

THIOCYANATOCOBALTOUS ACID AND ITS ALKALI SALTS.

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When an aqueous solution of $K_2Co(SCN)_4$, to which sufficient $KSCN$ has been added to make the solution 0.8-1.0 normal in thiocyanate, is shaken with sufficient 1:4 ethyl alcohol-ether to form a separate layer, only traces of a blue compound pass into the ether layer. If the solution be now acidified with mineral acid, practically all the blue compound passes into the ether layer. As the blue color has been shown by Rosenheim and Cohn¹ to be due to a bivalent complex negative ion, $Co(SCN)_4^{--}$ it appears probable that in the acid solution the free acid, $H_2Co(SCN)_4$, may be formed which is readily soluble in ether while its potassium salt is nearly insoluble. Two similar acids, $H_2Hg(SCN)_4$ ² and $HAu(SCN)_4 \cdot 2H_2O$ ³, have been isolated in solid, crystalline form. Preliminary attempts to isolate the acid in solid form, by evaporation of the ether solution in an evacuated desiccator, showed that large amounts of $HSCN$ were evolved as the solution concentrated. A mixture was deposited consisting of long slender needles of deep blue color which showed a strong acid reaction when moistened with water and short needles of a bluish green color. No method of separating the two sufficiently for analysis has been found up to this time. In order to obtain some information as to the nature of the ether-soluble blue compound, experiments were made to determine the partition of acid, thiocyanate and cobalt between the aqueous and ether layers at 25° C.

Preliminary determinations were made of the partition of sulfuric acid and of thiocyanic acid. These are recorded in the following tables.

TABLE 1. Partition of H_2SO_4 between water and 1:4 alcohol (EtOH)-ether (Et₂O).

Expt. No.	Normality of acid.	
	Aq. layer	Et ₂ O Layer
1	0.8005	0.0037
2	1.7112	0.0074

The solubility of H_2SO_4 in aqueous ether is very small and in comparison with the large solubility of $HSCN$ shown in the next table is negligible at total concentrations not above 1.5 normal.

¹ Z. anorg. Chem., 27, 280 (1900).² Rosenheim and Cohn, loc. cit.³ Bjerrum and Kirschner, Die Rhodanide des Goldes, Mem. acad. roy. sci. lettres, Danemark, 8me serie, V, No. 1, p. 20.

TABLE 2—Partition of HSCN between water and 1:4 EtOH-Et₂O.

In each experiment 10 cc. 4 normal NaSCN (SCN=0.04 equiv.)

Expt. No.	5-N. H ₂ SO ₄ cc.	Volume cc.		Acid normality		SCN normality		Ratios		
		aq.	Et ₂ O	aq.	Et ₂ O	aq. (by dif.)	Et ₂ O	Et ₂ O H ⁺ to aq. H ⁺	Et ₂ O SCN to aq. SCN	Et ₂ O SCN to Et ₂ O H ⁺
1	0	*	*	0.0	0.0		0.0087			
2	1	32	26	.0440	.1651	1.108	.1744	3.75	0.157	1.056
3	3	26.5	24.5	.1908	.4801	1.042	.5060	2.52	.486	1.054
4	5	24	24	.3890	.7230	0.9078	.7590	1.86	.836	1.050
5	7	22	24.5	.6680	.9360		.7736	1.40	1.212	1.002
6	9	19	25	1.082	1.098		.5850	1.15	1.974	1.052
7	20	32	30	2.280	1.122		.1625	1.160	0.49	7.139

*Not recorded.

In the above table, experiment 1 shows that NaSCN has a very small but appreciable solubility in aqueous ether. Unfortunately, the volumes of the aqueous and the ether layers in this experiment were not recorded so that the ratios in the last column could not be corrected for dissolved salt. The slight excess of thiocyanate is undoubtedly due to this cause. The close approximation of the last ratio to unity shows that the ether-soluble substance is practically all HSCN. The data clearly show that this acid is far more soluble in ether than in water. A small excess of mineral acid is sufficient to force nearly all the thiocyanate into the ether layer as HSCN.

The data recorded in table 3 were obtained as follows. In a tall glass-stoppered cylinder were placed 25 cc. of an aqueous solution of K₂Co(SCN)₆, in which the cobalt content was 71.0 mg., 10 cc. of 4 normal KSCN, the recorded volumes of 5 normal H₂SO₄, (in Expt. 9, 5 cc. of 33 normal acid) and sufficient 1:4 ethyl alcohol-ether to give approximately equal layers. The cylinder was placed in a bath at 25° C. and frequently shaken until equilibrium was reached. In separate portions of the ether layer acidity was determined by titration with NaOH and phenolphthalein, SCN by titration with AgNO₃ and ferric alum, and cobalt by evaporation with H₂SO₄ and weighing as CoSO₄. Acid in the aqueous layer was also determined. In experiment 9, only 20 cc. of the K₂Co(SCN)₆ solution were taken.

