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Certain Interactions between Transition Metal Ions and the NCS Group in Chromium(III) Isothiocyanato Complexes. II. Reinecke's Salt Type Complexes Involving Nickel(II), Manganese(II) and Iron(III) Ions*1

Hisaya OKI, Eishin KYUNO and Ryokichi TSUCHIYA

Department of Chemistry, Faculty of Science, Kanazawa University, Kanazawa

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Nickel(II), manganese(II) and black iron(III)-tetraisothiocyanatochromate(III) were prepared by the reaction of nickel(II) nitrate, manganese(II) sulfate and iron(III) chloride with Reinecke's salt, respectively. Each salt exhibits a gradual color change from reddish-purple to brownish-orange, red and black, respectively, when exposed to dry air after preparation, except for the orange iron(III) salt prepared in hydrochloric acid solution, which shows no color change from the original orange. Their absorption spectra give evidence that each salt will dissociate into a metal cation and Reinecke's anion in aqueous solution. Splittings due to the C–N stretching vibration were not observed in the IR spectra. The effective magnetic moments were evaluated as 3.96, 5.13, 5.0 and 4.81 B. M. for the nickel(II)-, the manganese(II)-, the black iron(III)- and the orange iron(III)-salts, respectively. They show that the salts are nearly low spin types, or a type somewhere between low and high spin. From X-ray diffraction analyses, the unit cell of all the salts were found to be tetragonal.

In a preceding paper,1) cobalt(II) and copper(II) isothiocyanatochromate(III) were prepared and it was concluded that the gradual color change from reddish-purple to grayish-green for the cobalt(II) salt was due to the appearance of an interaction between cobalt ion and the sulfur atom of an NCS group in Reinecke's anion, and that the formation of the insoluble, yellow copper(II) salt showed the presence of the assumed π-bonding between copper ion and an NCS group.

In the present work, the preparation of the nickel(II), manganese(II) and iron(III) salts of Reinecke's salt type has been carried out, and the structures of these compounds discussed with respect to the interaction between the transition metal cations and NCS groups in Reinecke's anion on the basis of electronic and IR spectra, magnetic susceptibility measurements and other chemical techniques.

Experimental

Nickel(II) Salt of Reinecke's Salt Type (called "Ni-salt"). To a solution of Reinecke's salt (1.5 g/100 m*l* of H_2O) at 60°C, crystals of nickel(II) nitrate (4 g) were added. After being kept in a refrigerator over night, reddish-purple scale-like crystal precipitated from the solution. After recrystallizing the precipitate obtained, it was washed with water. When the crystals were dried *in vacuo* over sulfuric acid at room temperature, their color changed to brownish-orange. If they were then heated at 68°C, the color changed further to greensih-brown, but the brownish-orange color was immediately reproduced when exposed to air.

Found: Cr, 14.07; Ni, 7.55; N, 22.96; H_2O, 2.4%. Calcd for $Ni[Cr(NCS)_4(NH_3)_2]_2 \cdot H_2O$: Cr, 14.32; Ni, 8.06; N, 23.56; H_2O: 2.52%.

Manganese(II) Salt of Reinecke's Salt Type (called "Mn-salt"). To a solution of Reinecke's salt (1.5 g/100 m*l* of H_2O) at 60°C, crystals of manganese(II) sulfate tetrahydrate (6 g) were added. When the solution was kept in a refrigerator over night, reddish-purple, scale-like crystals precipitated out. Separated by filtration, the crystals were washed with water. With drying *in vacuo* over sulfuric acid, their color changed to red, and the original color was reproduced when exposed to moist air.

Found: Cr, 13.84; Mn, 8.09; N, 22.91; H_2O, 5.0%. Calcd for $Mn[Cr(NCS)_4(NH_3)_2]_2 \cdot 2H_2O$: Cr, 14.29; Mn, 7.55; N, 23.10; H_2O, 4.95%.

