Spectrochemical Study of Microscopic Crystals. VI.[1] *Light Absorption of Non-planar Quadri-co-ordinated Complexes*

By Shoichiro YAMADA and Ryutaro TSUCHIDA

(Received June 16, 1954)

In the former reports,[1,2] the present authors studied dichroism in the visible and ultra-violet of metallic quadri-co-ordinated complexes possessing planar configuration, and established the common rules on the dichroism. It is known that some metals such as copper (II) and cobalt (II) form non-planar quadri-co-ordinated complexes in addition to planar ones: e.g., $Cu(H_2O)_4^{++}$ in the crystal of $CuSO_4 \cdot 5H_2O$ is square,[3] and $CuCl_4^{--}$ in the crystal of Cs_2CuCl_4 has a distorted-tetrahedral configuration.[4] Complexes with distorted-tetrahedral configuration would probably show more or less remarkable anisotropy of light absorption, whereas complexes with regular-tetrahedral configuration would exhibit very slight or no anisotropy. Measurements of pleochroism may, therefore, be expected to throw some light upon the nature of chemical linkages as well as upon the configuration. For the above purpose Cs_2CuCl_4, Cs_3CoCl_5 and $K_2Co(NCS)_4 \cdot 4H_2O$ have been studied. In the present work absorption spectra of the above compounds in the crystalline state have been quantitatively determined, and the results of the measurements have been discussed in relation to the configuration of the complex ions.

Experimental

Materials. — Cesium cobaltous pentachloride was prepared in blue tabular crystals by spontaneous evaporation at a room temperature of aqueous solution of cobaltous chloride and excess of cesium chloride.[5] The crystals, which belong to the tetragonal system, show straight extinction and very slight dichroism. Measurements of absorption spectra were made on the face (100) with polarized light having its electric vector along the directions of extinction.

Crystals of cesium tetrachloro-cuproate were obtained by evaporating at a room temperature an aqueous solution of cesium chloride and cupric chloride.[4] The orange, tabular crystals thus obtained show a dichroism; they appear orange with electric vector parallel to the b-axis, and yellow with that perpendicular to the above. Optical measurements were performed in the (101) face with reference to the above two directions.

Potassium tetrathiocyanato-cobaltoate tetrahydrate was prepared in blue prismatic crystals by the method of v. Grotthus.[6] The crystals of the orthorhombic system show a definite dichroism in the prism face; they appear blue with the electric vector along the direction of elongation and pale blue with that perpendicular to the above. Dichroism measurement was carried out in the prism face with reference to the above two directions. The absorption spectrum was also determined with its solution in 99% alcohol containing potassium thiocyanate.[7]

Measurements.—Quantitative measurements of absorption spectra of crystals were made at room temperature by Tsuchida-Kobayashi's microscopic method[8] with polarized light in the region covering 7500 to 2400Å. α represents the absorption coefficient of a crystal. Molecular absorption coefficients of a crystal, k, were calculated from the relation, $k=10\alpha M/\rho$, where M and ρ denote formula weight of a complex compound and density of a crystal, respectively.

Absorption spectrum in solution was determined with a Beckman DU quartz-spectrophotometer. ε represents extinction coefficient of the solution.

Results and Discussion

Cesium Tetrachlorocuproate. — According to the result of the crystal structure analysis,[4] the crystal consists of cesium ions and $CuCl_4^{--}$ anions having configuration of flattened tetrahedron. The maximum of the band at the longest wave-length could not be determined, since the band extends into the infra-red beyond the region of the measurement. Comparison of the absorption curve (Fig. 1) with previously reported data of other cupric complex compounds and analogy to cobaltic and chromic complexes indicate that the band with its maximum in

---

[1] Part V of this series, S. Yamada and R. Tsuchida, This Bulletin, **27**, 156 (1954).

[2] R. Tsuchida, S. Yamada and H. Yoneda, *J. Chem. Soc. Japan* **69**, 145 (1948); S. Yamada, *J. Am. Chem. Soc.*, **73**, 1182 and 1579 (1951); S. Yamada and R. Tsuchida, This Bulletin, **26**, 72 (1953).

