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Certain Interactions between Transition Metal Ions and the NCS Group in Chromium(III) Isothiocyanato Complexes. I. Reinecke's Salt Type Complexes Involving Cobalt(II) and Copper(II) Ions[*1]

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Cobalt(II) tetraisothiocyanatochromate(III), $Co[Cr(NCS)_4(NH_3)_2]_2$, was prepared from cobalt(II) chloride and Reinecke's salt in an aqueous solution. The absorption spectrum gave evidence that the so-called "cobalt-salt" dissociated into cobalt(II) cation and Reineck's anion in aqueous solution. The reflection spectrum showed a remarkably strong absorption band at $14.08 \times 10^{13}\,sec^{-1}$, which might be assigned to bonding between cobalt(II) and sulfur in an NCS^- ligand. The three absorption peaks observed at 2158, 2095 and 2065 cm^{-1} in the IR spectrum due to C–N stretching vibrations also emphasized the strong interaction between cobalt and sulfur. The effective magnetic moment estimated was 4.58 B. M. at 18.3°C. The corresponding copper(II) salt, $Cu(OH)[Cr(NCS)_4(NH_3)_2]$, was obtained from an aqueous solution of copper(II) sulfate and Reinecke's salt as a yellow powder. It was a sparingly soluble in water. In the reflection spectrum, the red-shifted band covered much of the first band region of Reinecke's salt and in the IR spectrum, the C–N band had only a small splitting. The magnetic moment was found to be 3.84 B. M. at 16.0°C, which is close to the predicted value in the complex when copper is reduced, becoming univalent. X-Ray diffraction analysis also showed a relatively stronger contraction of the unit cell in the copper salt than in the cobalt salt. On the basis of the above points, it was proposed that in the copper salt there is considerable π-bonding between copper and the two adjacent isothiocyanate groups.

It has already been reported1) that the so-called "cobalt(II) salt" prepared from cobalt(II) chloride and Reinecke's salt exhibited a gradual color change from reddish-purple to grayish-green when it was exposed to dry air, and the color changed back to the original purple upon absorption of water, while the corresponding "copper(II) salt" gave a yellow color quite different from Reinecke's salt, when it was prepared from copper(II) sulfate and Reinecke's salt. However, no further attempts to obtain information on the structures of these salts has been made.1)

The green color in the cobalt(II) salt in the dry, solid state and the yellow color in the copper(II) salt suggest the presence of a certain interaction between cobalt or copper ion and Reinecke's anion. Our interest lies particularly in investigating such color changes in the cobalt and copper salts in relation to a structural discussion based on the spectra, magnetic behavior and measurements of chemical properties.

Experimental

Preparation of Compounds. *Cobalt(II) Tetraisothiocyanatochromate(III)* (called "Co-salt"). To a solution of Reinecke's salt (8 g/800 ml of H_2O) at 60°C, a solution of cobalt(II) chloride hexahydrate (225 g/ 700 ml of H_2O) at 5°C was added. Being kept in a refrigerator over night, reddish-purple scale-like crystals precipitated out. After filtration, the crystals were washed with a small amount of ether, and when dried over sulfuric acid *in vacuo*, their color changed to grayish-green.

Found: Cr, 14.39; Co, 8.47; N, 23.64%. Calcd for $Co[Cr(NCS)_4(NH_3)_2]_2$, Cr, 14.94; Co, 8.47; N, 24.16%.

In reverse, the color changed back to the original upon washing with water.

Copper(III) Tetraisothiocyanatochromate(III). (called "Cu-salt"). To a solution of Reinecke's salt at 60°C, a solution of copper(II) sulfate pentahydrate was added in a stoichiometric ratio (1 : 1). As soon as both solutions were mixed together, a yellow powder was obtained. The color does not change in a dry or moist atmosphere. The crystal was insoluble in water, alcohol, ether, dioxane and several organic solvents.

When the solids of Reinecke's salt and copper(II) sulfate hydrate were mixed in a motar, the same salt was also obtained.

Found: Cr, 13.05; Cu, 15.84; N, 21.57; C, 12.27; H, 1.70%. Calcd for $Cu(OH)[Cr(NCS)_4(NH_3)]_2$: Cr, 13.03; Cu, 15.94; N, 21.07; C, 12.29; H, 1.75%.

Apparatus for Measurement. Molar conductivity, electronic and reflection spectra, IR and far-infrared absorption spectra, magnetic suceptibility and

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[*1] Presented at the 15th and 16th Symposiums on Coordination Compounds of the Chemical Society of Japan; Kanazawa, Oct., 1965 and Tokyo, Dec., 1966.