Iron(III) Salts of Reinecke's Salt Type. *a) Black Iron(III) Salts of Reinecke's Salt Type* (called "black Fe-salt"). To a solution of Reinecke's salt (1.5 g/100 m*l* of H_2O) at 60°C, a solution of iron(III) chloride hexahydrate (8 g/10 m*l* of H_2O) was added. When the solution was kept in a refrigerator over night, reddish-purple, scale-like crystals pricipitated out, which were then separated by filtration. After being washed with a small amount of water, and dried *in vacuo* over sulfuric acid, the color of the crystals changed from reddish-purple to black. As recrystallization was repeated in water, the color of the crystal was gradually changed from black to purple or somewhat reddish-purple. This

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*1 Read in part at the 16th Symposium on Coordination Compounds of the Chemical Society of Japan, Tokyo, Dec., 1966.

1) H. Oki, E. Kyuno and R. Tsuchiya, This Bulletin, **41**, 2357 (1968).

is probably due to the sublimation of iron(II) trithiocyanate, produced as the result of the partial decomposition of the black Fe-salt, leaving a small amount of ferric oxide. Thus, recrystallization was unsuccessful even in an acidic solution.

Found: Cr, 11.87; Fe, 9.60; N, 23.53%. Calcd for $Fe[Cr(NCS)_4(NH_3)_2]_3 \cdot Fe(NCS)_3$: Cr, 12.57; Fe, 9.00; N, 23.70%.

b) Orange Iron(III) Salt of Reinecke's Salt Type (called "orange Fe-salt"). To a solution of iron(III) chloride hydrate (8 g/10 m*l* of 8 N HCl), a solution of Reinecke's salt (10 g in 6 N hydrochloric acid) at 60°C was added. When the solution was kept in a refrigerator over night, a reddish-orange or orange powder separated out, which was filtered and washed with a small amount of ether. The orange crystals did not show any color change, even when upon drying, differing from the black Fe-salt described above.

Found: Cr, 13.06; Fe, 6.69; N, 22.17; Cl, 9.24%. Calcd for $FeHCl_2[Cr(NCS)_4(NH_3)_2]_2$: Cr, 13.60; Fe, 7.30; N, 21.98; Cl, 9.28%.

Apparatus for Measurement. Conductivity, visible and UV absorption spectra, IR and far-IR absorption spectra, reflection spectra, magnetic susceptibility and X-ray diffractions were measured with the same apparatus described in the preceding paper.[1)]

Results and Discussion

Conductivities and Behavior toward Ion Exchangers. Values of the molar conductivity of the salts per equivalent Reinecke's anion in aqueous solution at 25°C are listed in Table 1. They suggest, first, that the Ni- and Mn-salts are 1:2 valency types which can dissociate into a metal cation and two Reinecke anions in aqueous solution.

TABLE 1. THE MOLAR CONDUCTIVITY (at 25°C)

Sample	Concentration mol/*l*	Molar conductivity cm^2ohm^{-1}	Type
Reinecke's salt	2×10^{-2}	103.1	1 : 1
Ni-salt	5×10^{-2}	115.3	1 : 2
Mn-salt	2×10^{-2}	106.3	1 : 2
Black Fe-salt	4×10^{-2}	194.8	1 : 3
Orange Fe-salt	4×10^{-2}	374.8	

On the other hand, the condutivity of the black Fe-salt per equivalent Reinecke anion was found to be much greater than expected for 1:3 type salts in general. This can be explained reasonably by their behavior toward ion exchangers.

When an aqueous solution of the black Fe-salt was poured onto a column of anion exchange resin (Dowex 1×8), pink solution passed through, leaving some red material adsorbed on the exchanger. It is thought that the pink solution, in part, contains $Fe(NCS)_3$ and the appearance of the red color on the exchanger is due to the adsorption of Reinecke's anion. The presence of $Fe(NCS)_3$ in the pink solution was verified by detecting the chromium ion formed by the reaction of Reinecke's anion with ferric ion.

Moreover, the orange Fe-salt has the largest molar conductivity of all the complexes, as given in Table 1. This is due to the presence of hydrogen ion which is capable of dissociation in aqueous solution, as indicated by the formula proposed in the Experimental section.

When an aqueous solution of the orange Fe-salt was poured onto the column of the same exchanger as was used above, yellow solution passed through, leaving red material on the exchanger. It is thought that the yellow color of the solution indicates the presence of iron(III) ion, and the red material on the exchanger indicates the adsorption of Reinecke's anion.

