2O$ and $Na_2IrCl_6,6H_2O$ in 4M-HCl; the extinction coefficient values are based on concentrations calculated from solution values. Figure 1 also shows the same sample at *ca.* 10 K.

The purpose of this examination of $K_2IrCl_6,6H_2O$ was to identify the cause of the splitting of the second band (23,500 cm^{-1}) observed in the absorption spectra.[6] This splitting is not found in the spectrum of the t-butylammonium salt.[4] A splitting is observed in the m.c.d. of this band of the $(MeNH_3)_2SnCl_6$ crystals but here $IrCl_6^{2-}$ experiences a D_{3d} crystalline distortion.[5] It was therefore decided to study the potassium salt in a medium where no regular distortion exists but could be examined at helium temperatures.

The m.c.d. of $RuCl_6^{3-}$ is reported here for the first time (Figure 2); the spectrum shown is of $(PhNH_3)_3RuCl_6$ in 12M-HCl. It is identical to that reported by Jørgensen [6] and agrees with the reflectance spectrum of the solid. The m.c.d. of $RuBr_6^{3-}$ is also reported (Figure 3) since although this has been published [4] there was some doubt about the purity of the sample which was produced from Na_2RuCl_5,H_2O. Here the spectrum is of $(PhNH_3)_3RuBr_6$ in 40% HBr.

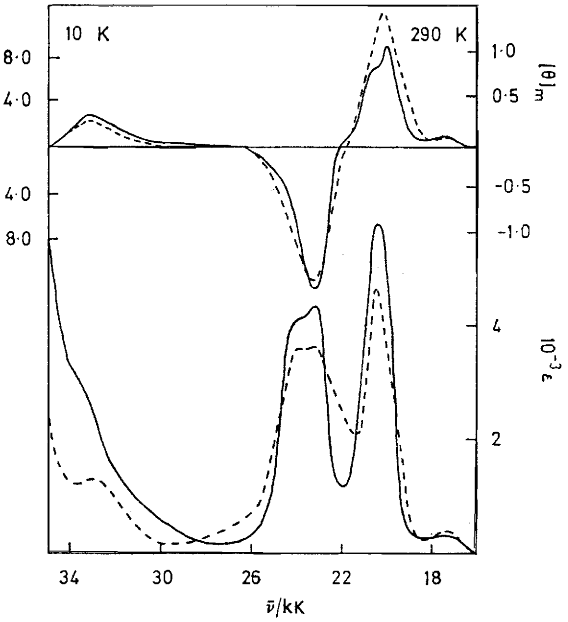

FIGURE 1 Absorption and m.c.d. spectra of $K_2IrCl_6,6H_2O$ in polymethyl methacrylate at room temperature (broken line) and 10 K (solid line). ε Is the molar extinction coefficient/(l mol^{-1} cm^{-1}). $[\theta]_m$ Is the molar ellipticity/° dl dm^{-1} mol^{-1} G^{-1}

The sample of $Ru(NH_3)_6Cl_3$ was kindly donated by Professor H. Taube of Stanford University.

THEORY

The theoretical interpretation of the m.c.d. of these octahedral systems has been reported in detail in references 4, 5, and 7 and is discussed only in outline here.

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[1] M. D. Rowe, A. J. McCaffery, R. Gale, and D. N. Copsey, *Inorg. Chem.*, 1972, **12**, 3090.

[2] R. Gale and A. J. McCaffery, *J.C.S. Dalton*, 1973, 1344.

[3] M. D. Rowe and A. J. McCaffery, *J. Inorg. Nuclear Chem.*, to be published.

[4] G. N. Henning, A. J. McCaffery, P. N. Schatz, and P. J. Stephens, *J. Chem. Phys.*, 1968, **48**, 5636.

[5] A. J. McCaffery, P. N. Schatz, and T. E. Lester, *J. Chem. Phys.*, 1969, **50**, 379.

[6] C. K. Jørgensen, *Mol. Phys.*, 1959, **2**, 309.

