Spectrochemical Study of Microscopic Crystals. XI.[1] *The Structure and Polarized Absorption Spectra of Some Metallic Compounds with Remarkable Interaction between Metal Atoms through Anions*

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These several years the present authors have been particularly interested in those inorganic compounds which display in the crystalline state much deeper colours than would be expected from the colours of their components in solution. In one type of the compounds, the metal-to-metal interaction was concluded to exist, causing the unusual deepening of the colour[2]. In the compounds of another type, there was supposed to be interaction between metal atoms through anions[3]. In the study of the above compounds, the measurement of polarized absorption spectra has proved to be a feasible means, since the interaction was found to cause enormous changes in the direction along which the interaction was known to exist between the metal atoms. We have taken up those compounds in which there would be expected to be infinite chains of metal atoms connected with anions as bridging groups. In the present work, polarized absorption spectra of $Pd(NH_3)_2Cl_3$, Pt $(en)Cl_3$[4] and $(NH_4)_3AgAuCl_7$ have been quantitatively determined and the results have been discussed with relation to the structure of the compounds.

Experimental

Materials.—Trans-$[Pd(NH_3)_2Cl_2]$ was prepared in orange crystals of moderate size by spontaneous evaporation of an aqueous solution of $[Pd(NH_3)_4]Cl_2$[5]. The crystals show a straight extinction. They appear yellow with the electric vector along the *c*-axis, and orange with the electric vector normal to the *c*-axis. The measurement was made along the two directions. The X-ray study of the crystal structure[5] indicates that the *c*- and *a*-absorption denote absorption with the electric vector along and normal to the complex molecules, respectively.

$[Pd(NH_3)_2Cl_2][Pd(NH_3)_2Cl_4]$ was prepared according to the method of Cohen et al.[6] The crystals obtained in black needles belong to the orthorhombic system, showing a straight extinction and a remarkable dichroism. They appear quite dark with the electric vector along the *c*-axis, and yellow with the electric vector normal to the *c*-axis. There were sometimes grown crystals with a different habit, which exhibited a dichroism different from the above. The dichroism measurement was made with the crystals of the former type.

$[Pt(en)Cl_2]$ was prepared in yellow powder according to the method of Basolo[7]. Crystals of

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[1] Part X of this series, S. Yamada and R. Tsuchida, This Bulletin, 29, 289 (1956).

[2] S. Yamada and R. Tsuchida, *J. Chem. Soc. Japan*, 70, 142 (1949); S. Yamada, *J. Am. Chem. Soc.*, 73, 1579 (1951); This Bulletin, 24, 125 (1951); S. Yamada and R. Tsuchida, *J. Am. Chem. Soc.*, 75, 6351 (1953); This Bulletin, 27, 156 (1954).

[3] S. Yamada, Y. Shimura and R. Tsuchida, This Bulletin, 26, 72 (1953); R. Tsuchida and S. Yamada, *Nature*, 174, 1064 (1954).

[4] The notation, en, denotes a molecule of ethylenediamine.

[5] F.G. Mann, D. Crowfoot, D.C. Gattiker and N. Wooster, *J. Chem. Soc.*, 1935, 1642.

[6] A.J. Cohen and N. Davidson, *J. Am. Chem. Soc.*, 73, 1955 (1951).

[7] F. Basolo, ibid., 72, 2433 (1950).

a moderate size suitable for the absorption measurement could not be obtained. Its absorption spectrum was determined in the aqueous solution with a Beckman DU spectrophotometer.

$[Pt(en)Cl_4]$ was prepared in pale yellow powder by the method of Basolo⁷⁾. The measurement of the polarized absorption spectra with the crystals could not be made, since the crystals large enough for the measurement were not available. Its absorption spectrum was determined using the aqueous solution.

$Pt(en)Cl_3$ was prepared by oxidizing $[Pt(en)Cl_2]$ with ammonium persulphate according to the method of Tschugaeff et al.⁸⁾ or by allowing to cool a hot, mixed solution of $[Pt(en)Cl_2]$ and $[Pt(en)Cl_4]$. Red, plate-like crystals thus obtained were strongly dichroic; purplish-red and pale yellow with the electric vector along and normal to the *c*-axis, respectively. The measurement of the polarized absorption spectra was performed along the above two directions. The *a*- and *c*-absorption have the same meaning as the above.