1) O. Christensen, *J. pr. Chem.*, **45**, 371 (1892).

X-ray diffraction were measured with a Yokogawa Universal Bridge BV-Z-13A, a Hitachi EPU-2A spectrophotometer with a standard reflection attachement, a Nippon Bunko IR Spectrometer DS-301 and a Hitachi ERI-101 Grating IR Spectrometer, a Gouy balance and a Rigaku-denki Geigerflex X-ray Analyser, respectively.

Results and Discussion

Conductivity and pH Measurements. The value of the molar conductivity of the "Co-salt" was 196.4 cm²ohm^{-1}(1×10^{-2} mol/*l*) at 25°C and that of Reinecke's salt 103.1 cm²ohm^{-1} (2×10^{-2} mol/*l*). This suggests that the Co-salt is a 1 : 2 valency type salt, being capable of dissociating into a cobalt cation and Reinecke's anion in aqueous solution according to the following equation,

$$\mathrm{Co[Cr(NCS)_4(NH_3)_2]_2} \rightarrow \mathrm{Co^{2+}} + 2\mathrm{[Cr(NCS)_4(NH_3)_2]^-}.$$

For the corresponding Cu-salt, the conductivity could not be measured because of its insolubility in water. Christensen[1] reported that copper was univalent in the salt, but in the present work, it was concluded that the Cu-salt involves a hydroxyl group, as indicated by the chemical formula $\mathrm{Cu(OH)[Cr(NCS)_4(NH_3)_2]}$.

In order to ascertain the composition of the Cu-salt, the following experiments were carried out.

Solutions of different concentrations of Reinecke's salt were added to solutions containing a constant number of moles of copper(II) sulfate pentahydrate. The precipitation formed was filtered off and the absorbancy of the filtrates measured at peaks of both the first and second absorption bands in Reinecke's salt. The results are shown in Fig. 1. It suggests that the Cu-salt obtained above has a simple mole ratio 1 : 1 as confirmed by the elementary analysis.

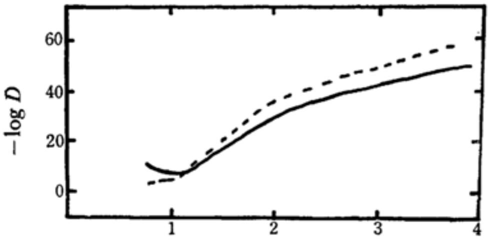

Fig. 1. The absorbancy of the filtrates after the Cu-salt formation.
---- at 520 m (the first band of Reinecke's salt)
—— at 392 m (the second band of Reinecke's salt)

The pH values of Reinecke's salt and copper(II) sulfate hydrate were found to be 4.84 and 4.50, respectively, in their aqueous solutions, whereas that of the filtrate was found to be in the range 2.70 to 2.50. In addition, it was found that the tendency to form the Cu-salt was extremely decreased in strongly acidic solutions. These results also indicate the existence of a hydroxo group in the Cu-salt.

Visible and UV Spectra. The visible and ultraviolet absorption spectra of the Co-salt measured are shown in Fig. 2, together with those of Reinecke's salt; numerical values are 57.69 ($\log\varepsilon=2.03$), 76.53 ($\log\varepsilon=2.00$) and 99.67×10^{13} sec^{-1} ($\log\varepsilon=4.12$) for the Co-salt, and 57.69 ($\log\varepsilon=2.01$), 76.53 ($\log\varepsilon=1.96$) and 99.67×10^{13} sec^{-1} ($\log\varepsilon=4.14$) for Reinecke's salt, respectively.

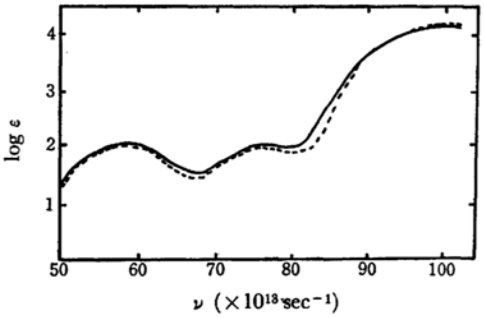

Fig. 2. The absorption spectra of the Co-salt (——) and Reinecke's salt (----).

It is obvious in Fig. 2 that the absorption spectrum of the Co-salt is in approximate agreement with that of Reinecke's salt within the range of wavelength measured. This may support the assumption concerning the dissociation of the Co-salt as a 1 : 2 valency type, since the contribution of the spectrum of cobalt(II) cation in aqueous solution to that of the Co-salt is very small in the corresponding wavelength region.

