

Reflection Spectra of Rhenium(IV), Osmium(IV), and Iridium(IV) Hexahalides

CHR. KLIXBÜLL JØRGENSEN

Cyanamid European Research Institute, Cologne (Geneva), Switzerland

Powdered samples of A_2MX_6 ($A = K, Cs, N(CH_3)_4, N(C_4H_9)_4, As(C_6H_5)_4$; $M = Re(IV), Os(IV), Ir(IV)$ or co-precipitated mixtures of these ions with larger amounts of $Pt(IV), Sn(IV)$ or $Pb(IV)$; $X = Cl, Br$) show reflection spectra with absorption maxima at lower wavenumbers than of aqueous solutions of MX_6^{2-} , and comparable to or lower than MX_6^{2-} in organic solvents. In the case of $A = Tl$ and Ag , new electron transfer bands occur at much lower wavenumbers as also in silver chromate and permanganate. In the case of cubic crystals, X-ray data for the unit cell parameter are indicated. The energy levels are compared with the deductions from the concept of optical electronegativities.

We are going to compare the spectra of solids containing clusters of atoms MX_6 with the absorption spectra of solutions of isolated complex ions MX_6^{2-} . It is expected that a localized description of the solids is appropriate whereas the energy band method is not expected to be adequate¹⁻³. However, it is of some interest to study whether some co-operative effects between adjacent clusters MX_6 can be perceived in the crystalline state.

Varying cation size. Table 1 gives the absorption maxima (shoulders in parentheses) in the reflection spectra of crystalline powders of the general composition A_2MX_6 , A being a colourless alkali metal ion or quaternary ion, M being either pure Ir or mixture of Ir with quadrivalent Pt, Sn, Pb or Ce , and X being chloride. The second column of Table 1 gives the wavelengths of the strongest of the maxima. This is the band used to divide the compounds into various classes according to its behaviour in different environments. In aqueous solution,^{4,5} the wavelength is seen to be as low as $487\text{ m}\mu$, whereas it is $\cong 497\text{ m}\mu$ in organic solvents⁶ and in solids containing large organic cations. On the other hand, the group with $A = Cs^+, NH_4^+$ and K^+ have maxima around $515\text{ m}\mu$.

The quite characteristic colour shift when going from the orange-brown $IrCl_6^{2-}$ in solution or in salts containing large ions A to brick-red cesium salts and purple ammonium and potassium salts is not so much caused by the shift

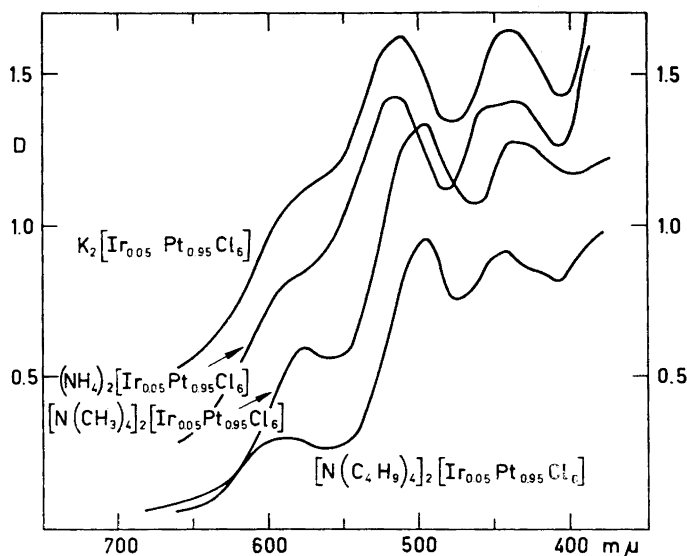


Fig. 1. Reflection spectra of IrCl_6^{2-} in A_2PtCl_6 with different ionic size of A.

of the second band as by the increasing intensity of the shoulder $\sim 580 \text{ m}\mu$. (See Fig. 1). It is even doubtful whether this shoulder corresponds to the same transition as the comparatively much weaker maximum at $590\text{--}570 \text{ m}\mu$ occurring in salts with large A. Whereas the latter transition presumably^{4,6} is the parity-forbidden electron transfer even γ_4 (π localized mainly on the ligands) \rightarrow even γ_5 (partly filled shell), the former, much intenser shoulder may be caused by a genuine co-operative effect to be discussed below. This shoulder is much more pronounced in the dark-brown mixtures with hydrated Na_2SnCl_6 showing a strong shoulder at $640 \text{ m}\mu$ (*cf.* also Balchan and Drickamer's high-pressure measurements⁷). However, since these latter crystals probably show deviations from cubic symmetry, the data are less valuable.