The ratio $\frac{1}{2}$ Co:SCN, together with the data of columns 8 and 12, indicates a small solubility of Co(SCN)₂ in aqueous ether containing a little alcohol. This was confirmed using a sample of the purple Co(SCN)₂·3H₂O which, although not very pure as shown by analysis, showed all the reactions of this salt. When placed in ether the latter assumed only a faint tinge of blue. The solubility calculated from the data of experiment 1 is 0.347 mg. per cc. for the anhydrous salt.

The ratios, H⁺: $\frac{1}{2}$ Co:SCN and (SCN- $\frac{1}{2}$ Co): H⁺, confirm the conclusion from table 2 that HSCN is largely soluble in ether and that its concentration in the ether layer increases rapidly as the mineral acid in the aqueous layer is increased.

The data throw no light on the formula of the ether-soluble, blue cobalt compound. In not too acid solutions about 20 mols. of HSCN for each mol. of Co(SCN)₂ are present. This may indicate either a

TABLE 3. Partition of Co and HSCN between water and 1:4 alcohol-ether. In each experiment 10 cc. 4 N KSCN. In experiments 1-8, 71.0 mg. Co=0.020404 equiv.; total SCN=0.080808 equiv. In experiment 9, 0.016323 equiv. Co and 0.072646 equiv. SCN.

Expt. No.	5-N H ₂ SO ₄ cc.	Volume cc.		Acid normality		SCN normality		CoSO ₄ mg. per cc.		Cobalt normality		Ratio in Ether layer			Ratio		Fraction of total Co in Et ₂ O layer
		aq.	Et ₂ O	aq.	Et ₂ O	aq. by dif.	Et ₂ O	aq. by dif.	Et ₂ O	aq. by dif.	Et ₂ O	H ⁺ to	½ Co	to SCN	(SCN— ½ Co)	to H ⁺	
1.....	0	51	42	0.0	0.0	1.581	0.004	3.402	0.312	0.0439	0.004	0.0	1	1	—	—	—
2.....	1	50	44	0.0330	0.0945	1.521	0.109	3.020	0.808	0.0389	0.0104	9.086	1	10.48	1	1.0435	0.211
3.....	3	49	48	0.0945	0.2496	1.367	0.288	1.986	1.860	0.0256	0.0240	10.04	1	12.00	1	1.058	0.4837
4.....	5	49	48	0.2090	0.3590	1.265	0.392	1.308	2.552	0.0168	0.0329	10.91	1	11.91	1	1.0003	0.661
5.....	7	50	48	0.363	0.4476	1.135	0.502	0.764	3.092	0.0099	0.0398	11.24	1	12.60	1	1.0310	0.802
6.....	9	51	46	0.495	0.5280	1.030	0.593	0.571	3.424	0.0074	0.0442	10.94	1	13.39	1	1.0395	0.857
7.....	11	53	45	0.646	0.580	0.984	0.637	0.641	3.392	0.0083	0.0438	13.24	1	14.54	1	1.1023	0.841
8.....	15	55	44	0.910	0.653	0.865	0.755	0.705	3.360	0.0091	0.0438	14.90	1	17.21	1	1.089	0.827
9.....	5cc. 33 N	35	57	3.630	0.770	0.797	0.785	1.574	1.652	0.0203	0.0213	36.15	1	36.80	1	0.992	0.512

definite compound, $H_{2x}Co.(SCN)_{4x}$, a mixture of several such acids, or an acid of definite formula along with a large excess of HSCN. That upon evaporation the ether solution deposits deep blue crystals having a strong acid reaction makes it probable that a definite acid, $H_{2x}Co.(SCN)_{4x}$, is present and that it is capable of existence in solid crystalline form. The problem of obtaining this compound sufficiently pure for analysis is being further investigated.

The conclusion drawn from table 1 of the preceding paper on Vogel's reaction, that the fraction of cobalt which passes into the ether layer reaches a maximum at moderate concentrations of mineral acid and then decreases as the acid is increased, is clearly verified by the data of table 3 above, as shown in the last column.

Alkali salts of Thiocyanatocobaltous Acid. Deep blue double thiocyanates of cobalt and alkali metals have been prepared in crystalline form by Treadwell¹ and by Rosenheim and Cohn.² These investigators agree in assigning to these salts the empirical formula, $Co(SCN)_2 \cdot 2RSCN$, in which R may be NH_4 , K or Na, but they differ as to their properties and hydration. By transference experiments Rosenheim and Cohn proved that the blue color was due to a complex anion, $Co(SCN)_4^{2-}$. Treadwell, working with organic solvents, obtained the potassium and ammonium salts in anhydrous condition and found them to be quickly decomposed by water and even by moist air. Rosenheim and Cohn prepared 12-14% solutions of HSCN by action of H_2S on concentrated solutions of $Hg(SCN)_2$ and by action of this acid on $CoCO_3$ prepared cobalt thiocyanate in violet rhombic crystals of composition $Co(SCN)_2 \cdot 3H_2O$. By addition of the calculated amounts of the various alkali thiocyanates to aqueous solutions of this salt they obtained in well defined crystalline form the potassium and ammonium salts, each with 4 molecules of water, and the Na and Ba salts each with 8 molecules of water. They found all these salts to be soluble in methyl, ethyl and amyl alcohol and in acetone and that they could be recrystallized from concentrated aqueous solution without decomposition. They also prepared the anhydrous salts by Treadwell's methods and from aqueous solutions of these obtained the hydrated salts without decomposition. It seemed worth while to investigate these discrepant statements.