[3] C. A. Beevers and H. Lipson, *Proc. Roy. Soc.*, London A**146**, 570 (1934).

[4] L. Helmholz and R. F. Kruh, *J. Am. Chem. Soc.*, **74**, 1176 (1952).

[5] H. M. Powell and A. F. Wells, *J. Chem. Soc.*, **1935**, 359.

[6] T. v. Grotthus, "Gmelins Handb. d. anorg. Chem.," 8. Aufl., 1932, **58**$_3$, 431.

[7] The authors are indebted to the Analytical Laboratory of our department for the measurement of the solution with a Beckman spectrophotometer.

[8] R. Tsuchida and M. Kobayashi, "The Colours and the Structures of Metallic Compounds," Osaka, 1944, p. 180.

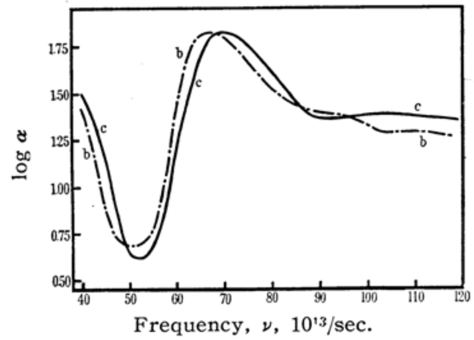


Fig. 1. Absorption spectra of Cs_2CuCl_4.

the infra-red region (band A) is considered to be due principally to electronic transitions of co-ordination electrons around the core of the metal atoms, and the band with its maximum at ν = about 70×10^{13}/sec. (band B) may be due largely to the existence of the negative ions in trans-positions.[9]

It is seen from the result of the crystal structure analysis that the b-absorption, absorption with electric vector parallel to the b-axis, is more abundant with the z-component than with the x-component (Fig. 2.), and that the c-absorption is richer in the x-component. From the configuration of the complex anion, anisotropy is expected for the crystal. The expectation is satisfied by the present measurement, which indicates that for the band B and also possibly for the band A the Z-absorption is bathochromic to the X-absorption. (Table I)

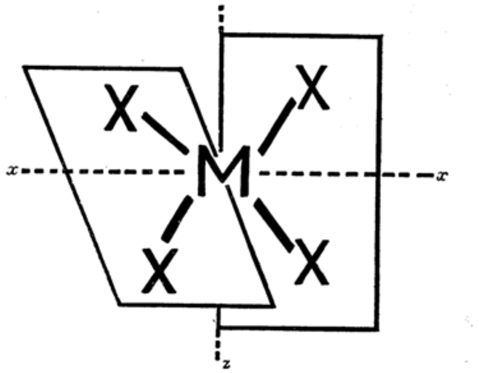


Fig. 2. Flattened-tetrahedral configuration of quadri-co-ordinated complexes.

TABLE I

ABSORPTION MAXIMA OF Cs_2CuCl_4 IN THF CRYSTALLINE STATE

	ν,10^{13}/sec.	logα	M
b–abs.	67.0	1.82	9.11×10^4
c–abs.	70.0	1.82	9.11×10^4

The qualitative absorption spectrum of the compound was reported by Helmholz et al.[4] with the solid suspended in the mineral oil, but their results are not in good agreement with ours where a single crystal is used instead of powdered solid in oil.