Electronic Absorption Spectra. The electronic absorption spectra of the Ni(II)- and Mn(II)-salts of Reinecke's salt type were in approximate agreement with that of Reinecke's salt itself, which supports their complete dissociation to Ni(II) or Mn(II) cations and Reinecke's anion in aqueous solution. The numerals of the electronic spectra of these complexes are listed in Table 2, including those of both Fe-salts described below.

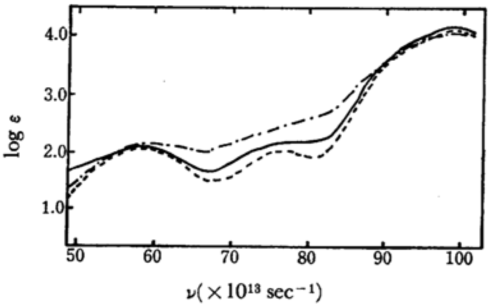

Fig. 1. The absorption spectra of the black Fe-(——), and the orange Fe-salts (— - —) and Reinecke's salt (- - -).

The electronic spectra of the black and orange Fe-salts are shown in Fig. 1, together with that of Reinecke's salt. As seen in this figure, the spectra of these compounds are also similar to that of Reinecke's salt except for the second band being changed to a shoulder. It shows that both Fe-salts dissociate into iron(III) cations and Reinecke's anions in an aqueous solution, the same as the Ni- and Mn-salts, but some amount of hydroxo-iron(III) is formed.

Reflection Spectra. Absorption spectra of the Ni-, Mn- and orange Fe-salts in the solid state were measured by the diffusion-reflection method and are shown in Fig. 2 together with that of Reinecke's salt. In the Ni- and Mn-salts, only the first band corresponding to that of Reinecke's salt is observed, the second band being undetectable probably because of the shift of the intense charge transfer band to the visible region, which can not

TABLE 2. THE ABSORPTION SPECTRA OF THE REINECKE'S TYPE SALTS

	The first band		The second band		The specific band	
	$\nu(10^{13}\,\mathrm{sec}^{-1})$	$(\log \varepsilon)$	$\nu(10^{13}\,\mathrm{sec}^{-1})$	$(\log \varepsilon)$	$\nu(10^{13}\,\mathrm{sec}^{-1})$	$(\log \varepsilon)$
Reinecke's salt	57.69	(2.01)	76.53	(1.96)	99.67	(4.14)
Ni-salt	57.69	(2.01)	76.53	(1.96)	99.67	(4.14)
Mn-salt	57.69	(2.03)	76.53	(1.96)	99.67	(4.14)
Black Fe-salt	57.69	(2.05)			99.01	(4.18)
Orange Fe-salt	60.00	(2.11)			99.01	(4.11)

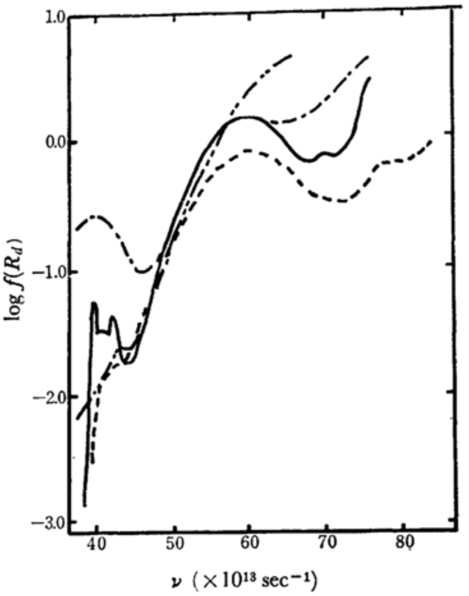

Fig. 2. The reflection spectra of the Mn-salt (——), the Ni-salt (— — —), the orange Fe-salt (— - - - —) and Reinecke's salt (- - -).

be observed in the visible absorption spectra of these compounds in aqueous solution.

In the Mn-salt, an absorption peak which seems assignable to the second absorption band of manganese sulfate in aqueous solution is also faintly observed at $69.77\times10^{13}\,\mathrm{sec}^{-1}$. Besides, three absorption bands are observed in the frequency range from $38.71\times10^{13}\,\mathrm{sec}^{-1}$ to $44.44\times10^{13}\,\mathrm{sec}^{-1}$, which are thought probably due to the overlapping of the electron spin forbidden band with the first bands of manganese(II) cation and Reinecke's anion.