Table 1. Absorption maxima (shoulder in parentheses), wavelengths in $\text{m}\mu$.

Aqueous solution ^{4,5} of IrCl_6^{2-}	590	478	434, 410
IrCl_6^{2-} in dichloroethane ⁶	586	497(475)	440
$[\text{As}(\text{C}_6\text{H}_5)_4]_2 \text{IrCl}_6$	588	499(460)	440
$[\text{N}(\text{C}_2\text{H}_5)_4]_2 \text{Ir}_{0.05}\text{Pt}_{0.95}\text{Cl}_6$	588	496	442
$[\text{N}(\text{CH}_3)_4]_2 \text{Ir}_{0.05}\text{Pt}_{0.95}\text{Cl}_6$	575	496	435
$\text{Cs}_2 \text{Ir}_{0.05} \text{Ce}_{0.95} \text{Cl}_6$	(575)	507	422
$\text{Cs}_2 \text{Ir}_{0.05} \text{Pb}_{0.95} \text{Cl}_6$	575	510	425
$\text{Cs}_2 \text{Ir}_{0.02} \text{Sn}_{0.98} \text{Cl}_6$	570	508	425
$\text{Cs}_2 \text{Ir}_{0.05} \text{Pt}_{0.95} \text{Cl}_6$	(580)	514	430
$\text{Cs}_2 \text{IrCl}_6$	(580)	514	425
$(\text{NH}_4)_2 \text{Ir}_{0.02} \text{Sn}_{0.98} \text{Cl}_6$	585	~ 510	~ 425
$(\text{NH}_4)_2 \text{Ir}_{0.05} \text{Pt}_{0.95} \text{Cl}_6$	(590)	517	458, 440
$\text{K}_2 \text{Ir}_{0.05} \text{Pt}_{0.95} \text{Cl}_6$	(585)	515	442
$\text{Na}_2 \text{Ir}_{0.02} \text{Sn}_{0.98} \text{Cl}_6, (6\text{H}_2\text{O}?)$	(640)	525	425
$\text{Nr}_2 \text{Ir}_{0.01} \text{Pt}_{0.99} \text{Cl}_6, 6\text{H}_2\text{O}$	(630)	(530)	—

The Goldschmidt ionic radii for Ir(IV) 0.66 Å, Pt(IV) 0.65 Å, Sn(IV) 0.74 Å, Pb(IV) 0.84 Å and Ce(IV) 1.02 Å suggest that the cluster IrCl_6 is relatively least compressed in the large Cs_2CeCl_6 matrix and most compressed in the pure salt and in Cs_2PtCl_6 host lattice. Unfortunately, we did not succeed in introducing IrCl_6^{2-} into the more compressed Cs_2TiCl_6 . It was expected that such a compression (which also seems to occur in organic solvents⁶) would have the same effect as decreasing radius of A. Actually, there is a red shift in the direction $\text{Ce} < \text{Sn} < \text{Pb} < \text{Pt} \sim \text{Ir}$. For reasons which are explained below, it is interesting to note that the first electron transfer band of the host lattice MCl_6 groups have wavenumbers⁴ increasing in the order $\text{Ir} \ll \text{Ce} < \text{Pb} < \text{Pt} < \text{Sn}$. The concentration of IrCl_6^{2-} is held so high in the mixtures with PtCl_6^{2-} that the 80 fold weaker band at 452 $m\mu$ of the latter complex ion is without much importance for at least the two first bands observed*.