Tricesium Cobaltous Pentachloride.—According to the X-ray analysis of the crystal,[5] the crystal consists of $CoCl_4^{--}$ cesium and chloride ions, $CoCl_4^{--}$, being regular-tetrahedral. Therefore, very slight or no anisotropy of light absorption can be anticipated for the crystal of the compound. Actually very slight anisotropy of absorption was observed (Fig. 3. and Table II). Slight dichroism may be attributed to the dissymmetrical crystalline field. The above result lends a further support to the regular-tetrahedral configuration of the quadri-co-ordinated complex in this crystal.[5] Recently Katzin et al.[10] reported reflection spectra with powdered solid of dipyridinium and dicesium tetrachloro-

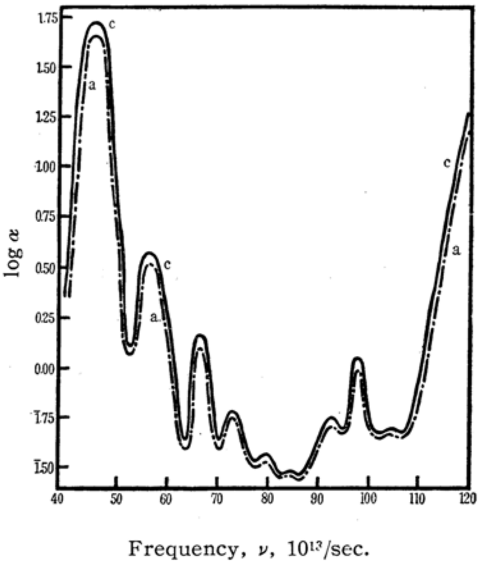


Fig. 3. Absorption spectra of Cs_3CoCl_5.

TABLE II

ABSORPTION MAXIMA OF THE CRYSTAL OF Cs_3CoCl_5

ν,10^{13}/sec.	45.0	56.8	66.6	73.2	80.0	84.3	92.8	98.0
logα_a	1.65	0.51	0.10	$\bar{1}$.75	$\bar{1}$.53	$\bar{1}$.43	$\bar{1}$.69	$\bar{1}$.57

---

[9] R. Tsuchida, This Bulletin, **13**, 436 (1938). Such a kind of band was named "third absorption band". See also, F. Basolo, *J. Am. Chem. Soc.*, **70**, 2634 (1948); ibid., **72**, 4393 (1950).

[10] L. I. Katzin and E. Gebert, *J. Am. Chem. Soc.*, **75**, 2830 (1953).

[11] A. v. Kiss and M. Gerendas, *Z. physik. Chem.*, **A180**, 117 (1938).

cobaltoates, both containing $CoCl_4^{--}$ ions. Their results, however, were only qualitative and limited within the visible region, although the absorption maxima reported by them generally coincide with the results of our present measurement. A. v. Kiss et al.[11] also reported absorption spectra of aqueous solution containing cobaltous chloride and great excess of chloride ions in the visible and ultra-violet. They recorded a number of sharp peaks. Most of the absorption peaks which have been found in the present measurement almost correspond with those reported by them. There were reported, however, other peaks in their work which have not been observed in our measurements.

Inspection of absorption spectra of the crystal leads us to the idea that the absorption bands of the complex anion between $\nu=45$ and 85×10^{13}/sec. may form one series. As reported in our recent communication,[12] wave numbers of the absorption peaks in the above series can be expressed by the following equation,

$$\nu=\nu_0+am-bm(m+1), \qquad (1)$$

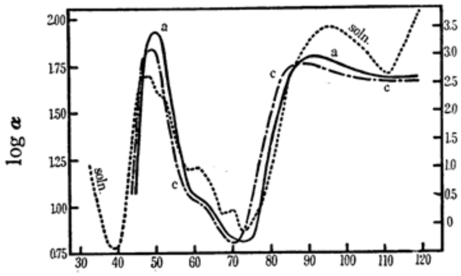
where $\tilde{\nu}$ represents the wave-number of a peak, $\tilde{\nu}_0$ the wave-number of the band head, a and b constants, and m positive integer including zero (Table III). The following values have been obtained for a and b: $a=4.37\times10^3$/cm. and $b=2.92\times10^2$/cm. The expression of the form (1) may be derived readily in the approximation, using a familiar expression for an anharmonic oscillator[13] and assuming (a) that the absorption peaks correspond to transitions from the ground electronic state with vibrational quantum number zero to the excited electronic state with m as the vibrational quantum number, and (b) that the vibrational frequency is altered very little in the electronic transitions. Judging from the order of the vibrational frequency and considering that the measurement was made at room temperature, the former assumption may be permissible. The intensity relation of the absorption series may be understood qualitatively on the basis of the above assumed mechanism of the transition.[14] Using the above derived constants and assuming the above mechanism of the transition, the dissociation energy of the complex ion is estimated,[15] in the rough approximation, as 40.2 kcal. per mol. The value thus obtained seems reasonable,[16] favouring the above assumption. The fact that the band peaks can be correlated with electronic-vibrational transitions supports the view that the series of band peaks is due principally to transitions of the coordination electrons of the complex anion.[17,18] A similar fine structure had been reported by Shibata et al.[19] with solution of several metallic compounds at the temperature of liquid air, and an equation had been given to represent wave-numbers of absorption peaks in the fine structure.