[7] S. B. Piepho, T. E. Lester, A. J. McCaffery, J. R. Dickinson, and P. N. Schatz, *Mol. Phys.*, 1970, **19**, 781.

Figure 1 (ref. 4) shows a schematic molecular orbital diagram based on that of Ballhausen and Gray[8] for O_h complexes, modified with the information obtained from m.c.d. experiments. The allowed charge-transfer states are shown in Figure 5 together with the effects of spin–orbit coupling and a low symmetry D_{4h} distortion.

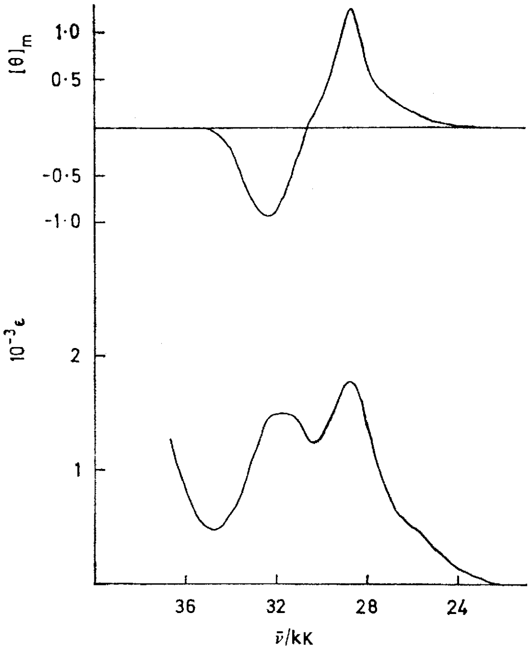

FIGURE 2 Absorption and m.c.d. spectra of $(PhNH_3)_3RuCl_6$ in 12M-HCl. Units as for Figure 1

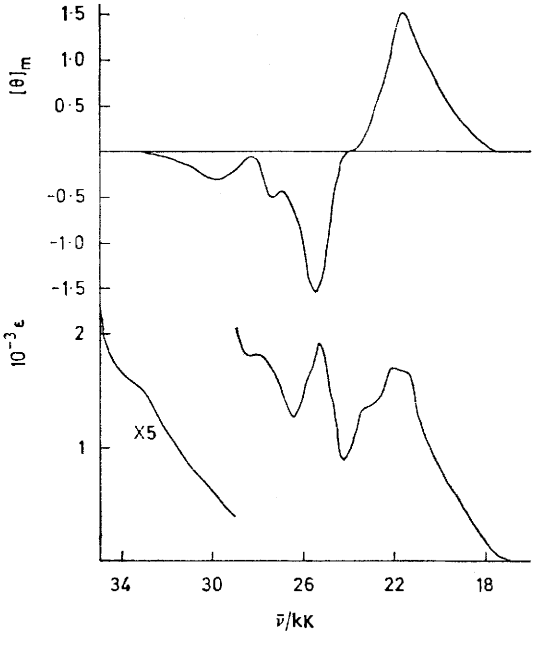

FIGURE 3 Absorption and m.c.d. spectra of $(PhNH_3)_3RuBr_6$ in 40% HBr. Units as for Figure 1

It is well known from variable temperature crystal studies[5] that the m.c.d. of $IrCl_6^{2-}$ is predominantly due to *C* terms arising from the ground-state degeneracy. *B* terms can arise[5] from mixing of the ground-state spin–orbit components *via* the magnetic field, but the magnitude of the spin–orbit splitting (ξ_d Ir^{IV} = 2000 cm^{-1}, Ru^{III} = 1100 cm^{-1}) makes the *B* term contributions small and they are not discussed further here.

