The Crystal Absorption Spectra of Some Hexachloroiridate(IV) Salts

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The absorption spectra of the single-crystals of several hexachloroiridate(IV) salts and the doped crystals of the hexachlorostannate(IV) salts and the hexachloroplatinate(IV) salt with the $IrCl_6^{2-}$ anion were measured. Distinct dichroisms appeared in the polarized absorption spectra of all the anisotropic crystals studied. The splittings of the bands and the dichroisms of the spectra were interpreted in terms of the lowering of the symmetry of the $IrCl_6^{2-}$ anions in the crystal. The absorption bands at 19760 and 20000 cm^{-1} in the spectra of $(CH_3NH_3)_2Sn(Ir)Cl_6$ could be assigned to the $E'_g \rightarrow E''_u$ and $E'_g \rightarrow E'_u$ transitions respectively from their polarizations in the double group, D_{3d}*. Similarly, the bands at 23100, 23500, and 24500 cm^{-1} were assigned to the $E'_g \rightarrow E'_u$, $E'_g \rightarrow E''_u$, and $E'_g \rightarrow E'_u$ transitions respectively. The polarized absorption spectra of $Na_2IrCl_6 \cdot 6H_2O$ and $Na_2Pt(Ir)Cl_6 \cdot 6H_2O$ were also interpreted, assuming that the $IrCl_6^{2-}$ anions in these crystals were of the D_{4d} symmetry.

The nature of the electronic absorption spectra of the transition-metal hexahalogenocomplexes was first discussed by Jørgensen,[1] and since then many reports have appeared in this field, especially concerned with Ir(IV) complexes.[2] In these studies the absorption spectra and the magnetic circular dichroisms of the complexes have been measured in solution or by means of the doped crystals because of their large molar extinction coefficients ($\log \varepsilon > 3$). The hexahalogenostannate(IV) salts and the hexahalogenozirconate(IV) salts have been frequently employed as the host lattice. However, π(halogen)$\rightarrow t_{2g}$(metal) electron-transfer absorption bands of the complexes have been known to change considerably in their shapes and positions according to their matrices.[3] In fact, different absorption spectra have been obtained in these studies of Ir(IV) complexes doped into various host lattices and in solution.

One of the present authors (Y. K.) has previously measured the single-crystal polarized absorption spectra of $Na_2IrCl_6 \cdot 6H_2O$, and observed its remarkably distinct dichroism. This dichroism evidently indicates that the complexes are fairly much distorted from O_h in this anisotropic crystal. Therefore, for a detailed discussion of the absorption spectra, it seems important to study the absorption bands under a reduced symmetry of the complex, especially in the anisotropic crystals.

In the present work, the single-crystal absorption spectra of several hexachloroiridate(IV) salts and the doped crystals of the hexachlorostannate(IV) salts and of the hexachloroplatinate(IV) salt with $IrCl_6^{2-}$ anion were measured. The spectra thus measured were interpreted in terms of the lowering of the symmetry of the complexes in the crystal.

Experimental

The visible absorption spectra of the crystalline samples were measured by means of a microspectrophotometer composed of a Hitachi EPS-3T spectrophotometer and a specially-designed stainless-steel box containing a microscope. For the low-temperature studies, the box could be evacuated and was equipped with a stainless-steel cylinder that could hold *ca.* 500 ml of liquid nitrogen. The liquid nitrogen flowed from this cylinder to a specially-designed cooling stage of the microscope through a copper tube. Depending on the cross-section of the crystalline sample, a condenser and an objective with an appropriate power (×4, ×10: ordinary glass objective, ×20, ×40: reflection type optics; Zeiss-Jena) were used. The slit image of the spectrophotometer on the stage of the microscope was about 0.15 mm, as the ×4 lens system was employed, while the ×40 lens system could condense it to about 15 μm in length. The crystalline sample should be large enough to cover the slit image on the stage completely for the measurement. For some doped crystals, the low-temperature absorption spectra were measured. These doped crystals were mounted over a hole in an aluminum plate, which was then placed on the cooling stage of the microscope. Apiezon N grease ensured good thermal contact between the crystal, the aluminum plate, and the cooling stage. The thermocouple indicated that the samples were cooled to about 90 K.