Reflection Spectra. Reflection spectra of the Co- and Cu-salts were measured for powdered crystals, the latter being especially meaningful due to its lesser solubility in water. The results are shown in Figs. 3 and 4 for the Co- and Cu-salts, respectively, in which the logarithm of $f(R_d)$ coordinate is equal to $(1-R_d)^2/2R_d$ in the Kubelka-Munk equation, where R_d is the relative diffuse-reflection index.

The reflection spectrum of the grayish-green Co-salt showed two bands: the one appearing at 42.55×10^{13} sec^{-1} ($\log f(R_d)=0.67$) may probably be assigned to charge transfer from sulfur to cobalt, which could not be found in Reinecke's salt, and the other, at 60.00×10^{13} sec^{-1} ($\log f(R_d)=0.068$), may correspond to the first absorption band of Reinecke's salt. On the other hand, the band corresponding to the second band of Reinecke's salt could not be observed in the Co-salt.

In the Cu-salt, the first absorption band corresponding to that of Reinecke's salt is only observed as a shoulder, but the second band could not be observed due to the great shift of the charge transfer

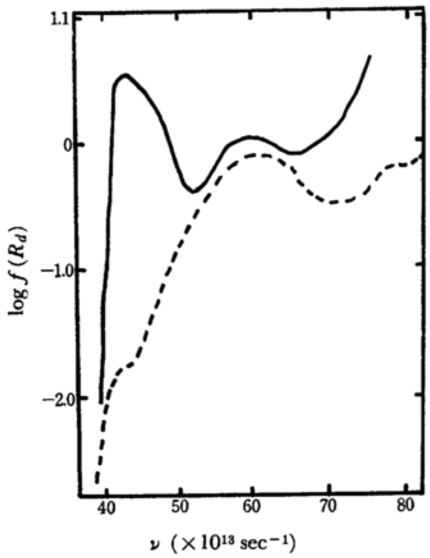

Fig. 3. The reflection spectra of the Co-salt (——) and Reineck's salt (----).

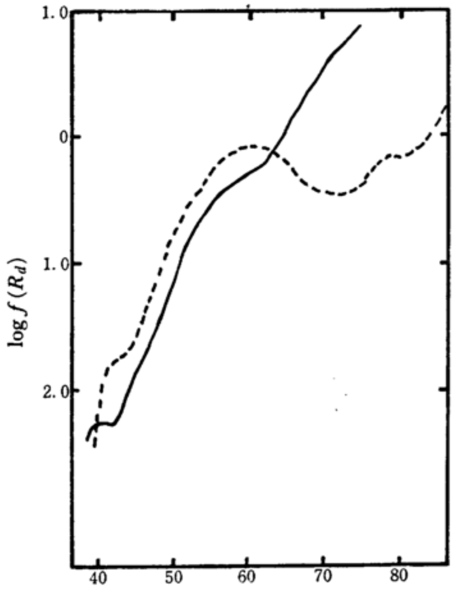

Fig. 4. The reflection spectra of the Cu-salt (——) and Reinecke's salt (----).

band to the visible region. Such a great shift suggests a strong interaction between the copper ion and Reinecke's anion.

IR Spectra. The bond between metal ions and isothiocyanate groups has been known and is classified according to the following three types:

1) a bond through the nitrogen atom in NCS, like M–NCS

2) a bond through the sulfur atom in NCS, like M–SCN

3) a bond through an NCS group bridge with an another metal, like M–NCS–M′, where M and M′ are two different metals.

Jones[2] has reported on the three normal vibrational modes of thiocyanate ion in KNCS. Mitchell and Williams[3] proposed that the stretching frequencies of C–N bonding in isothiocyanato type complexes increase in the order $NCS^- <$ M–NCS $\leqslant$ M–SCN $<$ M–NCS–M′, and that, especially, the frequencies in the bridged M–NCS–M′ become higher as the electronegativity of M′ becomes smaller.

Lewis, Nyholm and Smith,[4] on the other hand, noted that the C–S stretching frequency peak of 2) appears in a region lower than that of 1). It may be expected from such information that the peak due to C–S stretching in 3) will appear between the peaks in the above two cases.

The IR spectra of the Co- and Cu-salts with respect to C–N and C–S stretching vibrations are shown in Figs. 5 and 6, respectively, together with that of Reinecke's salt. Numerical data are summarized in Table 1, where data on a few Reinecke type salts by Fujita *et al.*[5] are cited for comparison with values obtained in the present work.