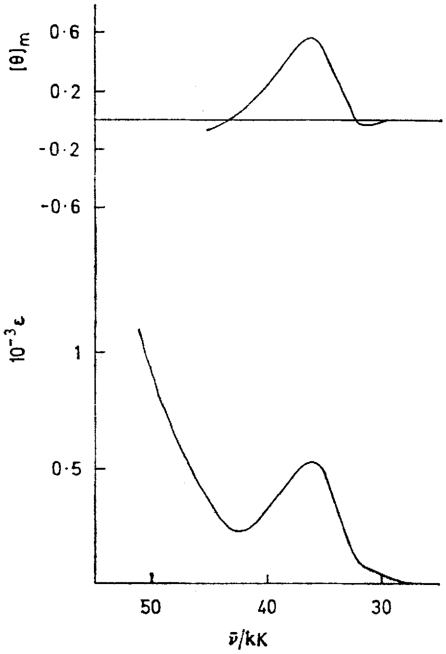

FIGURE 4 Absorption and m.c.d. spectra of $Ru(NH_3)_6Cl_3$ in aqueous solution. Units as for Figure 1

C terms calculated using the isotropic formula for the allowed charge-transfer transitions are given in Table 1 (ref. 7) together with the corresponding values of *D*, the dipole strength.

It is appropriate here to mention the magnitude of the

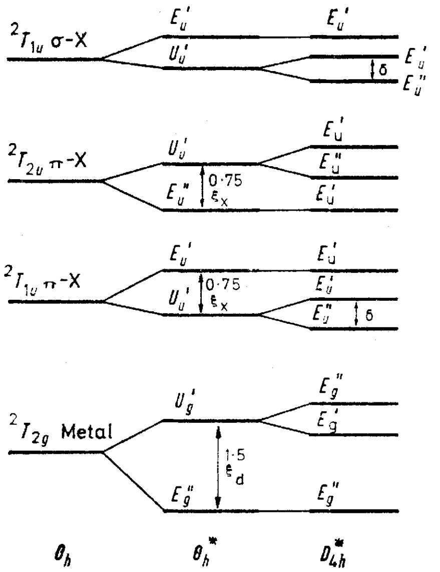

FIGURE 5 Ground and excited states of the d^5 hexahalide system showing spin–orbit and low-symmetry splittings

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[8] C. J. Ballhausen and H. B. Gray, 'Molecular Orbital Theory,' W. A. Benjamin, New York, 1965.

spin–orbit splitting of the ligand excited states. The splitting of the π ligand states is calculated by assuming that the only non-zero contribution comes from p orbitals on the same ligand; overlap terms are neglected. Similar considerations for the σ-ligand $^2T_{1u}$ state shows the spin–orbit splitting to be small since it is dependent only on overlap terms. The splitting shown in Figure 5 for this state is therefore only schematic.

DISCUSSION

$K_2IrCl_6,6H_2O$.—Figure 1 clearly shows the splitting of the band centred at 23,500 cm^{-1} in the absorption spectra into two components at 23,800 cm^{-1} and 23,200 cm^{-1}. The positive C term (negative $[\theta]_m$) lines up with the latter lower energy component in the absorption spectrum but there is no shoulder in the m.c.d. corresponding to the 23,800 cm^{-1} component seen in the absorption spectrum. In the 10 K m.c.d. the first band which is a negative C term at 20,400 cm^{-1} shows a well defined shoulder which has no equivalent in the absorption spectrum.

The increase in $[\theta]_m$ values at low temperature confirms the C term character of the m.c.d. although correct $1/T$ behaviour is not shown. As mentioned,[1] this is found for the C terms of many samples doped into plastic films and may be due to heating of the sample by the light beam or by radiation from the windows of the optical channel. Heating experiments with these polymers indicate that spin–lattice relaxation processes are very lengthy and the effective temperature of the excited molecules may be quite high.

Experimental C, D, and C/D values are given in the Table; for the reasons just mentioned we shall use the 10 K spectra only for its qualitative information.

If we concentrate on the room-temperature spectra, the m.c.d. band at 20,500 cm^{-1} with negative C term is due to the $^2T_{2g} \longrightarrow {}^2T_{1u}(\pi\text{-Cl})$ transition and involves both U_u' and E_u' spin–orbit states which are only split by up to 440 cm^{-1}, ξ_{Cl} being 590 cm^{-1}. The experimental C/D value for this band is $-0{\cdot}21$ which is a little low compared with the theoretical value of $-0{\cdot}45$.