Silver and thallium (5d group) hexahalides. Fig. 2 shows that the spectrum of $\text{Tl}_2\text{Ir}_{0.05}\text{Pt}_{0.95}\text{Cl}_6$ is entirely different from that of compounds containing $\text{A} = \text{Cs}^+$ or NH_4^+ of comparable radius. The broad maximum at 625 $m\mu$ of this blue-green powder corresponds to the electron transfer band previously described¹¹ to be found in the dark green Tl_2IrCl_6 . The only residue of the usual electron transfer bands in the visible is a broad shoulder $\sim 480 m\mu$. It may be remarked that the Tl^+ , $\text{N}(\text{C}_4\text{H}_9)_4^+$ and especially the Ag^+ salts prepared here

* Incidentally, it may be mentioned that one of the facts which led to the discovery of iridium was Foureroy and Vauquelin's observation of a variable red discoloration of yellow K_2PtCl_6 . Quite generally, the lattice A_2MX_6 is so stable as to permit many otherwise unstable compounds and mixtures to be isolated. Thus, $\text{Cs}_2\text{Rh}_x\text{Pt}_{2-x}\text{Cl}_6$ has been studied^{8,9} and Day¹⁰ recently compared the reflection spectra of A_2MX_6 with M being mixtures of Sn(IV) with equimolar quantities of Sb(V) and of Sb(III), In(III) or Bi(III).

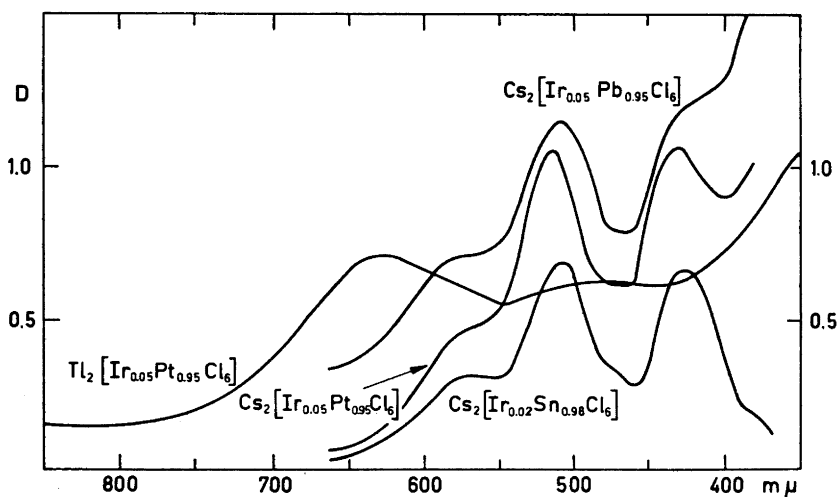


Fig. 2. Reflection spectra of one thallium(I) and three caesium salts of IrCl_6^{2-} mixed with other less coloured MCl_6^{2-} species.

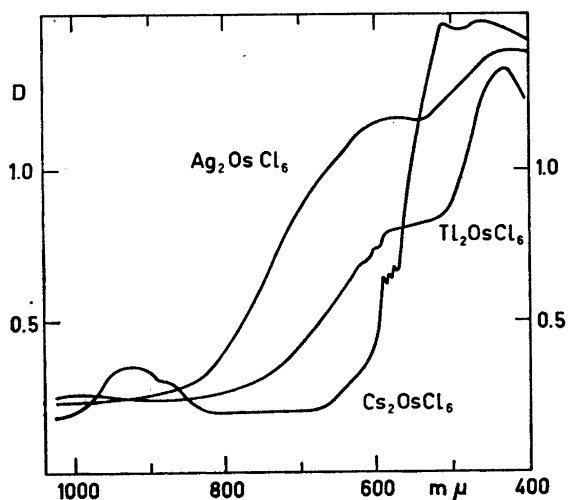


Fig. 3. Reflection spectra of various salts of OsCl_6^{2-} .

tend to form much smaller crystals than the other cations A, and hence the relative optical densities in reflection spectra do not give a true impression of the actual intensity.