TABLE III

A SERIES OF ABSORPTION PEAKS OF Cs_3CoCl_5 IN THE CRYSTALLINE STATE

m in eq.(1)	0	1	2	3	4	5
$(\tilde{\nu})$obs	15.0	18.9	22.2	24.4	26.7	28.0
$(\tilde{\nu})$cal	15.0	18.8	22.0	24.6	26.6	28.1

Potassium Tetrathiocyanato-cobaltoate Tetrahydrate.—The compound in the crystalline state shows bands at $\nu=50$ and about 100×10^{13}/sec. and one more band in the infra-red; no measurement of the latter band was made in the present work. From comparison of the absorption curves (Fig. 4. and



Frequency, ν, 10^{13}/sec.

Fig. 4.

Absorption spectra of $K_2Co(NCS)_4\cdot4H_2O$.

TABLE IV

ABSORPTION MAXIMA OF $K_2Co(NCs)_4\cdot4H_2O$

	ν,10^{13}/sec.	logα	M	ν,10^{13}/sec.	logα	M
a–abs.	49.8	1.98	2.18×10^5	91	1.79	1.46×10^5
c–abs.	49.2	1.84	1.58×10^5	88	1.76	1.36×10^5

---

[12] S. Yamada and R. Tsuchida, *J. Chem. Phys.*, **22**, 1273 (1954).

[13] See, for example, G. Herzberg, "Spectra of Diatomic Molecules," Van Nostrand Company, New York, 1950, p. 151, etc.

[14] For example, Ref. 13), p. 193, etc.

[15] See, for example, K. S. Pitzer, "Quantum Chemistry," Prentice-Hall, New York, 1953, p. 255. The equation for diatomic molecules is tentatively assumed in the present estimation.

[16] From spectroscopic study, Shibata et al. (Ref. 19) reported 48 kcal. for the dissociation energy of ($CoCl_2\cdot$ acetone).

[17] R. Tsuchida, This Bulletin, **13**, 388 (1938).

[18] A similar conclusion was formerly drawn by v. Kiss et al, (Ref. 11).

[19] Y. Shibata and K. Harai, *J. Chem. Soc. Japan*, **56**, 1 (1935).

Table IV) with that of tricesium cobaltous pentachloride, it is considered that the absorption band at $\nu=50\times10^{13}$/sec. corresponds to the band at $\nu=45\times10^{13}$/sec. in Cs_3CoCl_5, being due mainly to co-ordination electrons, and that the band stretching from $\nu=$about 80×10^{13}/sec. further into the ultra-violet may correspond to "specific band,"[20] which is principally due to the NCS^- ions in co-ordination. The absorption spectrum of cobaltous thiocyanate in aqueous solution containing excess of potassium thiocyanate was reported by Kiss et al.[21] Their data roughly coincide with our result, but differ in detail, probably because their measurements were made with the mixed solution, involving much more complicated factors as compared with ours. It is seen that the crystal of the compound shows the corresponding band peaks in the shorter wave-length than does the solution.