$Cs[AuCl_4]$ was prepared in yellow prisms from tetrachloro-auric acid and caesium chloride, which were purified by repeated recrystallization from water. A slight dichroism was observed with the crystals under the microscope. The measurement of the dichroism was made along the directions parallel and normal to the prism axis. The C- and A- absorption denote absorption with the electric vector along and normal to the prism axis, respectively. Measurement of absorption spectra was also made with the aqueous solution containing CsCl.

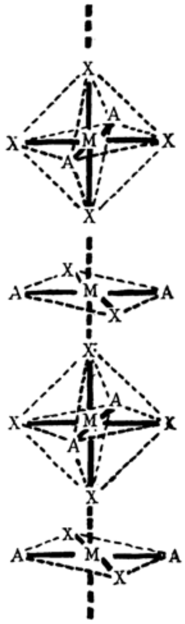
$Cs_2AgAuCl_6$ was obtained in black microcrystals by the method of Wells⁹⁾. To an aqueous solution of tetrachloro-auric acid acidified with hydrochloric acid was added silver nitrate and caesium chloride, followed by warming on a water bath. The precipitate of silver chloride, which was formed at first, again entered into solution, from which the black crystals sparated out. The crystals of a larger size suitable for the absorption measurement could not be obtained. The visual observation, however, could be made with some of them under the microscope. The crystals showing a straight extinction were strongly dichroic. They appear almost black with the electric vector along the *c*-axis, and yellow with the electric vector normal to the *c*-axis.

$(NH_4)_3AgAuCl_7$ was prepared in very dark crystals follwing the same procedure as that with the above caesium compound, except that ammonium chloride was used instead of caesium chloride¹⁰⁾. The reaction also proceeded in a way very similar to the case of the corresponding caesium compound. The needles of the compound, which belong to the orthorhombic system, showed a marked dichroism. They appeared quite dark along the *c*-axis, and yellow in the direction normal to the *c*-axis. The dichroism measurement was made with reference to the above two directions.

Measurement.—Quantitative dichroism measurements were made by Tsuchida-Kobayashi's microscopic method¹¹⁾ with polarized light in the regions covering 2400 to 8000 Å. The notations used are the same as those in the previous papers of this series¹⁾.

Results and Discussion

In 1948, Brosset¹²⁾ studied the crystal structure of $Pt(NH_3)_2Br_3$. The crystal analysis indicates that the crystal of the compound, which should be formulated as $[Pt(NH_3)_2Br_2]$ $[Pt(NH_3)_2Br_4]$, consists of infinite chains, each containing alternate planes of $[Pt(NH_3)_2Br_2]$ and octahedra of $[Pt(NH_3)_2Br_4]$, as illustrated in Fig. 1. From visual observation of the crystals under the microscope and examination of their magnetic property, Cohen et al.⁶⁾ supposed that the crystal of $Pd(NH_3)_2Cl_3$, which could be represented by $[Pd(NH_3)_2Cl_2]$ $[Pd(NH_3)_2Cl_4]$, would possess the same structure as that of $[Pt(NH_3)_2Br_2]$ $[Pt(NH_3)_2Br_4]$. This was confirmed later by the X-ray analysis of the crystal¹³⁾.



M: Pd or Pt A: ammonia or amine
X: halide or hydroxyl group
Fig. 1. Chain structure in the crystals of the compounds having the empirical formula, MA_2X_3.

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8) L. Tschugaeff and J. Tschernyaeff, *Z. anorg. allgem. Chem.*, 182, 159 (1929).

9) H. L. Wells, *Amer. J. Sci. Silliman*, (5) 3, 257 (1920); *Chem. Zentr.*, 1922, 239.

10) W.B. Pollard, *J. Chem. Soc.*, 117, 99 (1920).

11) R. Tsuchida and M. Kobayashi, This Bulletin, 13, 619 (1938); "The Colours and the Structures of Metallic Compounds", Zoshindo, Osaka, Japan (1944), p. 180.