Tl_2OsCl_6 is olive-green and has a weak shoulder $\sim 560 \text{ m}\mu$. The behaviour of the silver salts is rather conspicuous. Both Ag_2OsCl_6 and $\text{Ag}_2\text{Os}_{0.2}\text{Pt}_{0.8}\text{Cl}_6$ are dark brown (Figs. 3–4) with a very intense maximum at $590 \text{ m}\mu$. Ag_2ReCl_6 is reported to be orange¹² which is a pronounced deviation from the principle

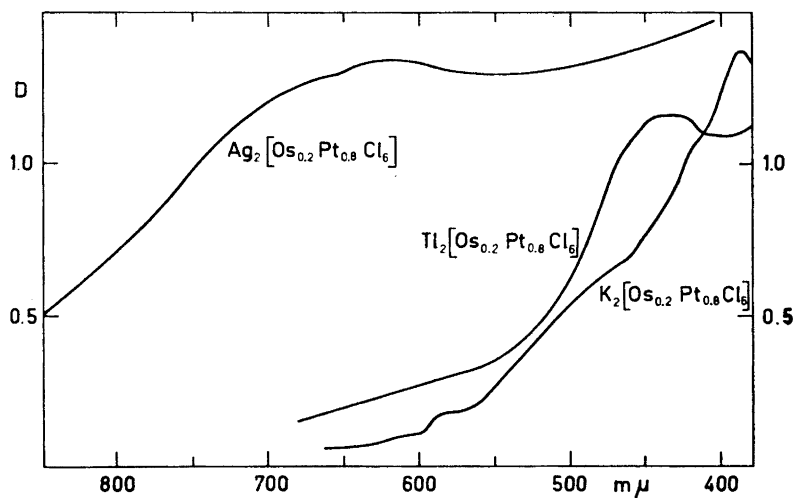


Fig. 4. Reflection spectra of various $\text{A}_2\text{Os}_{0.2}\text{Pt}_{0.8}\text{Cl}_6$.

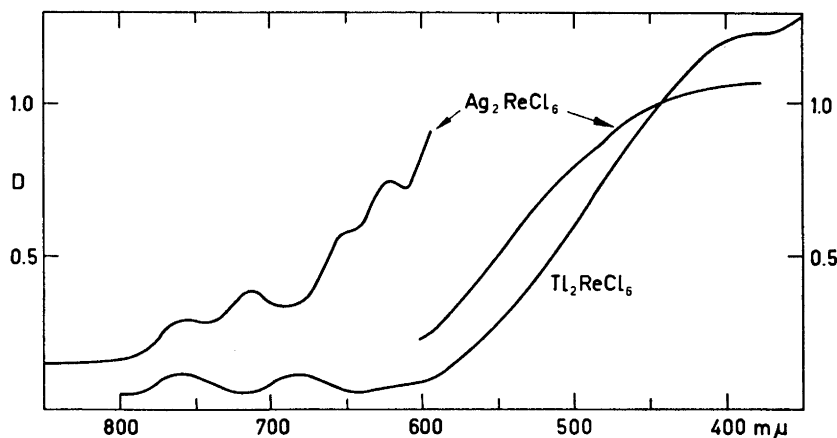


Fig. 5. Reflection spectra of silver(I) and thallium(I) rhenium(IV) hexachloride. The left-hand part of the spectrum of Ag_2ReCl_6 has the scale of optical density D four times expanded, for showing the weak details in the red.

of additivity of ionic colours, since ReCl_6^{2-} is pale green. Indeed, Ag_2ReCl_6 has a shoulder at $410\text{ m}\mu$ (Fig. 5).