Experimental m.c.d. parameters

Compound	Band/ cm^{-1}	C	D	C/D
$K_2IrCl_6,6H_2O$ in P.M.A.	20,400	$-0{\cdot}70$	3·32	$-0{\cdot}21$
290 K	23,500	$+0{\cdot}88$	4·90	$+0{\cdot}18$
	32,000	$-0{\cdot}12$	1·05	$-0{\cdot}11$
$K_2IrCl_6,6H_2O$ in P.M.A.	20,400	$-0{\cdot}15$	4·05	$-0{\cdot}04$
10 K	23,500	$+0{\cdot}19$	3·98	$+0{\cdot}05$
$(PhNH_3)_3RuCl_6$ in 12M-	28,700	$-0{\cdot}50$	1·72	$-0{\cdot}29$
HCl 290 K	32,000	$+0{\cdot}39$	1·30	$+0{\cdot}30$
$(PhNH_3)_3RuBr_6$ in 40%	21,600	$-1{\cdot}11$	2·74	$-0{\cdot}40$
HBr 290 K	25,300	$+0{\cdot}56$	1·30	$+0{\cdot}43$
$Ru(NH_3)_6Cl_3$ in H_2O 290 K	36,500	$-0{\cdot}54$	0·87	$-0{\cdot}62$

The band at 23,500 cm^{-1} with positive C term is due to the $^2T_{2g} \longrightarrow {}^2T_{2u}(\pi\text{-Cl})(E_u'' + U_u')$ transition; this has an experimental C/D of $+0{\cdot}18$ which is again somewhat low compared with the theoretical value of $+0{\cdot}45$.

The band at 33,000 cm^{-1} has been assigned to the $^2T_{2g} \longrightarrow {}^2T_{1u}(\sigma\text{-Cl})(E_u' + U_u')$ transition[4] since it has the correct sign of m.c.d. although the experimental C/D value observed here is also low.

The splitting of the band at 23,500 cm^{-1} has been observed in a single-crystal study of $Na_2IrCl_6,6H_2O$ by Jørgensen and Kondo[9] and the two components were strongly polarised, suggesting that the splitting arises from some kind of distortion, possibly tetragonal. The splitting cannot be due solely to spin–orbit coupling as it is not observed in the spectrum of $(Bu^n{}_4N)_2IrCl_6$ in dichloromethane solution.[4] Further, since this splitting is observed in aqueous solutions of the potassium salt as well as in the polymer film it cannot be due to a crystal lattice distortion. The e.s.r. of our doped PMA sample at 20 K shows only one isotropic g-value at $g = 1{\cdot}80$ in agreement with the values obtained for $IrCl_6{}^{2-}$ in cubic crystals.[10] The $^2T_{2g}$ metal ground state must then be undistorted, the metal atom being in a mainly octahedral environment.

If the splitting of the 23,500 cm^{-1} band is due to a distortion it seems likely that it must be a distortion of the excited state. It is possible that it arises from an interaction between the chlorine ligands and water molecules in the second co-ordination sphere. This would require that a similar interaction exists in the crystal as in solution. Such an interaction might be expected to affect the vibrational frequencies of the complex and show up in the i.r. and Raman spectra of these compounds. The far-i.r. and Raman spectra of K_2IrCl_6[11,12] have been interpreted in terms of undistorted octahedral symmetry although no mention was made of whether the compound was hydrated or not. Interestingly the vibrational spectra[12] of K_3RhCl_6,H_2O and K_3IrCl_6,H_2O indicate a possible D_{4h} distortion. N.q.r. studies have been carried out on K_2IrCl_6 presumably in the hydrated form since the sample was crystallised from aqueous solution. Only one resonance line was observed from the chlorine atoms, indicating that they are all crystallographically equivalent.