12) C. Brosset, *Arkiv Kemi Mineral. Geol.*, 25 A, No. 19 (1948).

13) E. W. Hughes, unpublished; private communication from Dr. A. J. Cohen; C. S. Adams, M. S. thesis, University of Sydney, 1952.

The result of the present measurement is shown in Fig. 2. Polarized absorption spectra of one component, *trans*-$[Pd(NH_3)_2Cl_2]$, are also given in Fig. 2. The other component, $[Pd(NH_3)_2Cl_4]$, is too unstable to be isolated in crystals. Its solution, however, is orange in colour. The crystal of $[Pd(NH_3)_2Cl_2]$ $[Pd(NH_3)_2Cl_4]$, therefore, is seen to show its absorption at much longer wavelength than would be expected from the absorption spectra of the components. This suggests that the component complexes would undergo specific effects in the crystal of $[Pd(NH_3)_2Cl_2][Pd(NH_3)_2Cl_4]$. Moreover, the present measurement shows that absorption is much more bathochromic with the electric vector along the chains, $\cdots Cl—Pd^{IV}—Cl\cdots Pd^{II}\cdots Cl—Pd^{IV}—Cl\cdots$, than that normal to the chain. This relation is seen to be reverse to that with the crystal of *trans*-$[Pd(NH_3)_2Cl_2]$. *It may be presumed from the above relations that in the crystals of* $[Pd(NH_3)_2Cl_2]$ $[Pd(NH_3)_2Cl_4]$ *there would be strong interaction between the metal atoms in different oxidation states through the anions.* Thus with the electric vector along the chain, absorption was observed at 30–45×10^{13}/sec., whereas the absorption in this region was not observed with the electric vector normal to the above chain. This absorption might be assumed to be a charge-transfer band[14] due to the chain, $\cdots Cl—Pd^{IV}—Cl\cdots Pd^{II}\cdots Cl—Pd^{IV}—Cl\cdots$.

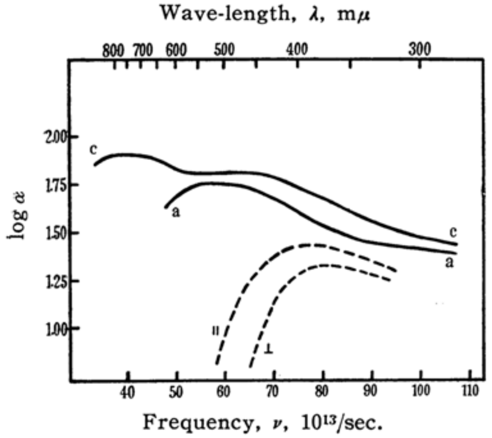

Fig. 2. Absorption spectra of $[Pd(NH_3)_2Cl_2]$ $[Pd(NH_3)_2Cl_4]$ (——) and *trans*-$[Pd(NH_3)_2Cl_2]$ (- - - -), both in crystalline state.

The compound, $Pt(en)Cl_3$, may be considered as a compound of a similar type. Thus the compound can be prepared from a mixed aqueous solution of $[Pt(en)Cl_2]$ and $[Pt(en)Cl_4]$. Further, magnetic examination[15] indicates that this compound is diamagnetic, involving no platinum in tervalent state. The above facts seem to show that the compound should be formulated as $[Pt(en)Cl_2][Pt(en)Cl_4]$.