There seems to be the regularity (Table 2) that the electron transfer band presumably caused by $(\text{Ag } 4d) \rightarrow (\text{even } \gamma_5 \text{ MCl}_6)$ and $(\text{Tl } 6s) \rightarrow (\text{even } \gamma_5 \text{ MCl}_6)$ has the wavenumber some 5000 to $10\,000\text{ cm}^{-1}$ below the first Laporte-allowed transition of the type $(\pi \text{ odd } \gamma_5 \text{ MCl}_6) \rightarrow (\text{even } \gamma_5 \text{ MCl}_6)$. If a treatment¹³ using optical electronegativities, x_{opt} , is attempted, Ag(I) is found to have $x_{\text{opt}} = 2.7$ or 2.8 , a little below the value for chloride. It is emphasized that these values refer to ionization energies in the same way as for ligands, whereas x_{opt} for ordinary metal atoms correspond to electron affinities. However, the consequences of this idea are that the electron transfer spectra of Ag_2MX_6 should be independent of x_{opt} for the halogen X. This does not seem to be the case; Tl_2OsBr_6 is an intensely black powder which has a very high optical density in the whole visible range and only starts to reflect some radiation above $800\text{ m}\mu$. A direct proof for the dependence of the electron transfer bands on X would be if Ag_2IrF_6 was shown to have no strong absorption bands in the visible.

The question is now whether the orbital from which the electron comes in the $\text{Ag} \rightarrow \gamma_5$ and $\text{Tl} \rightarrow \gamma_5$ bands is (1) delocalized to some extent on the six first neighbour atoms X and to a smaller extent on the A atoms, or whether (2) the orbital is predominantly localized on the A atoms. In case (1), the $4d$

Table 2. Approximate wavenumbers in cm^{-1} of the first strong electron transfer band.

	Ag_2MCl_6	Tl_2MCl_6	MCl_6^{2-}
M = Re(IV)	24 000	25 000	35 600
Os(IV)	17 000	18 000	27 000 ⁴
Ir(IV)	15 000 ¹¹	16 000	20 500 ⁴

orbital energy of Ag or 6s of Tl in the compound might be changed much due to the delocalization, whereas, in case (2) this would not be expected to occur. The red shift of the new band in Tl_2OsBr_6 as compared to Tl_2OsCl_6 might suggest possibility (1); the much larger bandwidth and other characteristics of the new band makes the present writer prefer possibility (2). This does not, of course, rule out a certain delocalization which after all is the only mechanism possible for producing an electric dipole moment (*cf.* Robin's study¹⁴ of $\text{Fe}(\text{CN})_6\text{Fe}^-$). A similar electron transfer band²¹ occurs for $\text{Tl}_3(\text{CN})_6$.

Silver permanganate and chromate. Symons and Trevalion¹⁵ have recently studied CrO_4^{2-} and MnO_4^- in various environments. We had previously made some measurements of mixtures of Ag_2CrO_4 and Ag_2SO_4 and our results also show that it is the strong absorption band $\sim 450 \text{ m}\mu$ which produces the characteristic brick-red colour of these compounds. We believe that this band is caused by a $\text{Ag}(4d) \rightarrow \text{CrO}_4(\gamma_3)$ transition in analogy to the hexahalides discussed above. Similar colour is found in Tl_2CrO_4 . It is interesting to observe that the chromates of the isoelectronic species Cd(II) and Pb(II) are yellow, indicating that the low wavenumber electron transfer band is caused by removal of an electron from the metal ions. Fig. 6 shows the reflection spectrum of the pale blue mixed crystal of AgClO_4 with traces of AgMnO_4 . Symons and Trevalion¹⁵ observed the red shift of the vibrational structure of the $\pi \gamma_4 \rightarrow \gamma_3$ ordinary electron transfer band, compared to other salts of MnO_4^- , and assumed that the $\text{Ag} \rightarrow \gamma_3$ absorption occurs at $400 \text{ m}\mu$. We find rather a new broad band without resolved vibrational structure $\sim 710 \text{ m}\mu$, again at some 5000 cm^{-1} below the first ordinary electron transfer band of isolated MnO_4^- .