A simpler method of preparing the potassium salt and also $Co(SCN)_2 \cdot 3H_2O$ was worked out. The work described below verifies the statements of Rosenheim and Cohn but it was found that the tri-hydrate is the form of the potassium and ammonium salts which is stable in air at the temperature of the laboratory, although, as stated by Rosenheim and Cohn, the tetra-hydrate separates from aqueous solution. The loss of one molecule of water is not accompanied by any change in the appearance of the crystals. The sodium complex salt was not prepared.

EXPERIMENTAL.

To concentrated aqueous solution of $CoSO_4$ was added the amount of KSCN calculated to form the double salt and then ethyl alcohol in

¹ *Z. anorg. Chem.*, 26, 108 (1900).

² *Loc. cit.*

large excess. Most of the K_2SO_4 precipitates and can be filtered off. The deep-blue alcoholic solution was evaporated on a water bath nearly to dryness and alcohol added. More K_2SO_4 could now be removed and three or four repetitions of this process proved sufficient for the complete removal of sulfate. The sulfate-free alcoholic solution was evaporated with occasional additions of a little water until the alcohol was removed and the concentrated aqueous solution allowed to crystallize at room temperature. Crystals of the potassium salt several centimeters long were thus obtained. Analysis of the crystals, removed from the mother liquor and dried by pressing between filter paper, gave: SCN=52.65%; Co=13.53%. $K_2Co(SCN)_4 \cdot 4H_2O$ requires SCN=52.61; Co=13.35.

After exposure to air: 24 hours, SCN=54.99%; Co=13.69%; 96 hours, SCN=55.09%, Co=14.29%; 144 hours, SCN=55.15%, Co=14.04%. $K_2Co(SCN)_4 \cdot 3H_2O$ requires SCN=54.85%, Co=13.92%. Evidently the trihydrate, and not the tetrahydrate, is the form stable in air at room temperature.

The ammonium complex salt was prepared in anhydrous form by precipitation from its acetone solution by chloroform and dried in air. Found, SCN=69.17%; $(NH_4)_2Co(SCN)_4$ requires SCN=70.97%. The salt was dissolved in water and the solution, when evaporated at low temperature, yielded fine blue needles often several centimeters long. This material, when removed from the mother liquor and dried by pressing between filter paper, gave SCN=60.75%; after exposure to air 48 hours, 60.44%; after 72 hours, 61.03%; after 96 hours, 61.22%. The tetrahydrate requires SCN=58.16%; the trihydrate requires SCN=60.91%. The trihydrate appears to be the form of the ammonium salt also which is stable in air at room temperature.

By the same method of removal of alkali sulfate by alcohol it was found possible to obtain the purple $Co(SCN)_2 \cdot 3H_2O$ by adding to concentrated aqueous solutions of $CoSO_4$ the calculated amount of NaSCN. The product was well crystallized and contained only a spectroscopic trace of sodium. In appearance and reactions it corresponded exactly with the description of Rosenheim and Cohn but analysis gave Co=22.17%, SCN=54.19%. $Co(SCN)_2 \cdot 3H_2O$ requires Co=25.77%, SCN=50.66%. This salt is unstable in air and passes into a yellow-brown substance, readily soluble in alcohol to a deep-blue solution and in appearance corresponding to the hemihydrate, $Co(SCN)_2 \cdot \frac{1}{2}H_2O$, described by Rosenheim and Cohn.

SUMMARY.

1. The partition of cobalt between water and aqueous-alcoholic-ether in presence of thiocyanic acid was studied. The ether layer was found to contain equivalent proportions of cobalt and thiocyanate, in addition to large amounts of thiocyanic acid, but to dissolve practically no cobalt thiocyanate or alkali thiocyanate.

2. The data obtained in this study do not permit definite conclusion as to the formula, or formulas, of the extremely ether-soluble blue cobalt compounds, although the evidence makes it highly probable that one or more complex acids having cobalt in the anion are present.

3. Both the blue complex alkali thiocyanatocobaltites and the purple trihydrate of cobalt thiocyanate can be prepared by double decomposition in aqueous solution starting from the sulfate of cobalt and removing alkali sulfates by means of alcohol. This simple method avoids the use of thiocyanic acid which is not easy to prepare in at all concentrated solution and is rather unstable in aqueous solution.

4. It is shown that at laboratory temperature the trihydrate, and not the tetrahydrate, is the form stable in air for the ammonium and potassium thiocyanatocobaltites. In all other respects the statements of Rosenheim and Cohn were confirmed. Treadwell is in error as to the instability of these salts. That the purple trihydrate of cobalt thiocyanate changes into the yellow-brown hemihydrate rather rapidly when exposed to the air of an artificially warmed room has not been previously recorded.