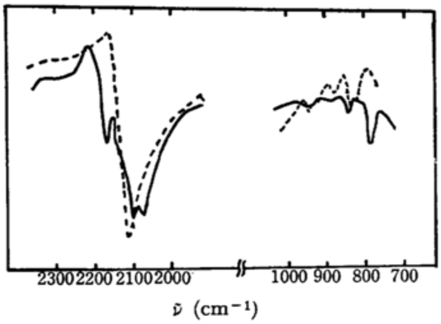

Fig. 5. IR spectra of the Co-salt (——) and Reineck's salt (----).

The presence of peaks at 2158 cm^{-1} and 795 cm^{-1}, assigned to the C–N and C–S stretching vibrations, respectively, in the Co-salt, as shown in Table 1, suggest a relatively strong bond between cobalt(II) ion and the sulfur atom in the NCS^- group, forming a bridged structure such as Cr–NCS–Co, analogous to a Reinecke type Hg-salt, owing to the complete similarity of the IR spectra of these two salts.

On the other hand, in the Cu-salt, the peak assigned to the C–N stretching vibration did not

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2) L. H. Jones, *J. Chem. Phys.*, **25**, 1069 (1956).

3) P. C. H. Mitchell and R. J. P. Williams, *J. Chem. Soc.*, **1960**, 1912.

4) J. Lewis, R. S. Nyholm and P. W. Smith, *ibid.*, **1961**, 4590.

5) J. Fujita, K. Nakamoto and M. Kobayashi, *J. Am. Chem. Soc.*, **83**, 4157 (1961)

TABLE 1. THE INFRARED ABSORPTION PEAKS OF THE REINECKE'S TYPE SALTS

	ν_{C-N}			ν_{C-S}		δ_{NCS}			
Reinecke's salt	2120	2080							by Fujita *et al.*[5]
Cholin-salt	2180								
Ba-salt	2000	2130							
Hg-salt	2160	2098	2073						
Reinecke's salt	2119			840	860	467			by authors
Co-salt	2158	2095	2065	795	855	471	464	444	
Cu-salt	2110	2095	2075	810	825	475	460		
Hg-salt	2160	2095	2065	798	845				

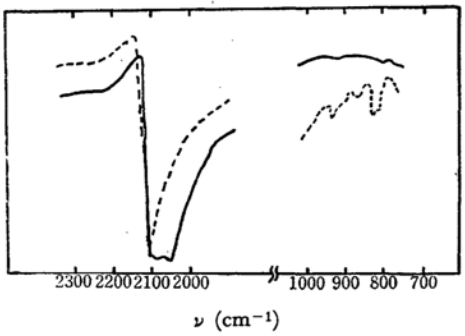

Fig. 6. IR spectra of the Cu-salt (——) and Reinecke's salt (----).

shift from the corresponding one in Reinecke's salt. Therefore, the bridged structure concluded for the Co-salt, M–NCS–M′, must be excluded for the Cu-salt.

However, since the band in the C–N stretching region is found to split into three peaks and the C–S band shifts to a lower wave number region than that of Reinecke's salt, but not so low as that of the Co-salt, another kind of the interaction should be considered between the copper(II) ion and Reinecke's anion.

Thus, a structure in which the copper is weakly coordinated to Reinecke's anion through two sulfur atoms in both adjacent NCS^- groups square planar around the copper atom can be assumed. But such a structure may also be unacceptable, since X-ray analysis data[6] give about 7 Å for the S–S distance between the two sulfur atoms in the adjacent NCS^- groups.

Taking into account also the reflection spectra of the Cu-salt, a structure may be conclusively proposed in which the copper(II) ion is not bound to sulfur atoms, but to the NCS^- groups as a whole, concluding considerable π-bonding character due to the transfer of the π-electron spread over the NCS^- group to the copper ion. Although such a structure, allowing π-bonding with respect to the NCS^- groups, is unknown to date, it may be most reasonable, and is also supported by the far-infrared absorption spectra described below.

Far-IR Absorption Spectra. The far-infrared absorption spectrum of the Co-salt is shown in Fig. 7, togehter with that of Reinecke's salt. The absorption band at 500 cm⁻¹ in Reinecke's salt may be assigned to the Cr–N stretching vibrations on the ammonia, since it did not shift even when ammonium ion was replaced by cobalt ion, and it is coincident with the corresponding band in the ammine complexes.

The band at 467 cm⁻¹ in Reinecke's salt may be assigned to the NCS bending vibration since it is in good agreement with the corresponding band which has been reported by Sabatini *et al.*[7] concerning metal cyanato, thiocyanato and selenocyanato complexes. In the Co-salt, the corresponding band splits into three peaks, which may be due to the NCS bending vibration free from the counter cation and due to some interactions with the counter cation through the bridged Cr–NCS–Co bond.