Dr. Peter Day, Inorganic Chemical Laboratory of Oxford, was so kind as to draw the attention to the anhydrous, moderately soluble silver perhenate as a suitable host lattice for MnO_4^- . Actually, the blue-green crystals containing 1 molar percent permanganate show a reflection spectrum with a broad band centered at $600 \text{ m}\mu$ (its tail ends at $900 \text{ m}\mu$) with a relatively weak vibra-

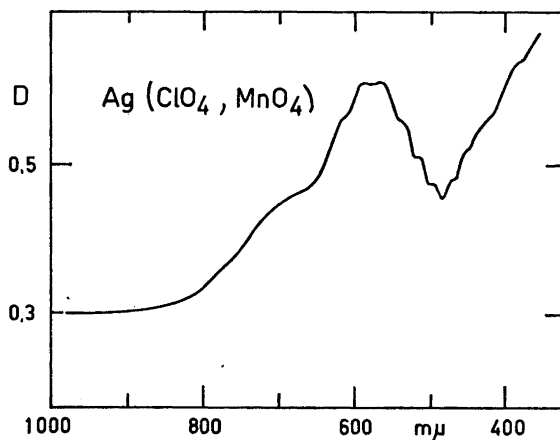


Fig. 6. Reflection spectrum of the pale blue crystals of AgClO_4 containing a trace of MnO_4^- . The measurements are slightly perturbed by the high hygroscopicity.

tional structure superposed in the region 560—580 $m\mu$. The following maximum occurs at 430 $m\mu$. Presumably, AgReO_4 is less compressed than AgClO_4 with respect to the dimensions imposed on an included permanganate anion, and the new electron transfer band occurs at a higher wavenumber.

Potassium osmium(IV) hexachloride. The dark red colour of K_2OsCl_6 previously described¹⁶ persists to some extent in $\text{K}_2\text{Os}_{0.2}\text{Pt}_{0.8}\text{Cl}_6$ as seen on Fig. 4. This would seem to disprove the description of this phenomenon (also found in $\text{K}_2\text{Ir}_{0.05}\text{Pt}_{0.95}\text{Cl}_6$) as due to the specific interaction between the tightly compressed OsCl_6^{2-} or IrCl_6^{2-} groups. As previously suggested^{4,11} the dark colour may be due to interactions between a given MX_6 with its twelve nearest, adjacent MX_6 groups. This would broaden the set of energies of the highest filled orbitals, especially if the neighbour M have nearly the same x_{opt} as Ir(IV) or Os(IV). However, since the strong 580 $m\mu$ shoulder of the K^+ and NH_4^+ iridium(IV) containing salts is rather independent of the choice of host component, Sn(IV), Pb(IV), Pt(IV), or Ir(IV), a delocalization (case (1) above) do not appear to be important.

A better hypothesis is therefore that IrCl_6^{2-} and OsCl_6^{2-} , whenever compressed, tend to displace their absorption towards relatively low wavenumbers.

The general red shift of electron transfer bands (where the electron is going to a sub-shell which is not σ -antibonding) when the internuclear distances are decreased^{6,7} can formally be described as an increasing x_{opt} of the central atom. This is also the case in tetrahedral 3d complexes¹⁷ having higher x_{opt} than the corresponding octahedral complexes with larger internuclear distances. Dr. J. Ryan, Hanford, was also so kind to inform me that NpCl_6^{2-} has a much higher x_{opt} by about 0.3 unit, than $\text{NpCl}(\text{H}_2\text{O})_x^{3+}$ reported by Sykes and Taylor¹⁸ again possibly changing the Np—Cl distance, either because the coordination number is different or because the latter complex is an outer-sphere ion-pair.

Intra-subshell transitions in osmium(IV) and rhenium(IV). On Figs. 3—4, the internal transitions ${}^3\Gamma_4 \rightarrow {}^1\Gamma_3$ and ${}^1\Gamma_4 \sim 900 m\mu$ and ${}^3\Gamma_4 \rightarrow {}^1\Gamma_1 \sim 600 m\mu$ in the lowest sub-shell configuration of OsCl_6^{2-} are observed also in the solid compounds such as also previously reported¹⁶. Fig. 5 shows the similar transition ${}^4\Gamma_2$ to the Γ_7 and Γ_8 components of ${}^2\Gamma_5$ in Tl_2ReCl_6 at slightly lower wavenumbers than in²⁶ K_2ReCl_6 and without resolved vibrational structure. Ag_2ReCl_6 exhibits four weak bands in this region, suggesting a strong distortion from cubic symmetry. This seems very probable when compared with the crystallographic data now to be discussed.

Table 3. Dimension of unit cell a in Å of cubic lattices.