In the orange Fe(III)-salt, both the first and second bands corresponding to those of Reinecke's salt could not be observed, and only an electron spin forbidden band was found.

In the reflection spectrum of the black Fe(III) salt, no positive peak was detected because of the black color due to an intense absorbance over all wavelengths measured.

IR Spectra. The infrared absorption spectra of the Ni- and Mn-salts, which are very similar, are shown in Fig. 3, together with those of the Co-salt1) and Reinecke's salt. Since the absorption peaks assigned to the C–N stretching vibration of the Ni- and the Mn-salts does not shift so greatly, and the peaks due to C–S stretching are also observed in a higher wave number region than that of the Co-salt,1) but lower than that of Reinecke's salt, the bond between the sulfur atom in an NCS group and nickel(II) or manganese(II) ion is not so strong as the corresponding bond in the Co-salt.

The IR spectra of the black and orange iron(III)-salts are shown in Fig. 4. In the black Fe(III)-salt, two peaks, assigned to C–N stretching at 2117 and 2075 cm^{-1}, are observed; the former peak may be due to an appreciable interaction between the sulfur in coordinated NCS and iron,

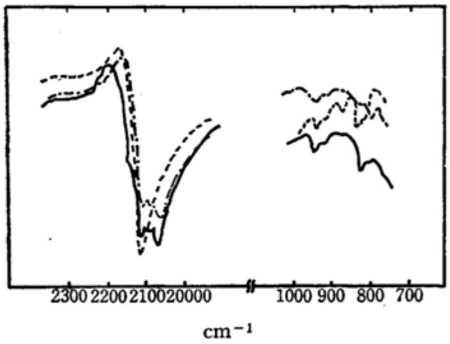

Fig. 3. The infrared spectra of the Mn-salt (——), the Ni-salt (— — —) and Reinecke's salt (- - -).

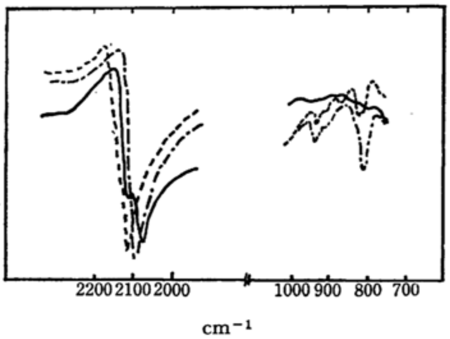

Fig. 4. The infrared spectra of the black Fe-salt (——), the orange Fe-salt (— — —) and Reinecke's salt (- - -).

TABLE 3. THE ANALYSES OF THE X-RAY DIFFRACTION AND DENSITY OF THE REINECKE'S TYPE SALTS

	c/a	a(Å)	c(Å)	ρ		Z
				Calcd	Found	
Reinecke's salt	1	13.42	13.42	1.50		6
Ni-salt	1.3	13.08	17.35	1.59	1.53	8
Mn-salt	0.96	11.41	10.95	1.69	1.12	4
Black Fe-salt	0.9	15.81	14.23	1.55	1.60	8
Orange Fe-salt	1.2	12.24	14.70	1.73	1.45	8

but assumably it will be weaker than that in the corresponding Co-salt; the latter should be independent of such an interaction.

There was found, on the other hand, only one peak at 2098 cm^{-1} due to the C–N stretching vibration in the orange iron(III)-salt as shown in Fig. 4. This may be attributed to the iron being surrounded by large coordinated chloride atoms, as pointed out by Fujita *et al.*[2] In the cholin-salt, the effective charge is small, since the positive charge on the nitrogen atom is screened by bulky aliphatic groups and so the interaction between the thiocyanate group and cholin ion may be negligibly small.

Far-IR Absorption Spectra. The far infrared absorption spectra of the Ni(II)-, Mn(II)-, black Fe(III)- and orange Fe(III)- salts are shown in Fig. 5. In the Ni(II)- and Mn(II)-salts, the band near 500 cm^{-1} assigned to the Cr–N stretching vibration involving NH_3 does not shift or split, whereas the band appearing in the region immediately to lower wave number than that of the former band assigned to NCS bending slightly splits into two peaks, but the splitting is not so large as that in the Co-salt. Thus it is thought that the nickel and manganese ions bind weakly with isothiocyanate groups through the sulfur atom.