Excellent single-crystals of the hexachloroiridate(IV) salts were obtained when one drop of the 6M HCl solution of the salt was put between two plates of the quartz slide and the plates were then allowed to stand overnight in air in order to evaporate the solvent. The crystals thus obtained were examined under a polarizing microscope, and the absorption spectra of the appropriate samples were measured. The thickness of the samples was not measured in the present studies. However, it could be estimated to be less than 1 μm, assuming that the molar extinction coefficient of the complexes in solution does not change in the crystal. Doped crystals of various hexachlorostannate(IV) salts and sodium hexachloroplatinate(IV) with the $IrCl_6^{2-}$ anion were grown from a slowly-evaporating solution of the salts in 6M HCl containing small quantities (*ca.* 0.05%) of the $IrCl_6^{2-}$ anion. It was found that, in most cases, the $IrCl_6^{2-}$ anions were condensed into the host crystals to some extent. Crystals about 0.5 mm thick were selected and used for the measurements. The polarized absorption spectra of the anisotropic crystals were measured on their extinction directions using a Rochon polarizer. The Raman spectra of the solid powder of the hexachlorostannate(IV) salts were obtained by a laser excited Raman spectrometer. The X-ray crystallographic studies were done with a Weissenberg camera.

Results and Discussion

K_2IrCl_6, $(NH_4)_2IrCl_6$, $K_2Sn(Ir)Cl_6$, $(NH_4)_2Sn(Ir)Cl_6$. These crystals of the hexachloroiridate(IV) salts and the host hexachlorostannate(IV) salts belong to the cubic crystal system, with the space group *Fm3m*.[6] The crystallographically-required symmetry of the complexes in these crystals is O_h. The absorption spectra

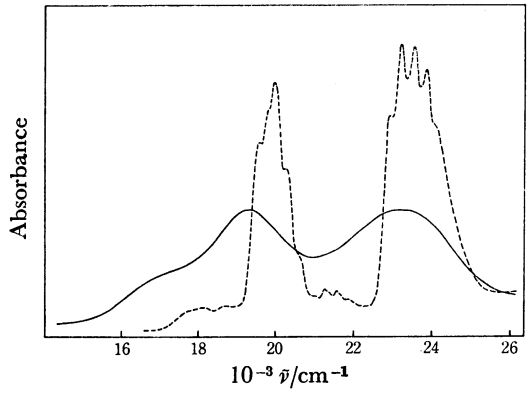

Fig. 1. Crystal absorption spectra of K_2IrCl_6 (——), and $K_2Sn(Ir)Cl_6$ at 90 K (------).

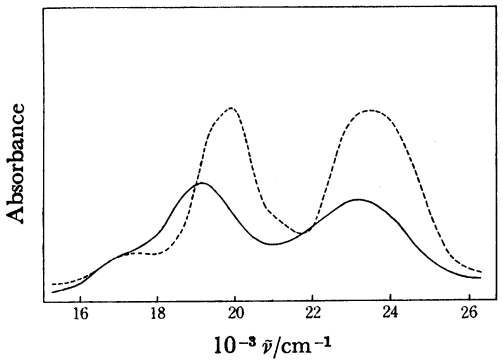

Fig. 2. Crystal absorption spectra of $(NH_4)_2IrCl_6$ (——), and $(NH_4)_2Sn(Ir)Cl_6$ (------).

of the single-crystals and the doped crystals are shown in Figs. 1 and 2. The familiar intense absorption bands of the $IrCl_6^{2-}$ anion were observed in the 20000 and 23500 cm^{-1} regions in all the cases; also, in some cases, there were weak absorption bands in the 17000 and 21500 cm^{-1} regions. Schatz *et al.*[7-9] investigated the absorption spectra and the magnetic circular dichroisms of π(halogen)$\rightarrow t_{2g}$(metal) electron-transfer absorption bands of the $IrCl_6^{2-}$ anion and concluded that the intense absorption bands in the 20000 and 23500 cm^{-1} regions could be assigned to the $^2T_{2g}\rightarrow{}^2T_{1u}$ and $^2T_{2g}\rightarrow{}^2T_{2u}$ transitions respectively, assuming the $IrCl_6^{2-}$ anion