	K^+	Cs^+	$\text{N}(\text{CH}_3)_4^+$	Tl^+
SnCl_6^{2-}	9.98 ²⁰	10.35 ²⁰	12.87 ²⁰	9.97 ²⁰
PbCl_6^{2-}	—	10.42 ²⁰	—	—
PtCl_6^{2-}	9.73 ²⁰	10.19 ²⁰	12.72	9.76 ²⁰
IrCl_6^{2-}	—	10.20	—	—
OsCl_6^{2-}	9.73 ²⁰	10.23	—	9.80
OsBr_6^{2-}	10.30 ²⁰	—	—	10.26
ReCl_6^{2-}	9.86 ²⁰	—	—	9.84

X-Ray crystallographic measurements. Table 3 gives the values of the lattice parameter a of the cubic structure A_2MX_6 determined in literature²⁰ and by Dr. Elfriede Rittershaus here at CERI. It is seen that in all cases, the Tl salts have nearly the same value of a as the corresponding K salts. It is interesting to note that the silver(I) compounds Ag_2ReCl_6 , Ag_2OsCl_6 and $Ag_2OsCl_xI_{6-x}$ discussed in a following note¹⁹ all showed strong deviations from cubic symmetry; Ag^+ has probably a too small ionic radius and dislikes the high coordination number of 12 chlorides imposed by the antifluorite structure¹¹. The only cubic silver compound possibly found here was Ag_2OsBr_6 . It was not too well crystallized and did not show several of the weaker lines expected on the X-ray film; if it is interpreted as an antifluorite lattice, it has $a = 9.98 \text{ \AA}$. This is a remarkably small value when compared with $a = 10.26 \text{ \AA}$ for Tl_2OsBr_6 and 10.30 \AA for K_2OsBr_6 . However, it is more probable that it is simply $AgBr$ crystallizing in NaCl lattice with the value of $a\sqrt{3}$ times smaller, that is 5.755 \AA ²⁷.

The value $a = 12.72 \text{ \AA}$ for $[N(CH_3)_4]_2PtCl_6$ given in Table 3 really refers to the mixture containing 5% $IrCl_6^{2-}$. There is no doubt that this substitution has only a very small influence on a , the measurement was made in order to show that these crystals are indeed still cubic, and not trigonally distorted as is the case, say with the UCl_6^{2-} salt.

Conclusions. The spectacular colour changes observed in 5d group hexahalides with colourless cations (orange-brown $IrCl_6^{2-}$ forming brick-red Cs_2IrCl_6 , purple K_2IrCl_6 , dark green Tl_2IrCl_6 , dark blue Ag_2IrCl_6 ; yellow $OsCl_6^{2-}$ forming orange Cs_2OsCl_6 , red K_2OsCl_6 , olive-green Tl_2OsCl_6 and dark brown Ag_2OsCl_6 ; or tomato-red $OsBr_6^{2-}$ forming black Tl_2OsBr_6) can be ascribed to two main phenomena: a broadening and shift of the first electron transfer band when the M—Cl distance is decreased in salts of small A, especially of potassium; and the appearance of a new electron transfer band in thallium(I) and silver(I) compounds. There has been found no spectroscopic evidence for any particular co-operative effects from distant MX_6 clusters, and the optical excitations seem much too localized in small chromophores for any energy-band-like description to be appropriate.

EXPERIMENTAL

Stock solutions of 0.1 M $Na_2PtCl_6 \cdot 6H_2O$ (H. Drijfhout & Zoon, Amsterdam) in 0.5 M HCl, and of 0.1 M $Na_2IrCl_6 \cdot 6H_2O$ (H.D.Z.) in 1 M HCl once saturated with Cl_2 (cf. the warnings by Poulsen and Garner⁵) were used for precipitations with solutions of $CsCl$, $TlClO_4$, $N(CH_3)_4Cl$ (Fluka), etc. The mixed anions were formed from Na_2SnCl_6 (B.D.H.) or from a solution of $SnCl_4$ in conc.HCl; from PbO_2 dissolved in ice-cold HCl; and from 0.74 g $CeCl_3 \cdot 6H_2O$ (Thorium Ltd., London) with 20 ml H_2O and 10 ml 1 M NaOH, $Ce(OH)_3$ oxidized to pale yellow $Ce(OH)_4$ with 6 ml bromine water, repeatedly washed with H_2O , and dissolved in 10 ml hydrochloric acid kept saturated with HCl at 0°C. This dark red solution was mixed with 1 ml of the $IrCl_6^{2-}$ stock solution and dropwise added to a solution of 1 g $CsCl$ in 5 ml ice-cold HCl.

