Spectrochemical Study of Microscopic Crystals. IX.[1] *Absorption Spectra and Structure of Cobalt(II) Mercury(II) Tetrathiocyanate*

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The structure of cobalt(II) mercury(II) tetrathiocyanate has long been discussed by a number of chemists[2,4]. In 1947 Jeffery[3] investigated the crystal structure with X-ray, showing that the sulphur atoms of the SCN-groups were attached to the mercury atom in tetrahedral co-ordination. However, he did not touch on the possibility of the linkage between the cobalt atom and NCS-groups, only stating that a cobalt atom is surrounded by nitrogen atoms. The present work was undertaken in order to clarify the structure of the compound in the crystalline state. In this paper polarized absorption spectra of the compound have been determined, and the results discussed in relation to the structure of the compound.

Experimental

Materials.—Cobalt(II) mercury(II) tetrathiocyanate, $CoHg(SCN)_4$, was prepared by the method of Hantzsch and Shibata[4]. Indigo-blue, prismatic crystals thus obtained belong to the tetragonal system and show straight extinction on the prism face. A slight dichroism is observed on the prism face under the microscope. The measurements of the absorption spectra were made on the prism face with polarized light having its electric vector along and perpendicular to the needle axis.

Potassium tetrathiocyanato-mercurate(II) was prepared from mercuric thiocyanate and potassium thiocyanate according to the method of Rosenheim and Cohn[5]. Measurement of absorption spectrum was made with its aqueous solution containing an excess of potassium thiocyanate.

Measurements.—Quantitative measurements of absorption spectra of crystals were made by Tsuchida-Kobayashi's microscopic method[6] with polarized light in the region covering 7500 to 2400 Å. The notation, α, represents absorption coefficient per mm. 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 molar extinction coefficient.

Results and Discussion

The results of the measurements are shown in Fig. 1 and Table I. The a- and b-absorption represent absorption with the electric

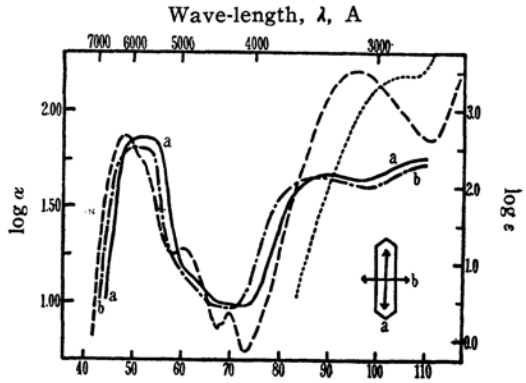

Fig. 1. Absorption spectra of $CoHg(SCN)_4$ in the crystalline state and its component complexes in solution. ———, $K_2[Co(NCS)_4]$, ·····, $K_2[Hg(SCN)_4]$. The curves in solution are taken from ref. 7.

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3) J.W. Jeffery, *Nature*, 159, 610 (1947).
4) A. Hantzsch and Y. Shibata, *Z. anorg. Chem.*, 73, 314 (1912).
5) A. Rosenheim and R. Cohn, ibid., 27, 281 (1901).
6) R. Tsuchida and M. Kobayashi, "The Colours and the Structures of Metallic Compounds," Zoshindo, Osaka, 1944, p. 180; This Bulletin, 13, 619 (1938).

vector parallel and perpendicular to the needle axis. The present measurement indicates that the crystal of the compound shows an absorption band at about 51×10^{13}/sec. and another band commencing at about 80×10^{13}/sec. Although the crystal analysis demonstrated the existence of the group, $Hg(SCN)_4$, the band at about 50×10^{13}/sec. can not be ascribed to the group, since the potassium salt, $K_2Hg(SCN)_4$, in aqueous solution shows absorption at far shorter wave-length. Alternatively, the band is considered to correspond to the band at the longer wave-length of the $Co(NCS)_4$-ion in the crystal of $K_2Co(NCS)_4\cdot4H_2O$ as well as alcoholic solution. It is concluded, therefore, that $CoHg(SCN)_4$ in the crystalline state should contain the group, $Co(NCS)_4$, as in the crystal of $K_2Co(NCS)_4\cdot4H_2O$[7,8]. In other words, four NCS-groups are attached to a cobalt atom through their nitrogen atoms. The linkage between the nitrogen atom and the cobalt atom is most likely to be largely electrostatic, judging from the tetrahedral configuration of the $Co(NCS)_4$-group[7].

The band at 50×10^{13}/sec. is found to be a little polarized. This fact shows that the co-ordination of four NCS-groups around a cobalt atom in the $Co(NCS)_4$-group deviates from regular tetrahedron. The similar conclusion was formerly obtained with the crystal of $K_2Co(NCS)_4\cdot4H_2O$[7]. Moreover, the dichroism for the band at 50×10^{13}/sec. of $CoHg(SCN)_4$ (Table I) is found to be similar

Table I

Absorption maxima of $CoHg(SCN)_4$

	ν, 10^{13}/sec.	$\log\alpha$	K	half width
a-abs.	51.6	1.86	117×10^2	10.2
b-abs.	50.6	1.80	102×10^2	10.5

to the dichroism of the potassium salt. That is, the absorption with its maximum at the shorter wave-length has larger absorption coefficient than the absorption with its maximum at the longer wave-length. This also seems to support the above conclusion.

The absorption of $CoHg(SCN)_4$ at about 80×10^{13}/sec. and shorter wave-length may be considered as superposition of the absorption of $Hg(SCN)_4$- and $Co(NCS)_4$-groups, since both the $Hg(SCN)_4$ and $Co(NCS)_4$ ions in the potassium salts exhibit absorptions in the above regions.

Summarizing the above consideration, a NCS-group of $CoHg(SCN)_4$ in the crystalline state combines through its sulphur atom with a mercury atom and through its nitrogen with a cobalt atom. The effect of combination of the sulphur atom with a mercury atom on the Co-NCS linkage may be observed, for example, in the absorption bands due to the $Co(NCS)_4$-group. The absorption spectra of the crystal of $CoHg(SCN)_4$ is different from that for $K_2Co(NCS)_4\cdot4H_2O$ in the following respects. (1) The width of the band at the longer wave-length is larger than that of the crystal of the potassium salt. (2) The band is slightly more hypsochromic than that in the potassium salt. These differences may be understood as due to the change in the electronic state of the nitrogen atom and consequently in its linkage to the cobalt atom, which would be caused by co-ordination of the sulphur atom to a mercury atom.

Summary

Polarized absorption spectra of $CoHg(SCN)_4$ in the crystalline state have been determined by Tsuchida-Kobayashi's microscopic method in the regions between 2400 and 7000 Å.

Absorption spectra of $HgCo(NCS)_4$ shows the existence of the $Co(NCS)_4$-group. Thus it has been concluded that the NCS-group is attached to a cobalt atom through a nitrogen atom, and to a mercury atom through a sulphur atom on the other end of the NCS-group.

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