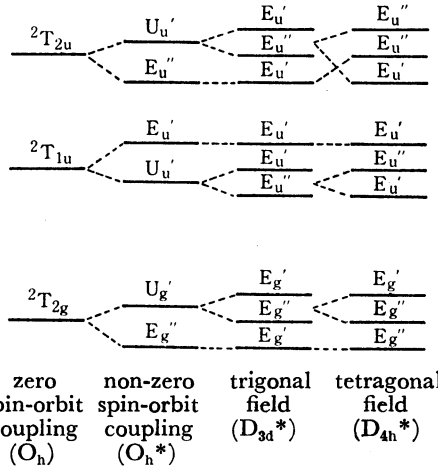

Fig. 3. Schematic energy level diagram of the electron transfer configurations of d^5 complex.

to have the O_h symmetry. Figure 3 shows the schematic energy levels of the electron-transfer configurations of the d^5 complex. It was found that the band maximum of the $^2T_{2g}\rightarrow{}^2T_{1u}$ transition of the pure crystals was always located at a lower wave number than that of the doped crystals. This fact has already been interpreted by Jørgensen in terms of the compression effect in the pure crystals. The absorption spectrum of $K_2Sn(Ir)Cl_6$ in Fig. 1 is consistent with that reported by Sleight[10] in 1968. That is, in the $^2T_{2g}\rightarrow{}^2T_{1u}$ absorption region, five components—at (1) 19570 cm^{-1}, (2) 19880(sh) cm^{-1}, (3) 20040 cm^{-1}, (4) 20350 cm^{-1}, and (5) 20650(sh) cm^{-1}—can be found. It can be considered that the (1) and (2) components form one set of vibrational fine structures, while the (3), (4), and (5) components form another set of vibrational structures. On the other hand, in the $^2T_{2g}\rightarrow{}^2T_{2u}$ absorption region, only one component, with its vibrational fine structures beginning at 22990 cm^{-1}, was observed. Sufficient evidence for the splitting of this band could not be obtained. However, it may be noted by a careful observation of the absorption spectra in Figs. 1 and 2 that each $^2T_{2g}\rightarrow{}^2T_{2u}$ band seems to have a shoulder on the higher-wave number side of the band. Measurements with higher resolution are necessary for any discussion of the band splittings of the complexes in the crystallographically-required O_h.

$(CH_3NH_3)_2IrCl_6$, $(CH_3NH_3)_2Sn(Ir)Cl_6$. The structure of $(CH_3NH_3)_2SnCl_6$ was determined by Wyckoff.[11] The crystals of $(CH_3NH_3)_2SnCl_6$ belong to the trigonal crystal system, with the space group *R3m*. The crystallographically-required symmetry of the complex is D_{3d}. The three-fold axis (z axis) of the complex should be normal to the well-developed face of the thin hexagonal plate of the crystal, in accord with the unique axis of the crystal. The crystals of $(CH_3NH_3)_2IrCl_6$, which also grow as thin hexagonal plates, must be isomorphous to $(CH_3NH_3)_2SnCl_6$, since they showed a similar Debye-Scherrer pattern in this work. The low-temperature absorption spectrum of $(CH_3NH_3)_2Sn(Ir)Cl_6$, with the light propagated along the unique axis of the crystal, has already been studied by Bird *et al.*[12] In the present work, using a carefully selected crystal, the polarized absorption spectra by

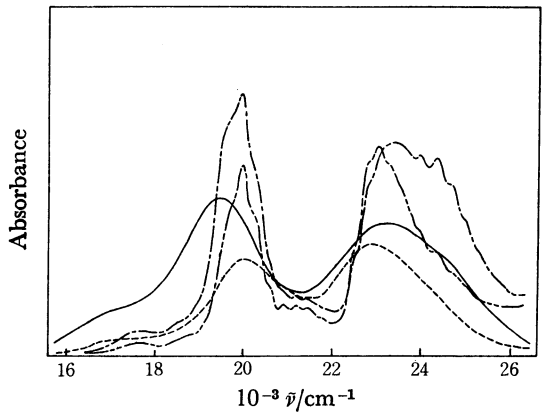

Fig. 4. Polarized absorption spectra of $(CH_3NH_3)_2IrCl_6$ (—— $\perp C_3$, ------ $// C_3$), and $(CH_3NH_3)_2Sn(Ir)Cl_6$ at 90 K (----- $\perp$ C_3, ——— $// C_3$).