The compound, $[Pt(en)Cl_2][Pt(en)Cl_4]$, in the crystalline state has much deeper colour than either of the component complexes; $[Pt(en)Cl_2]$ is pale yellow, and $[Pt(en)Cl_4]$ is also yellow. Thus the compound, $[Pt(en)Cl_2]$ $[Pt(en)Cl_4]$ dissolves in hot water to give a yellow solution, from which its red crystals separated. As may be expected from the colours, $[Pt(en)Cl_2][Pt(en)Cl_4]$ in the crystalline state is found to show its absorption at far longer wave-length than either of the component complexes (Fig. 3). This shows that the complexes are under remarkable effect in the crystalline state. The nature of the effect may be judged from the results of the dichroism measurement. The dichroism of the above compound, as given in Fig. 3, may be well understood, assuming that the red compound involves infinite chains similar to those in the crystal of $[Pd(NH_3)_2Cl_2]$ $[Pd(NH_3)_2Cl_4]$. That is, assuming the *c*-absorption to be the absorption along the infinite chains, $\cdots Cl—Pt^{IV}—Cl\cdots Pt^{II}\cdots Cl—Pt^{IV}—Cl\cdots$, and the *a*-absorption to be the absorption normal to the chain, then the absorption is seen to be much more bathochromic with the electric vector along the above chains than the absorption normal to the chains. This relation on the dichroism is found to be quite similar to that of $[Pd(NH_3)_2Cl_2]$ $[Pd(NH_3)_2Cl_4]$, and may be best understood in the same way as with the above palladium compound. *It is most likely that the crystal of* $[Pt(en)Cl_2][Pt(en)Cl_4]$ *involves the infinite chains along the c-axis, as assumed above.* The absorption at 50-65×10^{13}/sec.,

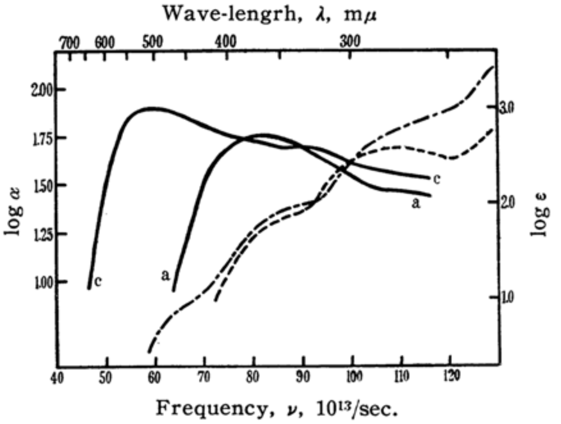

Fig. 3. Absorption spectra of $[Pt(en)Cl_2]$ $[Pt(en)Cl_4]$ (——), $[Pt(en)Cl_2]$ (- - - -) and $[Pt(en)Cl_4]$ (—·—·—).

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[14] See, for example, R.S. Mulliken, *J. Am. Chem. Soc.*, **72**, 605 (1950), etc.

[15] Y.K. Syrkin and V.I. Belova, *Žhur. Fiz. Khim.*, **23**, 664 (1949); *C.A.*, **43** 7277 (1949).

which is not observed with the electric vector normal to the chains, is observed with the electric vector along the chains. This absorption may be a charge transfer band due to the chains, $\cdots Cl-Pt^{IV}-Cl\cdots Pt^{II}\cdots Cl-Pt^{IV}-Cl\cdots$.

Besides the compounds described above, another type of compounds is known in which similar interaction may be found between metal atoms through anions. One of the compounds may be $Cs_2AgAuCl_6$. This crystal is very dark, almost black in colour. Elliott et al.[16] studied the crystal structure of the above compound, showing that the crystal of this compound involves infinite chains along the *c*-axis, each containing alternate planes of $[AuCl_4]^-$ and linear ions of $[Cl-Ag-Cl]^-$. The crystals of $Cs_2AgAuCl_6$ which we obtained were too small to be used for the dichroism measurement. We, however, could observe visually some of the crystals under the microscope. The observation showed that the crystals appeared almost black with the electric vector along the *c*-axis, and yellow with the electric vector normal to the *c*-axis. This fact seems to suggest that absorption with the electric vector along the infinite chains lies at much longer wave-length than that with the electric vector normal to the chains. Thus, it may be supposed that the crystal of $Cs_2AgAuCl_6$ exhibits dichroism of a type similar to that of $[Pd(NH_3)_2Cl_2][Pd(NH_3)_2Cl_4]$. The absorption at the longer wave-length, which would be allowed only with the electric vector along the infinite chains, $\cdots Au^{III}(Cl_4)\cdots Cl-Ag^{I}-Cl\cdots Au^{III}(Cl_4)\cdots$, may be a charge transfer band, characteristic of the above chains. This may be considered as showing that there would be a strong interaction between the metal atoms through the chlorine atoms.