Another possibility is that the splitting results from a Jahn–Teller distortion of the $^2T_{2u}(U_u')$ state *via* coupling with a suitable vibrational mode (e_g or t_{2g}). This type of effect has been suggested by Schatz *et al.*[7] to account for the splitting of the $^2T_{1u}(U_u')$ state of $IrBr_6{}^{2-}$ in various crystalline host lattices. The same authors, however, consider that structure in the m.c.d. and absorption spectra of the $^2T_{2u}(U_u')$ region of these systems is best explained in terms of a static distortion rather than a Jahn–Teller splitting. Bird *et al.*[13] have suggested that the bands at 18,500 cm^{-1} and 19,250 cm^{-1}

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[9] C. K. Jørgensen and R. Kondo, personal communication.

[10] J. H. E. Griffiths and J. Owen, *Proc. Roy. Soc.*, 1954, *A*, **96**, 226.

[11] D. M. Adams and H. A. Gebbie, *Spectrochim Acta*, 1963, **19**, 925.

[12] P. J. Hendra and P. J. D. Park, *Spectrochim. Acta*, 1967, **23**, 1635.

[13] B. D. Bird, P. Day, and E. A. Grant, *J. Chem. Soc.* (*A*), 1970, 100.

in the absorption spectrum of $(\mathrm{EtNH_3})_2\mathrm{SnBr_6{:}Ir^{4+}}$ crystals at low temperature are due to Jahn–Teller *splitting of the* $^2T_{2u}(U_u')$ state. However the m.c.d.[7] of these two bands are of opposite sign, in agreement with the sign of the *C* terms calculated for transitions to the $^2T_{2u}(U_u')[E'' + E']$ * states split by a static D_{4h} or D_{3d} distortion. The calculated *C* terms are shown in Table 1 (ref. 7) and it can be seen that *C* terms for the above states split by a Jahn–Teller effect are calculated to be of the same sign.

Before considering our experimental data, we should mention the recent study [14] of the m.c.d. of $\mathrm{Cs_2ZrCl_6{:}Ir^{4+}}$. The interpretation of the $^2T_{2g} \longrightarrow {}^2T_{1u}(\pi\text{-Cl})$ region follows the usual pattern, but in the $^2T_{2g} \longrightarrow {}^2T_{2u}(\pi\text{-Cl})$ region the authors claim that spin–orbit splitting is quenched *via* a Ham effect. This, in effect, means that the state experiences a Jahn–Teller distortion which is greater than spin–orbit coupling.[15] Diagonalisation of the functions under the Jahn–Teller effect results in the matrix elements of orbital angular momentum and hence spin–orbit coupling being off-diagonal and their magnitudes are reduced by a vibrational overlap integral.[15] The experimental evidence in support of the Ham effect [14] is observation of fine structure on the no-phonon line of the $^2T_{2g}(E_g'') \longrightarrow {}^2T_{2u}(E_u'')$ transition which the authors suggest to be the no-phonon line of the $^2T_{2g}(E_g'') \longrightarrow {}^2T_{2u}(U_u')$ transition, spin–orbit splitting having been reduced to 6 cm^{-1}.

We return to the spectra obtained in this study (Figures 1 and 2); if the splitting of the $^2T_{2u}(\pi\text{-Cl})$ band is caused by a Jahn–Teller mechanism then the splitting should increase with increasing temperature following the increasing amplitude of the vibration causing the splitting.[7,15] The spectra do not indicate this, since although the two clearly resolved peaks seen at room temperature at 23,200 cm^{-1} and 23,800 cm^{-1} become a peak and a well defined shoulder respectively at 10 K, this is only a very slight change for a 280 K temperature change and is probably due to the slightly greater increase in height of the 23,200 cm^{-1} peak. Further, if this is a Jahn–Teller splitting then it should also be observed in the spectrum of $(\mathrm{Bu^n{}_4N})_2\mathrm{IrCl_6}$ in dichloromethane,[4] although it is possible that the vibration responsible is influenced in some way by the water solvent cage or the water of hydration in the crystal lattice of $\mathrm{K_2IrCl_6,6H_2O}$.