The spectrum of the black Fe(III) salt resembles that of the Ni-salt, except for the appearance of a small band at 393 cm^{-1} which is probably due to slight contamination with $FeCl_3$. Hence, the interaction between iron and thiocyanate may have a strength similar to the Ni-salt.

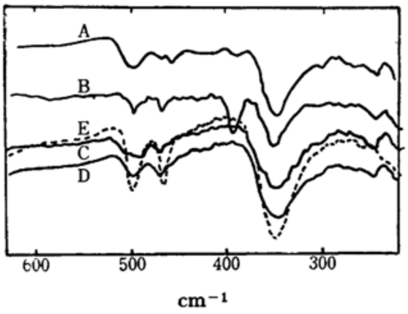

Fig. 5. The far infrared spectra of the Mn-salt (A), the orange Fe-salt (B), the black Fe-salt (C), the Ni-salt (D) and Reinecke's salt (E) (- - -).

The orange Fe(III)-salt has, on the other hand, a new band at 390 cm^{-1}, which has never been observed in the other Reinecke type salts. It consists of two absorption peaks. They are assigned to Fe–Cl stretching vibrations which are attached to hydrogen ion and which are not. Besides, the band assigned to the Cr–N stretching vibration involving an NCS group is commonly observed at 347 cm^{-1} in all Reinecke type salts, and Reinecke's salt itself treated in these papers.[1]

Magnetic Susceptibility. The calculated value of the effective magnetic moment from the magnetic susceptibility in the brownish-orange Ni-salt was 3.96 B. M. and the corresponding calculated value when the nickel is in a low spin state should be 3.87 B. M., which is in good agreement with the observed value described above. It may suggest that the nickel ion is probably surrounded by four sulfur atoms in a square planar arrangement. It is known that when the coordination of four sulfur atoms around nickel ion is square planar, the complex exhibits a brown or orange color; when it is tetrahedral, the complex becomes gray in color. Therfore, it can be predicted that when the former square planar complex is changed to the latter tetrahedral one, the value of the magnetic moment should increase. Nevertheless, the value of the magnetic moment in the Ni-salt heated at 68°C is found to be 4.01 B. M., being not so large as that calculated assuming a tetrahedral configuration around the nickel ion. This is probably due to the incompleteness of the structure change from square planar to tetrahedral.

The observed value of the magnetic moment in the Mn(II)-salt was 5.13 B. M. It is much smaller than the calculated value for a high spin state for manganese, 6.41 B. M. However, it is still larger than that for low spin type manganese, 4.39 B. M. The value of 5.41 B. M. is also expected for the square planar structure for the Mn-salt. These results, therefore, indicate that manganese ion is surrounded by four sulfur atoms in a square planar arrangement in the salt. However, such an interpretation is still inconsistent with that obtained from the reflection spectrum measurement. In addition, the bond between manganese ion and

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[2] J. Fujita, K. Nakamoto and M. Kobayashi, *J. Am. Chem. Soc.*, **78**, 3256 (1956).

sulfur atoms in a thiocyanate group is weak enough since no shift of the band due to the C–N stretching vibration can be detected in the infrared spectrum. At present, no successful explanation for these phenomena has been given without any discrepancies.

The effective magnetic moment of the black Fe(III)-salt was obtained as 5.0 B. M. The interpretation for the configuration of coordinated atoms around the iron(III) ion can not be appropriately given due to a mixing of iron(III) trirhodanate into the Fe(III)-salt.

The value obtained for the magnetic moment of the orange Fe(III) salt was 4.85 B. M. If iron atom is surrounded by two chloride ions and two Reinecke's anions forming a square planar structure, the calculated value obtained is 4.38 B. M. Therefore it is adequate to consider that this salt has a square planar structure and an ionic character.

X-Ray Diffraction Measurement. The results of an analysis of the X-ray diffraction patterns are summarized in Table 3.

The density of the Ni- and the black Fe-salt are nearly equal to that of Reinceke's salt. This indicates that these salts have not so strong a bond between the metal ions and Reinecke's anion as is the case in the Co- and Cu-salts. The values for the densities of the Mn- and orange Fe-salts obtained do not equal those of the salts mentioned above.

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