By following the same procedure as in the preparation of $Cs_2AgAuCl_6$ except that ammonium chloride was used instead of caesium chloride, a dark-coloured compound, $(NH_4)_3AgAuCl_7$, was obtained. The reaction proceeded in quite the same way as in the caesium compound. The crystal structure of $(NH_4)_3AgAuCl_7$ has not been determined as yet. But similarity to the corresponding caesium compound in the method of preparation and in the reaction of its formation seems to indicate that the crystals of $(NH_4)_3AgAuCl_7$ involve components similar to those of the corresponding caesium compound; that is, $[Cl-Ag-Cl]^-$ and $[AuCl_4]^-$ ions. The crystals of this compound are found to absorb in much longer wave-length than would be expected for the component complexes (Figs. 4 and 5). This indicates that the component complexes undergo some effects in the crystalline state.

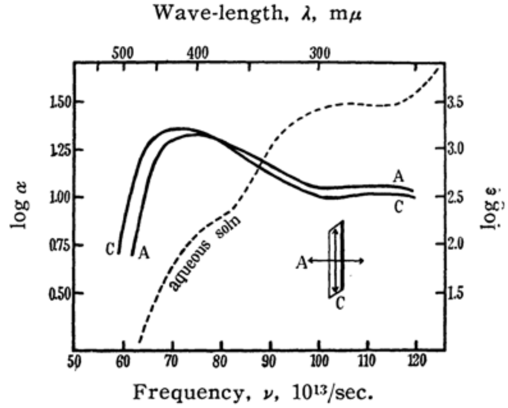

Fig. 4. Absorption spectra of $Cs[AuCl_4]$.

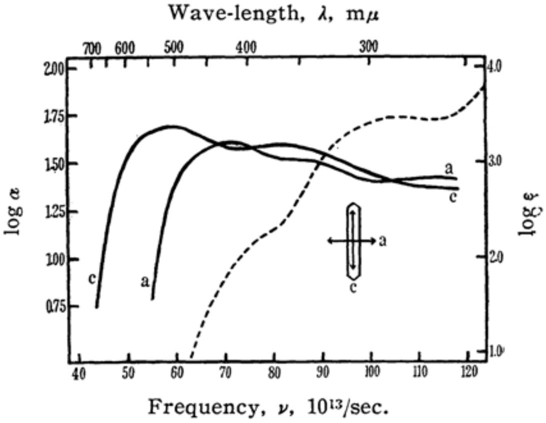

Fig. 5. Absorption spectra of $(NH_4)_3AgAuCl_7$ (——) and $Cs[AuCl_4]$ (- - - -).

It has also been found that the *c*-absorption is much more bathochromic and somewhat more hyperchromic than the *a*-absorption. These relations, which are similar to those with the crystals of $Pd(NH_3)_2Cl_3$, $Pt(en)Cl_3$ and $Cs_2AgAuCl_6$, seem to agree with the assumption that *the crystals of* $(NH_4)_3AgAuCl_7$ *may contain infinite chains of* $\cdots Au^{III}(Cl_4)\cdots Cl-Ag^{I}-Cl\cdots Au^{III}(Cl_4)\cdots$ *along the c-axis.* Thus the absorption at 55×10¹³/sec. for the *c*-absorption, which is not observed for the *a*-absorption, may be assigned to a kind of charge transfer band due to the above chains.

General Discussion

Surveying the above results, the following generalization may be induced. *Those compounds having infinite chains such as* $\cdots X-M^{m}-X\cdots M^{n}\cdots X-M^{m}-X\cdots$, *M and X being metal and halogen atoms, show at the*

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[16] N. Elliott and L. Pauling, *J. Am. Chem. Soc.*, 60, 1846 (1938).

longer wave-length a new absorption band, characteristic of the infinite chains and polarized along the chains. The new band may be interpreted as due to a charge transfer between the two components.