The 10 K m.c.d. of the $^2T_{1u}(\pi\text{-Cl})$ band at 20,300 cm^{-1} shows a shoulder at 20,500 cm^{-1}. The fact that such a shoulder does not appear in the absorption band together with the change in peak position compared with the room-temperature m.c.d. suggests that the shoulder is caused by a positive *C* term cutting in to a predominantly negative *C* term. This could be due to the forbidden $^2T_{2g}(E_g'') \longrightarrow {}^2T_{1u}(E_u')$ becoming allowed through mixing with the nearby U_u' or E_u'' allowed charge-transfer states through an e_g or t_{2g} vibration.[7] For $\mathrm{IrCl_6{}^{2-}}$ the nearest state available for mixing is the $^2T_{1u}(U_u')$ state since $0{\cdot}75\xi_{\mathrm{Cl}}$ is *ca.* 440 cm^{-1}. However the *C* term for the forbidden transition is then calculated to be negative.[7] Positive *C* terms can only arise for this forbidden transition *via* mixing with the $^2T_{2u}(E_u'')$ state [7] and since $^2T_{1u}(\pi_u\mathrm{Cl})$ and the $^2T_{2u}(\pi\text{-Cl})$ states are separated by *ca.* 3000 cm^{-1} this mixing is likely to be of less importance than with the $^2T_{1u}(U_u')$ state. Thus it is unlikely that the positive *C*-term trough at 20,500 cm^{-1} is due to the forbidden transition to the $^2T_{1u}(E_u')$ state.

The other alternative is that the structure of this band is due to the splitting of the $^2T_{1u}(U_u')$ state. A Jahn–Teller distortion would not explain the positive *C*-term trough since negative *C*-terms are calculated for transitions to both $^2T_{1u}(U_u')[E_u'' + E_u']$ states (Table 1, ref. 7). The m.c.d. can be explained on the basis of a D_{4h} or D_{3d} static distortion since, as can be seen in Table 1 (ref. 7), opposite-sign *C*-terms are calculated for the two split components of the $^2T_{1u}(U_u')$ state. The positive *C*-term trough is thus explained as being due to the partial resolution of the $+0{\cdot}225$ *C* term cutting in to the main $-0{\cdot}675$ *C* term. This requires a distortion splitting of *ca.* 400 cm^{-1} which is presumably not enough to be resolved in the absorption spectrum.

Turning to the split $^2T_{2u}$ absorption band centred at 23,500 cm^{-1}, we can assign the peak at 23,200 cm^{-1} which lines up with the m.c.d. positive *C*-term peak to the transition to the $^2T_{2u}(E_u'')$ state for which a *C* term of $+0{\cdot}60$ is predicted. The broad shoulder at 23,800 cm^{-1} in the 10 K spectrum clearly contributes less to the m.c.d. since the m.c.d. band tails away in this region. No shoulder occurs in the m.c.d. of this region although it is probable that transitions to the $^2T_{2u}(U_u')[E_u'' + E_u']$ states occur here with their small negative *C* term of $(+0{\cdot}075 - 0{\cdot}225) = -0{\cdot}15$ being swamped by the large positive *C* term of the $^2T_{2u}(E_u'')$ state.

The appearance of the splitting in the absorption band of this region can then be explained as arising from a combination of spin–orbit splitting and low-symmetry distortion. Now examining Table 1 (ref. 7) and Figure 5, assuming that the state with $D = \frac{1}{4}$ lies at highest energy and the state with $D = \frac{1}{12}$ lies between this and the $^2T_{2u}(E_u'')$ state with $D = \frac{2}{3}$, then we can explain the band shape observed in the absorption spectrum of this region. The observed splitting should be approximately equal to the separation of the states with $D = \frac{1}{4}$ and $D = \frac{2}{3}$. This separation is roughly $0{\cdot}75\xi_1 + \delta/2$ which is *ca.* 640 cm^{-1}, if we use $\delta = 400$ cm^{-1} as for the $^2T_{1u}(U_u')$ band and $0{\cdot}75\xi_{\mathrm{Cl}} = 440$ cm^{-1}.