light propagated perpendicular to the unique axis of the crystal could be obtained. Figure 4 shows the polarized absorption spectra of $(CH_3NH_3)_2IrCl_6$ and $(CH_3NH_3)_2Sn(Ir)Cl_6$. It was found that the two crystals showed distinct dichroisms with similar patterns, although $(CH_3NH_3)_2IrCl_6$ was studied at room temperature. This reasonably indicates that the $IrCl_6^{2-}$ anions are appreciably distorted in these crystals. Bird *et al.* considered that the $IrCl_6^{2-}$ anion doped into $(CH_3NH_3)_2SnCl_6$ does not suffer any appreciable distortion from O_h symmetry, since the splitting of the $\nu_5(t_{2g})$ line of the $SnCl_6^{2-}$ anion in the crystal could not actually be observed in their Raman studies. However, in the present work, the measurements of the Raman spectra of the powdered host stannate(IV) salts showed that the $\nu_5(t_{2g})$ line of the $SnCl_6^{2-}$ anion in $(CH_3NH_3)_2SnCl_6$ has a small shoulder. This fact also suggests that the symmetry of the $IrCl_6^{2-}$ anion doped into $(CH_3NH_3)_2SnCl_6$ is reduced from O_h. The Raman lines of the solid stannate(IV) salts are listed in Table 1.

TABLE 1. VIBRATIONAL FREQUENCIES (Raman active)

	$\nu_1(a_{1g})$	$\nu_2(e_g)$	$\nu_5(t_{2g})$
K_2SnCl_6	325.6 cm^{-1}	246.2 cm^{-1}	147.2 cm^{-1}
$(CH_3NH_3)_2SnCl_6$	316.0	241.1	174.0
			161.7 sh
$\{(CH_3)_2NH_2\}_2SnCl_6$	313.9	245.4	173.2
		236.7	159.3
$\{(CH_3)_3NH\}_2SnCl_6$	306.4	241.8	171.3
		232.1	162.7

The absorption spectrum of $(CH_3NH_3)_2Sn(Ir)Cl_6$, measured with polarized light whose electric vector was perpendicular to the unique axis, was essentially consistent with that given by Bird *et al.* However, as the crystal was cooled to 4 K in their studies, their spectrum appeared in a better resolution than ours, particularly in the $^2T_{2g}\rightarrow{}^2T_{1u}$ absorption region. They noted that the absorption band in this region consisted of three peaks centered at 19760, 20000, and 20300 cm^{-1}, but they considered that the peak at 20300 cm^{-1} belonged to the member of the vibrational fine structure of the component at 20000 cm^{-1}. Thus, they concluded that the spectrum contained two absorption components in this region, and they identified these two components arising from the excited state spin-orbit splitting in the O_h* double group. However, in the polarized absorption spectrum with its electric vector parallel to the three-fold axis of the complex, the component at 19760 cm^{-1} seemed to be considerably reduced in intensity compared with that at 20000 cm^{-1}. As is shown in Fig. 3, the $^2T_{1u}$ state is split into three levels, which transform as E_u', E_u'', and E_u' respectively in the D_{3d}*, double group while the ground state must still be E_g' because of the large spin-orbit coupling constant (ξ_{Ir}—3000 cm^{-1}). The Laporte allowed transitions of $E_g'\rightarrow E_u''$ and $E_g'\rightarrow E_u'$ should have their transition moments directed along xy and xyz respectively in the D_{3d}* double group. Therefore, the absorption component at 19760 cm^{-1}, the intensity of which along the z axis of the complex was remarkably reduced, must be due to the $E_g'\rightarrow E_u''$ transition. The component at

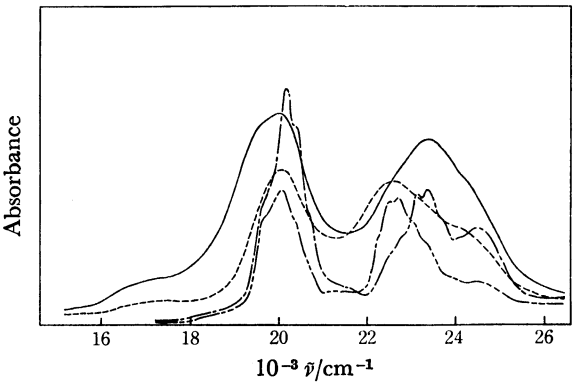

Fig. 5. Polarized absorption spectra of $\{(CH_3)_2NH_2\}_2$-$IrCl_6$ (——, ------), and $\{(CH_3)_2NH_2\}_2Sn(Ir)Cl_6$ at 90 K (-----, ——).