The band at 347 cm⁻¹ is probably due to the Cr–N stretching vibration in thiocyanate as suggested in the literature.[4,7] The bands observed in the wave number region, 270—245 cm⁻¹, may be assigned to Co–S stretching, but there is no further verification for it.

The far-infrared absorption spectra of the Cu-salt and of Reinecke's salt are shown in Fig. 8. The band near 490 cm⁻¹ is assigned to Cr–N stretching involving NH_3. It has a weak shoulder at 505 cm⁻¹, which was not detected in any other

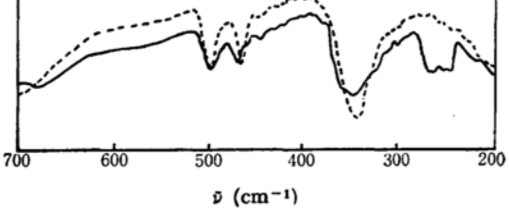

Fig. 7. The far infrared spectra of the Co-salt (——) and Reinecke's salt (----).

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6) Y. Takeuchi and Y. Saito, This Bulletin, **30**, 319 (1957).

7) A. Sabatini and I. Bertini, *Inorg. Chem.*, **4**, 959 (1965).

TABLE 2. THE ANALYSES OF THE X-RAY DIFFRACTION AND DENSITY OF THE REINECKE'S TYPE SALTS

	c/a	a (Å)	c (Å)	Density, ρ Calcd	Density, ρ Found	Z	Ref.
Reinecke's salt	1	13.25		1.50		6	6
Co-salt	1.1	10.30	11.34	1.96	1.87	8	
Cu-salt	0.89	9.03	8.07	2.01	1.96	2	

salts treated in the present work. However, it is not clear whether the shoulder is due to the distorted structure of Reinecke's anion in the crystal or not.

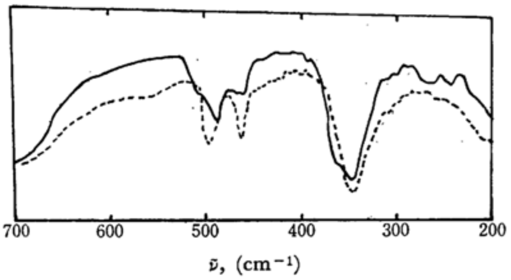

Fig. 8. The far infrared spectra of the Cu-salt (——) and Reinecke's salt (----).

The band assigned to the NCS bending vibration splits into two bands, but does not show the presence of a direct bond between the copper ion and a sulfur atom.

If the copper was bound to an NCS group through a sulfur atom, the absorption band assigned to the Cr–N stretching vibrations involving the NCS group should shift to a lower wave number range as is the case with the Co-salt. However, the corresponding bands were all shifted to a higher wave number region. From the various information described above, it may be reasonable to introduce the concept that the π-electron bond between an isothiocyanate group and copper ion plays an important role in the interaction between copper and Reinecke's anion in the Cu-salt.

Magnetic Susceptibility. From the magnetic susceptibility measurements, a value of 4.50 B. M. was obtained for the Co-salt as the effective magnetic moment. If the divalent cobalt ion is in a high spin state, the number of unpaired electrons contained may be amount to 4.5 (therein 3 for Cr and 1.5 for Co) per molecule of the salt, and then, the spin-only value should be 5.41 B. M. The value obtained in the present work seems to be remarkably small compared with that in the high spin state of cobalt. This supports in addition to the results from absorption and IR spectra, some kind of "superexchange interaction" between Co and Cr ions through an NCS$^-$ group.

The magnetic moment of the Cu-salt is expected to be 4.9 B. M. by evaluating the total number of spins contained. But the value obtained is 3.84 B. M. at 16°C, which is smaller. It may also alow that the copper is bound to Reinecke's anion through the π-electron in the NCS$^-$ groups as explained above on the basis of the IR spectra.

X-Ray Diffraction Measurement. The results of analysis of the X-ray diffraction patterns for the Co- and Cu-salts are summarized in Table 2, together with those for Reinecke's salt already published by Y. Saito *et al.*⁶⁾ The structures of these salts are indicated to be tetragonal, except for Reinecke's salt which has a cubic structure. The density of the Co-salt was measured in Nujol, whereas that of the Cu-salt, in water. The result that the Cu-salt has the largest density of these three salts suggest that there is the strongest contraction of the unit cell in the Cu-salt.

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