This may be taken as showing that *in those crystals there would exist some interaction between metal atoms through anions.* In the above instances, the halogen atoms are supposed to act as bridges, facilitating the electron transfer between the metal atoms. Assuming the picture of the electron transfer between metal atoms, the interaction would be stronger between atoms in different oxidation states of the same or similar elements than between atoms of different elements. The interaction between the metal atoms in the above compounds, however, seems to be slightly different from the interaction between metal atoms in μ-peroxodicobalt-compounds, magnetite or prussian blue[17]. That is, in the groups of the latter compounds all the metal atoms are almost or completely equivalent and undistinguishable, while in the former there are involved two kinds of the metal atoms which are clearly unequivalent. The electronic migration between the two metal atoms would occur much more readily in the compounds of the latter type than in those of the former.

It is to be noted that the complex, $[Pd(NH_3)_2Cl_4]$, is rather stable in the crystal of $[Pd(NH_3)_2Cl_2][Pd(NH_3)_2Cl_4]$, although the former has never been isolated in solid under any ordinary condition. In the same way, the $[Cl{-}Ag{-}Cl]^-$ anion seems to be much more stable in the crystal of $Cs_2AgAuCl_6$ and $(NH_4)_3AgAuCl_7$ than in other compounds of an ordinary type involving the anions. The remarkably enhanced stability of the above complexes in the present compounds may be closely associated with the interaction between the metal atoms through the anions.

It is suggested that a number of compounds having platinum or palladium in apparently tervalent state would involve similar chains. Thus, in the crystals of $Pt(NH_3)_2(OH)Cl_2$ there would be similar chains, in which the atom of bivalent platinum would be connected with the atoms of quadrivalent platinum through OH^- or Cl^- ions. In fact, according to Bokii et al., the crystals of $Pt(NH_3)_2(OH)Cl_2$ appears black with polarized light having its electric vector along the needle axis, and very pale with the electric vector normal to the needle axis[18]. This seems to indicate that the compound in the crystalline state displays in the visible region an absorption band which would be polarized in the direction of the needle axis. It is most probable that the band at the longer wave-length may be a charge transfer band due to the possible chains, $\cdots X{-}Pt^{IV}{-}X\cdots Pt^{II}\cdots X{-}Pt^{IV}{-}X\cdots$, indicating the interaction between the bivalent and quadrivalent platinum atoms through negative ions such as OH^- or Cl^- ions (Fig. 1).

The so-called copper-coloured oxalatoplatinum compounds[19] and the Wolffram's compound[20], $Pt(NH_2\cdot C_2H_5)_4Cl_3\cdot 2H_2O$, also are believed to belong to the same type of compounds involving similar chains. Polarized absorption spectra which were determined lately[21,22] are found to support the above presumption. The detailed reports on those compounds will be submitted later.

Summary

Polarized absorption spectra of $[Pd(NH_3)_2Cl_2]$ $[Pd(NH_3)_2Cl_4]$, $Pt(en)Cl_3$ and $(NH_4)_3AgAuCl_7$ in the crystalline state have been determined by Tsuchida-Kobayashi's microscopic method in the regions betwen 2400 and 8000 Å.

The crystals of the above compounds which are supposed to involve infinite chains of a type, $\cdots X{-}M^m{-}X\cdots M^n\cdots X{-}M^m{-}X\cdots$, have been found to display absorption at longer wave-length than any of the respective component complexes. This absorption at the longer wave-length has been shown to be completely polarized along the direction of the supposed chains in the crystals.

The above results show that in these crystals there would be rather strong interaction between the metal atoms through the anions along the infinite chains.

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[17] S. Yamada, Y. Shimura and R. Tsuchida, This Bulletin, **26**, 72 (1953); P.E. Fielding and D.P. Mellor, *J. Chem. Physics*, **22**, 1155 (1954), etc.

[18] G.B. Bokii and G.I. Distler, *Doklady Akad. Nauk S.S.S.R.*, 56, 923 (1947).

[19] A. Werner and E. Grebe, *Z. anorg. Chem.*, **21**, 381, 387 (1899), etc.

[20] H. Wolffram, Dissertation, Königsberg, 1900.

[21] R. Tsuchida and S. Yamada, read before the annual meeting of the Chemical Society of Japan, Kyoto, April, 1953.

[22] To be submitted later.