20000 cm^{-1} must be assigned to $E_g'\rightarrow E_u'$, as it has the transition moment also along the z axis. Two E_u' levels arise from $^2T_{1u}$, but it cannot be determined easily which E_u' level corresponds to this component. However, according to the calculations by Piepho *et al.*,[13] the $E_g'\rightarrow E_u'(D_{3d}^*)[U_u'(O_h^*)]$ must have a dipole strength of $D=1/4$. Therefore, this electronic transition must contribute largely to the absorption band at 20000 cm^{-1}.

The intense absorption-band group between 22500 and 26000 cm^{-1} has been considered to be due to the $^2T_{2g}\rightarrow{}^2T_{2u}$ transition in O_h. There have been several discussions concerning the composition of the band group in this region.[8,12] However, the absorption spectrum with the light polarized parallel to the unique axis of the crystal clearly revealed an absorption maximum at 23100 cm^{-1}, while this maximum did not appear in the spectrum with the light propagated along the unique axis. Thus, the band group in this region seems to consist of three components—namely, a band with some vibrational fine structures centered at 23100 cm^{-1}, a structureless band at 23500 cm^{-1}, and a band representing the extensive vibrational structures centered at 24500 cm^{-1}. The component appearing clearly at 23100 cm^{-1} in the z spectrum seems to have its intensity also in the xy direction; therefore, it could be considered to be of the xyz polarization. The vibrational fine structures centered at 24500 cm^{-1} could be seen also in the z spectrum; this component was overlapped with the slope of the band at 23500cm^{-1} to increase its intensity apparently in the xy spectrum. Therefore, the component centered at 24500 cm^{-1} could be regarded as the xyz polarization. Three levels which transform as E_u', E_u'', and E_u' in the D_{3d}* double group arise from the $^2T_{2u}$ state. The present polarization studies suggest the following assignments: the bands centered at 23100, 23500, and 24500 cm^{-1} are the components due to $E_g'\rightarrow E_u'$ (xyz polarization), $E_g'\rightarrow E_u''$ (xy polarization), and $E_g'\rightarrow E_u'$ (xyz polarization) respectively. Referring again to the dipole strength (D) calculated by Piepho *et al.*, the band at 23100 cm^{-1} can further be assigned to $E_g'\rightarrow E_u'(D_{3h}^*)[E_u''(O_h^*)]$-$(D=2/3)$, and that at 24500 cm^{-1}, to $E_g'\rightarrow E_u'(D_{3h}^*)$-$[U_u'(O_h^*)](D=1/12)$. McCaffery *et al.*[8] studied the MCD spectra of this doped crystal with the light

propagated along the unique axis of the crystal. These spectra showed two negative $[\theta]_M$ maxima, at 23000 and 24500 cm^{-1}, and may be interpreted in terms of the overlapping of the peaks corresponding to $E_g' \rightarrow E_u'$-($C=0.60$), $E_g' \rightarrow E_u''$($C=-0.225$), and $E_g' \rightarrow E_u'$($C=0.075$) respectively in the D_{3d}* double group.

The single-crystal of $(CH_3NH_3)_2IrCl_6$ showed polarized absorption spectra with a pattern similar to that of the doped crystal. As the crystal is isomorphous to the host one, the same statements can be made concerning these spectra.

$\{(CH_3)_2NH_2\}_2IrCl_6$, $\{(CH_3)_2NH_2\}_2Sn(Ir)Cl_6$.
Figure 5 shows the polarized absorption spectra of $\{(CH_3)_2NH_2\}_2IrCl_6$ and $\{(CH_3)_2NH_2\}_2Sn(Ir)Cl_6$. The crystals of $\{(CH_3)_2NH_2\}_2SnCl_6$ belong to the orthorhombic crystal system, with the space group of Pnn2 or Pnnm. The complex in this crystal is crystallographically required to possess one of three symmetries, C_1, C_s, or C_2. Solid $\{(CH_3)_2NH_2\}_2IrCl_6$ gave a Debye-Scherrer pattern similar to that of $\{(CH_3)_2NH_2\}_2SnCl_6$. Both Raman lines, $\nu_2(e_g)$ and $\nu_5(t_{2g})$, of the $SnCl_6^{2-}$ anion in the $\{(CH_3)_2NH_2\}_2SnCl_6$ were found to be clearly split, as is shown in Table 1. This suggests that the complex must have suffered a severe distortion force in the crystal to convert it to a low symmetry. The single-crystal and the doped crystal showed polarized absorption spectra with similar patterns. It was found that the $^2T_{2g} \rightarrow {}^2T_{2u}$ absorption band was clearly split into three components in the spectra of the doped crystal at 90 K. However, a detailed discussion of the polarized absorption spectra is not possible because the actual symmetry of the complex is not known.