According to the result of the crystal analysis,[22] the crystal consists of potassium ions, $Co(NCS)_4^{--}$ anions and molecules of crystallization water, $Co(NCS)_4^{--}$ ions being determined as tetrahedral. The crystal has been found to exhibit a marked dichroism. That is, as to the band at $\nu=50\times10^{13}$/sec. a-absorption is hyperchromic and hypsochromic to c-absorption, and with the specific band a-absorption is hypsochromic to c-absorption. In consequence, it is readily concluded that the configuration of the anion, $Co(NCS)_4^{--}$, in this crystal deviates considerably from regular-tetrahedron. It is most likely that the complex anion should possess a configuration of distorted-tetrahedron. From analogy to dicesium tetrachlorocuproate, it is supposed that the a-absorption of this crystal corresponds to the X-absorption and that the c-absorption corresponds to the Z-absorption of the $Co(NCS)_4^{--}$ ion.

It is to be noted that there can be found a series of sharp bands with this compound in alcoholic solution as in the crystal of tricesium cobaltous pentachloride. Some of the peaks in the shorter wave-length may be covered under the specific band, since the specific band comes very close to the band series. Though peaks which appear separated from the specific band seem to be rather small in number, wave-numbers at the series of peaks can be represented by the equation of the form (1). The following values have been obtained for a and b; $a=4.8\times10^3$/cm. and $b=4\times10^2$/cm., dissociation energy of the complex being estimated, in the same way as in tricesium cobaltous pentachloride, approximately as 34 kcal.

General Considerations.—It seems of significance that those series of sharp peaks in the above two compounds can be expressed by the equation of a similar form and may reasonably be correlated with electronic-vibrational transitions directly related to the co-ordination linkages in the quadri-co-ordinated complex ions. There have been reported very few metallic complexes which show at room temperature a corresponding electronic absorption band consisting of a series of sharp peaks. One such example, besides the above two compounds, may be found with potassium permanganate in aqueous solution.[23]

The appearance at room temperature of a fine structure in an electronic absorption band of such a kind is probably due to many factors. But the following may be cited as one of the principal factors.[24] Since to a first approximation the only vibrations for which Δv, v being the vibrational quantum number, differs from zero in polyatomic electronic spectra are the totally symmetrical vibrations, the electronic absorption spectra of those complex ions, which have a very small number of totally symmetrical vibrations, will show a simplified vibrational structure. Thus $CoCl_4^{--}$ in the crystal of $CsCoCl_5$ and $M_nO_4^-$ in aqueous solution of potassium permanganate, both being regular-tetrahedral, have only one totally symmetrical vibration and, moreover, contain only simple ions as ligands. Therefore, their electronic absorption might be expected to be more simple than in other complexes of more complicated structure. As for $K_2Co(NCS)_4\cdot4H_2O$, $Co(NCS)_4^{--}$ in this crystal has been presumed, from dichroism measurement, to have flattened tetrahedral configuration. This, however, might be ascribed, at least partly, to the effect of the crystalline field upon the complex ion, and the complex ion in alcoholic solution might be assumed to be nearly regular-tetrahedral. In agreement with the assumption seems to be the fact that the crystal of this compound has been found to be slightly hypsochromic to the solution, and that the splitting of the absorption band is less marked in the crystalline state.

Another point which deserves attention

---

[20] R. Tsuchida, This Bulletin, **13**, 471 (1938).

[21] A. v. Kiss and P. Csokan, *Z. physik. Chem.*, A**186**, 239 (1940).

[22] G. S. Zhdanov and Z. V. Zvonkova, *Zhur. Fiz. Khim.*, **24**, 1339 (1950); *C. A.*, **45**, 6001e (1951).

[23] B. Lange and C. Schusterius, *Z. physik. Chem.*, A**159**, 295 (1932).

[24] For example, see G. R. Harrison, R. C. Lord and J. R. Loofbourow, "Practical Spectroscopy," Prentice-Hall, New York, 1948, p. 291.

may be the fact that the above three complex compounds all involve relatively weak linkages. The weakness of the linkage seems to have some relation to the appearance of the electronic band with a fine structure.