Solutions of K_2OsCl_6 in 1 M HCl and of K_2ReCl_6 in 6 M HCl were used for the precipitations. Ag_2ReCl_6 was made from $[As(C_6H_5)_4]_2ReCl_6$ in ethanol and aqueous $AgClO_4$; Ag_2OsCl_6 and $Ag_2Os_{0.2}Pt_{0.8}Cl_6$ were made from solutions not containing excess HCl; Ag_2OsBr_6 and Tl_2OsBr_6 was made from $[N(C_4H_9)_4]_2OsBr_6$ dissolved in ethanol.

The reflection spectra of crystalline samples were measured on a Beckman DU spectrophotometer at every 5, 10, or 20 $m\mu$ according to the amount of structure present in the spectrum.

The X-ray crystallographic measurements were made with a Guinier-De Wolf camera (Copper $K\alpha$ radiation), from Enraf-Nonius, Delft, and were standardized with the cubic lattice of silicon.

Acknowledgements. I would like to thank Mr. Georges Casaro and Mr. Bernard Dusonchet for their assistance by measuring the reflection spectra, and Miss Elfriede Rittershaus for the crystallographic work. Finally, I thank Dr. A. L. Peiker and Professor C. J. Ballhausen for various clarifying stylistic improvements.

REFERENCES

1. Jørgensen, C. K. *Physica status solidi* **2** (1962) 1146.
2. Jørgensen, C. K. Lectures given at the Battelle Institute symposium in Geneva July 1962, "Local properties of perfect crystals".
3. Goodenough, J. B. *Magnetism and Crystal Structure in Nonmetals*. Technical Report No. 267 from the Lincoln Laboratory, M.I.T., 24 April 1962.
4. Jørgensen, C. K. *Mol. Phys.* **2** (1959) 309.
5. Poulsen, I. A. and Garner, C. S. *J. Am. Chem. Soc.* **84** (1962) 2032.
6. Jørgensen, C. K. *J. Inorg. Nucl. Chem.* **24** (1962) 1587.
7. Balchan, A. S. and Driekamer, H. G. *J. Chem. Phys.* **35** (1961) 356.
8. Jørgensen, C. K. *Mol. Phys.* **4** (1961) 231.
9. Kiriyaama, R., Ogawa, K. and Azumi, M. *J. Chem. Soc. Japan* **82** (1961) 328.
10. Day, P. *Inorg. Chem. In press.*
11. Jørgensen, C. K. *Mol. Phys.* **4** (1961) 235.
12. Brauer, G. and Allardt, H. D. *Z. anorg. Chem.* **316** (1962) 134.
13. Jørgensen, C. K. *Orbitals in Atoms and Molecules*. Academic Press, London 1962.
14. Robin, M. B. *Inorg. Chem.* **1** (1962) 337.
15. Symons, M. C. R. and Trevalion, P. A. *J. Chem. Soc.* **1962** 3503.
16. Jørgensen, C. K. *Acta Chem. Scand.* **16** (1962) 793.
17. Jørgensen, C. K. *Mol. Phys.* **6** (1963) 43.
18. Sykes, K. W. and Taylor, B. L. *Proc. 7 ICCS*, Stockholm 1962, p. 31.
19. Jørgensen, C. K. *Acta Chem. Scand.* **17** (1963) 1043.
20. Landolt-Börnstein *Tabellen*, 6. Aufl., I. Band, 4. Teil. Kristalle. Springer-Verlag Berlin 1955.
21. Brateman, P. S., Phipps, P. B. P. and Williams, R. J. P. *Proc. Chem. Soc.* **1963** 12.

Received November 25, 1962.