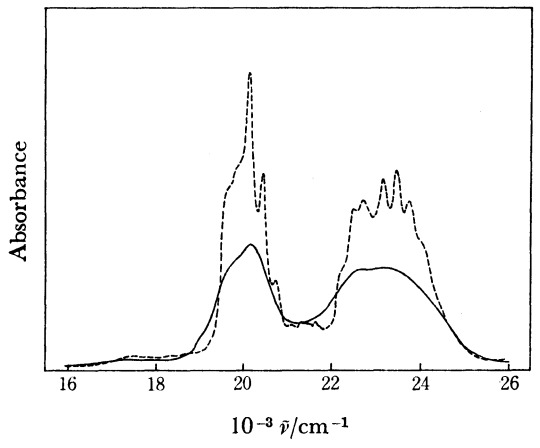

Fig. 6. Crystal absorption spectra of $\{(CH_3)_3NH\}_2IrCl_6$ (——), and $\{(CH_3)_3NH\}_2Sn(Ir)Cl_6$ at 90 K (------).

$\{(CH_3)_3NH\}_2IrCl_6$, $\{(CH_3)_3NH\}_2Sn(Ir)Cl_6$.
Figure 6 shows the absorption spectra of $\{(CH_3)_3NH\}_2IrCl_6$ and $\{(CH_3)_3NH\}_2Sn(Ir)Cl_6$. The host crystal of $\{(CH_3)_3NH\}_2SnCl_6$ belongs to the cubic crystal system with the space group *Pa3*.[6] The crystallographically-required symmetry of the complex is D_{3d}. The Debye-Scherrer photograph of $\{(CH_3)_3NH\}_2IrCl_6$ is similar to that of $\{(CH_3)_3NH\}_2SnCl_6$. As is shown in Table 1, not only the $\nu_5(t_{2g})$ but also $\nu_2(e_g)$ Raman lines of $SnCl_6^{2-}$ in the host crystal were found to be split. This indicates that the complex in this crystal may have a lower symmetry than D_{3d}, contrary to the results of the X-ray studies. It was found in the spectrum of the doped crystal that the bands due to both $^2T_{2g} \rightarrow {}^2T_{1u}$ and $^2T_{2g} \rightarrow {}^2T_{2u}$ were split into two components with clear vibrational structures. The absorption spectrum of $\{(CH_3)_3NH\}_2IrCl_6$ appeared to be almost the same as that of the doped crystal at room temperature. However, as the crystals belong to the cubic crystal system, polarized absorption studies were not possible.

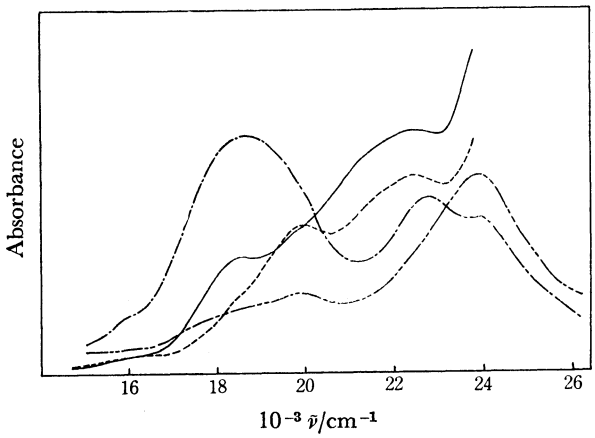

Fig. 7. Polarized absorption spectra of $Na_2IrCl_6 \cdot 6H_2O$ (------: A direction, ———: B direction), and $Na_2Pt(Ir)Cl_6 \cdot 6H_2O$ (——: A direction, ------: B direction).