It is of significance that there have been found complex-ions with distorted-tetrahedral configurations, intermediate between planar and regular-tetrahedral ones, in contrast to the generally accepted fact that as to magnetic properties there may usually be drawn a sharp line between tetrahedral and planar hybridization. Quadri-co-ordinated cupric and cobaltous complexes are expected to be square when ordinary hybridization of bond orbitals is assumed.25) In fact this is found not to be the case. One of the reasons for the above fact may be that the linkages between the metal atom and the ligands are too weak to enter into planar hybridization of an ordinary type.26)

The configuration of complex molecules would naturally be closely related to the hydbridization of bond orbitals in the molecule. The existence of these distorted-tetrahedral complexes, therefore, points to the possibility that the hybridization of bond orbitals, intermediate between tetrahedral and planar ones, may occur with the $CuCl_4^{--}$ and $Co(NCS)_4^{-}$ ions in these crystals. It is noteworthy that the same central metallic ion has been found to form complexes of different configurations with ligands of varying natures on the one hand, and that with the same ligands different metallic atoms as a centre form complexes of different configurations on the other. Thus it is readily recognized27) that the natures of both metal atoms and ligands are in close relation to the state of hybridization, the stability of the bonds, and the configurations of the complex ions.

Summary

Absorption spectra of crystals of dicesium tetrachlorocuproate, tricesium cobaltous pentachloride and potassium tetrathiocyanatocobaltoate tetrahydrate have been quantitatively determined in the visible and ultraviolet region by the microscopic method with polarized light.

In accordance with the flattened-tetrahedral configuration of tetrachlorocuproate anion, the crystal of $C_{s2}CuCl_4$ exhibits anisotropy of light absorption.

It has been found that crystals of Cs_3CoCl_5 are almost isotropic, supporting the regular-tetrahedral configuration of the $CoCl_4^{--}$ ion in this crystal.

It has also been found that $K_2Co(NCS)_4 \cdot 4H_2O$ in the crystalline state shows a marked dichroism. It is concluded from this observation that $Co(NCS)_4^{--}$ ions in this crystal are distorted-tetrahedral, just like the $CuCl_4^{--}$ ions in the crystal of $C_{s2}CuCl_4$.

It has been found that Cs_3CoCl_5 in the crystalline state and $K_2Co(NCS)_4 \cdot 4H_2O$ in alcoholic solution show their second absorption band with a series of sharp peaks, which have been shown to be correlated with electronic-vibrational transitions. This fact is in harmony with the idea on the origins of the absorption bands of metallic co-ordination compounds proposed by one of the authors.

The authors wish to thank the Ministry of Education for a grant.

Department of Chemistry, Faculty of
Science, Osaka University,
Nakanoshima, Osaka

---

25) R. Tsuchida, *J. Chem. Soc. Japan*, **60**, 245 (1939); R. Tsuchida, M. Kobayashi and H. Kuroya, *Rev. Phys. Chem. Japan*, **13**, 151 (1939); N. V. Sidgwick and H. M. Powell, *Proc. Roy. Soc. London*, A**176**, 153 (1940); L. Pauling, "The Nature of the Chemical Bond", Cornell Univ. Press, Ithaca, New York, 1940.

26) Since the configurations of the above complex ions were determined in the crystalline state, we could not remove another possibility that those complex ions would be non-planar only in the crystalline state where electrostatic forces of surrounding ions on the complex ions might be so strong and the linkages in the complexes so weak that the planar configuration would not be held.

27) N. V. Sidgwick, *J. Chem. Soc.*, **1941**, 433; D. P. Mellor and D. P. Craig, *J. Proc. Roy. Soc. N. S.* Wales, **74**, 474 and 495 (1940); D. P. Mellor, *Chem. Revs.*, **33**, 137 (1943); L. G. Van Uitert and W. C. Fernelius, *J. Am. Chem Soc.*, **76**, 379 (1954).