Such a combination of spin–orbit coupling and low-symmetry distortion cannot cause a splitting in the absorption spectrum of the $^2T_{1u}$ band since one of the three states, the $^2T_{1u}(E_u')$ state, is theoretically forbidden with $D = 0$.

This explanation is not entirely satisfactory but it is a possibility that fits the facts and it is difficult to devise any other explanation without radically altering the

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* States in parentheses are O_h states; those in square brackets refer to the distorted lower symmetry states.

[14] S. B. Piepho, J. R. Dickinson, J. A. Spencer, and P. N. Schatz, *J. Chem. Phys.*, 1972, **57**, 982.

[15] M. D. Sturge, *Solid State Physics*, 1968, **20**, 91.

existing model for the electronic structure of this system. As to the origin of the distortion, one is left with some kind of interaction of water molecules with the chlorine ligands, the exact nature of which remains in doubt.

Finally, no mention has yet been made of the weak band at 17,300 cm^{-1}. This has been assigned [5,7] to the parity-forbidden $^2T_{2g} \longrightarrow {}^2T_{1g}(U_g' + E_g')(\pi\text{-Cl})$ charge-transfer transition, gaining intensity from an allowed charge transfer *via* an odd parity vibration.

$(PhNH_3)_3RuCl_6$.—Figure 2 shows the absorption spectrum and m.c.d. of $(PhNH_3)_3RuCl_6$ in 12M-HCl where, as already mentioned, it exists as $RuCl_6^{3-}$. There is nothing particularly remarkable about the m.c.d.; it is very similar to that of $IrCl_6^{2-}$ as would be expected. The whole spectrum is shifted towards the blue compared with that of $IrCl_6^{2-}$ owing to the lower oxidation state of $RuCl_6^{3-}$ outweighing the effect of changing to a metal lower in the Periodic Table which should result in a red shift. These band shifts are some confirmation of the charge-transfer character of the spectrum. One odd feature is the fact that although the $^2T_{2u}(\pi\text{-Cl})$ band is broad and seems to be tending towards the splitting observed for this band in K_2IrCl_6, the m.c.d. peak lines up with the blue side of the absorption band. To explain this on the basis of the interpretation given for K_2IrCl_6 would require the reversal of spin–orbit splitting which is not possible. It may be that δ is of opposite sign here and perhaps larger than spin–orbit splitting.

As seen in the Table the experimental C/D values are in reasonable agreement with the theoretical values given in Table 1 (ref. 7) for the octahedral symmetry, the assignments being as outlined for the room temperature m.c.d. of $IrCl_6^{2-}$.

The shoulder at 26,000 cm^{-1} in the absorption spectrum is presumably due to the $^2T_{2g} \longrightarrow {}^2T_{1g}(\pi\text{-Cl})$ forbidden transition.

$(PhNH_3)_3RuBr_6$.—The m.c.d. of $RuBr_6^{3-}$ is shown in Figure 3. It is very similar to that previously published [4] apart from the greater resolution of the band at 27,500 cm^{-1}. The m.c.d. is broadly similar to that of $IrCl_6^{2-}$ and $RuCl_6^{3-}$ but as the spin–orbit coupling parameter for bromine is *ca.* $\xi_{Br} = 2460$ cm^{-1} we might expect to see the effects of this.

The absorption band centred at 22,000 cm^{-1} is similar to that observed in $IrBr_6^{2-}$ in solution and doped into various crystals [4,7,16] but with the three peaks less clearly separated. As in $IrBr_6^{2-}$ the two peaks at 21,500 cm^{-1} and 22,100 cm^{-1} can be assigned to the $^2T_{2g} \longrightarrow {}^2T_{1u}(U_u')$ transition with the splitting arising from a Jahn–Teller distortion, since as shown in Table 1 (ref. 7) calculation shows that transitions to both these states have negative C terms. Since no positive sign C term is seen cutting into the negative C term peak of this band this seems to be a reasonable assignment here also. The band at 23,000 cm^{-1} is analogous to that in the spectrum of $IrBr_6^{2-}$, assigned as forbidden charge transfer to the $^2T_{1g}(E_g')$ state gaining intensity from the $^2T_{2u}(E_u'')$ state. A positive C term is calculated [7] for this transition. In the m.c.d. reported here the signal goes to zero in the region of this band although it is possible that there is some overlap with the intense positive C term at 25,400 cm^{-1}. The overall C/D of this band centred at 21,600 cm^{-1} is $-0{\cdot}40$ (Table) which is in reasonable agreement with the theoretical value for transitions to the $^2T_{1u}(U_u') + (E_u')$ states (Table 1, ref. 7).