$Na_2IrCl_6 \cdot 6H_2O$, $Na_2Pt(Ir)Cl_6 \cdot 6H_2O$. Figure 7 shows the polarized absorption spectra of $Na_2IrCl_6 \cdot 6H_2O$ and $Na_2Pt(Ir)Cl_6 \cdot 6H_2O$. The crystals of $Na_2IrCl_6 \cdot 6H_2O$ and $Na_2PtCl_6 \cdot 6H_2O$ belong to the triclinic crystal system, being isomorphous with each other.[14] For both samples, the polarized absorption spectra measured were not related to their crystal axes. However, although, in the absorption spectra of the doped crystal, the $^2T_{2g} \rightarrow {}^2T_{2u}$ absorption region was overlapped with the slope of the strong absorption band of the $PtCl_6^{2-}$ anion, the patterns of the absorption spectra appeared to be comparable to that of $Na_2IrCl_6 \cdot 6H_2O$ in the $^2T_{2g} \rightarrow {}^2T_{1u}$ region. That is, the $^2T_{2g} \rightarrow {}^2T_{1u}$ absorption bands were split into two components, with strong dichroisms for both samples.

One of the present authors (Y. K.)[4] had previously measured the polarized absorption spectra of $Na_2IrCl_6 \cdot 6H_2O$, and had found a remarkably strong dichroism; hence, there has been a doubt as to the chemical composition of the fine crystals studied. Therefore, the sample crystals used in the course of this work were prepared by the evaporation of a 6M HCl solution of the salts in order to avoid any aquation of the complexes. Since all the crystals of $Na_2IrCl_6 \cdot 6H_2O$ thus obtained exhibited a distinct dichroism under the polarizing microscope, and since all the doped crystals of $Na_2Pt(Ir)Cl_6 \cdot 6H_2O$ prepared also showed a clear dichroism, it seems reasonable to say that the sample crystals certainly consist of $IrCl_6^{2-}$ anions. Griffith *et al.*[15] reported, on the basis of their ESR studies, that the $IrCl_6^{2-}$ anion doped into $Na_2PtCl_6 \cdot 6H_2O$

could be considered to be approximately of a D_{4h} symmetry. $Na_2IrCl_6 \cdot 6H_2O$ is isomorphous to $Na_2PtCl_6 \cdot 6H_2O$, and it showed polarized absorption spectra similar to those of $Na_2Pt(Ir)Cl_6 \cdot 6H_2O$, as has been described already. This suggests that the $IrCl_6^{2-}$ anion in the $Na_2IrCl_6 \cdot 6H_2O$ crystal can be considered to be approximately of a D_{4h} symmetry. The schematic energy levels in the D_{4h}* double group are shown in Fig. 3.

The bands at 18750 cm^{-1} ($Na_2IrCl_6 \cdot 6H_2O$) and at 18600 cm^{-1} ($Na_2Pt(Ir)Cl_6 \cdot 6H_2O$) which appeared in one polarization direction (the A direction in Fig. 7) would correspond to $E_g'' \rightarrow E_u'(D_{4h}^*)[U_h'(O_h^*)]$ (xy polarization). These distinct dichroisms observed in this region indicate that the $IrCl_6^{2-}$ anions of the D_{4h} symmetry lie in an ordering in the crystals favorable for the polarization studies. The band at 19850 cm^{-1} ($Na_2IrCl_6 \cdot 6H_2O$), which appeared as a shoulder in the spectrum of the A direction, almost covered by the slope of the band at 18750 cm^{-1}, could be considered to have its transition moment in either polarization direction of the spectra. The band at 19900 cm^{-1} ($Na_2Pt(Ir)Cl_6 \cdot 6H_2O$) clearly appeared in two directions of the spectra. These two bands can naturally be assigned to $E_g'' \rightarrow E_u''(D_{4h}^*)[U_u'(O_h^*)]$ (xyz polarization). On the basis of the evidence, the band at 22800 cm^{-1} ($Na_2IrCl_6 \cdot 6H_2O$) was considered to be of the xy polarization. Hence, it corresponds to $E_g'' \rightarrow E_u'(D_{4h}^*)[U_u'(O_h^*)]$. Different absorption maxima could be observed at 23950 cm^{-1} in the B direction and at 24040 cm^{-1} in the A direction of the polarized absorption spectra of $Na_2IrCl_6 \cdot 6H_2O$ shown in Fig. 7. This observation indicates that the actual symmetry of the complex in the crystal is reduced further than D_{4h}. However, assuming that the complexes are in the D_{4h} symmetry, these bands must correspond to the $E_g'' \rightarrow E_u''$ (xyz polarization) transitions arising from the $^2T_{2u}$ excited state.

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