The band at 25,400 cm^{-1} can be assigned to the $^2T_{2g} \longrightarrow {}^2T_{2u}(E_u'')$ transition, again in agreement with the assignment for the comparable band [7,16] in $IrBr_6^{2-}$. The experimental $C/D = +0{\cdot}43$ is lower than the calculated value of $+0{\cdot}90$. The forbidden $^2T_{2g} \longrightarrow {}^2T_{1u}(E_u')$ transition may also be under this band. Such a component has been resolved [7,16] in the spectrum of $IrBr_6^{2-}$ and is calculated to have positive C-term character *via* vibrational mixing with the $^2T_{2u}(E_u'')$ state.

The band at 28,000 cm^{-1} by analogy with the spectrum of $IrBr_6^{2-}$ should be the $^2T_{2g} \longrightarrow {}^2T_{2u}(U_u')$ transition but the m.c.d. in the region of this band is not readily explained. As already discussed the m.c.d. observed in this region for the $(EtNH_3)_2SnBr_6{:}Ir^{4+}$ crystal [7] has been interpreted in terms of a static distortion splitting the $^2T_{2u}(U_u')$ state. It is possible that the negative C-term trough at 27,000 cm^{-1} is due to transition to one split component of this state and the positive C-term peak at 27,400 cm^{-1} is due to transition to the other component since they are calculated to have opposite sign m.c.d. One cannot rule out the possibility that a Jahn–Teller distortion is present and that such a splitting of the $^2T_{2u}(U_u')$ state causes the negative C-term troughs at 27,000 cm^{-1} and 28,400 cm^{-1} (Table), the positive C-term peak at 27,400 cm^{-1} being only apparent and resulting from the 27,000 cm^{-1} component cutting into the $^2T_{2g} \longrightarrow {}^2T_{2u}(E_u'')$ band.

Either explanation could account for the low experimental C/D for the 25,300 cm^{-1} band. Low-temperature m.c.d. might help in distinguishing between the two alternatives.

$Ru(NH_3)_6Cl_3$.—One band at 36,500 cm^{-1} is observed in the solution spectrum of this compound in water (Figure 4). This is presumably the $^2T_{2g} \longrightarrow {}^2T_{1u}(\sigma\text{-NH}_3)$ charge-transfer transition since it has the correct sign m.c.d. The experimental $C/D = -0{\cdot}60$ is in reasonable agreement with the theoretical value. Comparing the spectrum of $RuCl_6^{3-}$ with that of $IrCl_6^{2-}$ one would predict that the $^2T_{2g} \longrightarrow {}^2T_{1u}(\sigma\text{-Cl})$ transition in the former should be at *ca.* 42,000 cm^{-1}. Thus charge transfer from the σ-NH_3 levels occurs at *ca.* 5500 cm^{-1} to the red of charge transfer from the σ-Cl levels. We would therefore predict that σ-NH_3 to Ir^{IV} charge transfer should occur at about 27,500 cm^{-1} which is in line with the findings of previous work on substituted Ir^{IV} chlorides [1] since this is to the blue of bands found for σ-pyridine levels. It should however be pointed out that the assignment of the 36,500 cm^{-1} band to a charge-

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[16] J. R. Dickinson, S. B. Piepho, J. A. Spencer, and P. N. Schatz, *J. Chem. Phys.*, 1972, **56**, 2668.

transfer transition is based on the agreement of the experimental and theoretical *C*/*D* values. It is however not impossible that this band is due to a *d*–*d* transition. Temperature-variation studies might confirm this point.

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