data by the method of least squares. Wt. % solubilities computed from this equation are given in column 3 of Table I; the % deviations of the experimental values from those calculated are recorded in column 4.

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Solvent Extraction Separation of Cobalt and Nickel with Thiocyanate and the Preparation of Nickel-free Cobalt Salts[1]

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In the course of a spallation study on cobalt,[3] it was necessary to prepare very pure cobalt metal foil targets for cyclotron bombardments. The best reagent grade cobalt salts available[4] contained about 0.25% alkali salts and 0.15% nickel as principal impurities. The alkali impurities were removed in the electrolytic process used to produce the foils but the nickel impurity persisted and interfered with the spallation experiments. No convenient procedure appears to be in the literature for the preparation of comparatively large quantities of nickel-free cobalt, although the converse can be achieved readily since cobalt forms an anionic complex with chloride which can be retained on an ion-exchange column.

As early as 1879 Vogel[5] reported the extraction of a cobalt thiocyanate complex into a 1:1 mixture of amyl acetate and ethyl ether. Subsequent study by many investigators[6-8] established the thiocyanate extraction as a standard colorimetric procedure for determining cobalt. Sandell[9] showed that nickel in considerable excess did not interfere in the colorimetric determination of cobalt with thiocyanate in an acetone–water medium due to the feeble color of the nickel–thiocyanate complex. He also found no interference from 100-fold excesses of nickel in the colorimetric extraction procedure.

Although the above observations were no guarantee that nickel was not extracting under the specified conditions, preliminary experiments with Ni^{57} tracer showed that the distribution coefficient for nickel from aqueous thiocyanate solutions into various organic solvents was indeed low. Further experiments were done using Ni^{57} and Co^{60} tracers and a variety of solvents to find the optimum conditions for removing traces of nickel from cobalt salts.

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Experimental

Materials.—Mallinckrodt Analytical Reagent Grade salts were used throughout. The ethyl acetate, ethyl ether, isoamyl alcohol and n-butyl alcohol were Merck and Co. reagent grade. The butyl acetate was Eastman Kodak Co. White Label material, while the methyl isobutyl ketone (hexone), methyl n-amyl ketone and tributyl phosphate were obtained from Commercial Solvents Corporation.

The Co^{60} tracer was high specific activity processed material obtained from Oak Ridge National Laboratory. The Ni^{57} tracer was prepared by bombarding 100 mg. cobalt foils with 45 Mev. protons in the internal circulating beam of the Harvard synchrocyclotron. The Ni^{57} activity was recovered by dissolving the cobalt foil in nitric acid containing 1 mg. of nickel carrier and removing the cobalt by extracting it into ethyl acetate from a solution 0.5 M in HNO_3 and 5 M in KSCN. The Ni^{57} tracer was purified by recovering it from the aqueous phase by precipitation with NaOH and by successive precipitations from acetic acid–acetate buffer with dimethylglyoxime. The nickel dimethylglyoxime precipitate was destroyed finally with HNO_3 and evaporated with H_2SO_4 to give the final tracer solution.

The Na^{22} tracer was prepared by bombarding 20 mg. of aluminum foils with 60 Mev. protons, dissolving the aluminum in HCl containing sodium carrier and precipitating the aluminum with NH_4OH. Evaporating the supernate with concd. HNO_3 gave Na^{22} as the nitrate.

Analyses.—Cobalt and nickel concentrations in the stock solutions were determined by adding H_2SO_4 to an aliquot of the concentrate, evaporating to dryness, and weighing the anhydrous sulfates. Thiocyanate concentrations were determined by titrating aliquots of the stock solutions against silver nitrate with ferric ion indicator.

Apparatus and Procedure.—Ten-ml. portions of aqueous solution were equilibrated with an equal volume of organic solvent by shaking for 30 seconds once every five minutes over a period of 30 minutes. The solutions were contained in four-ounce polyethylene bottles and were held at constant temperature ($\pm 0.5°$). After equilibration, 4-ml. aliquots of the two phases were pipetted into 5-ml. glass vials and counted in a well-type NaI (T1) scintillation counter. After subtracting background to obtain net activities, the distributing coefficient K_d was calculated as K_d = (net activity of organic phase aliquot)/(net activity of inorganic phase aliquot). The errors in the K_d values were less than 3% for $0.01 < K_d < 100$. Beyond these limits errors increased due to small interphase contaminations.

Results and Discussion

To allow economical purification of cobalt salts, cobalt and thiocyanate concentrations were chosen to allow the maximum cobalt concentration consistent with complete extraction. With trace amounts of cobalt, there was little point in using aqueous phases more than 2 M in thiocyanate as the K_d for cobalt increased only slowly beyond this point. In concentrated cobalt solutions, thiocyanate was consumed in complexing and about 13 moles SCN^-/mole Co over and above the 2 M value were needed for complete extraction. At 0° 0.35 M $Co(NO_3)_2·6H_2O$ with 5 M NaSCN gave the maximum cobalt concentration which was 99% extractable without precipitation in the aqueous phase. Slightly higher concentrations were possible with NH_4SCN.

Using NaSCN, thirteen solvents were tested with Ni^{57} tracer (see Table I). Diisobutyl ketone, dichlorodiethyl ether, 2-ethylhexanol and dichlorodiisopropyl ether gave precipitates under the stated conditions. Ethyl ether gave three phases as is observed in the ethyl ether extraction of high concentrations of iron from HCl solutions. In this case the middle phase was rich in cobalt and the bottom one rich in nickel. The three solvents giving the lowest K_d for nickel were hexone,

Table I

Extraction of Cobalt and Nickel with Thiocyanate[a]

Tracer	Salt concn. aq. phase	Co, M	Ni, M	Solvent[b]	Temp., °C	K_d'[a]	K_d^{Ni}	$\dfrac{K_d^{Co}}{K_d^{Ni}}$
Varying solvent								
Ni, Co	5 M NaSCN	0.35	0.35×10^{-3}	EtOAc	1	265	0.173	1530
Ni, Co	5 M NaSCN	.35	$.35 \times 10^{-3}$	MIBK	1	2420	.0106	228000
Ni, Co	5 M NaSCN	.35	$.35 \times 10^{-3}$	MNAK	1	868	.0061	142300
Ni, Co	5 M NaSCN	.35	$.35 \times 10^{-3}$	BuOAc	1	67.4	.0065	10370
Ni, Co	5 M NaSCN	.35	$.35 \times 10^{-3}$	TBP	1		.210	
Ni, Co	5 M NaSCN	.35	$.35 \times 10^{-3}$	Et$_2$O[c]	1		.073	
Ni, Co	5 M NaSCN	.35	$.35 \times 10^{-3}$	IAA	1		.224	
Ni, Co	5 M NaSCN	.35	$.35 \times 10^{-3}$	75% IAA, 25% Et$_2$O	1		.147	
Ni, Co	5 M NaSCN	.35	$.35 \times 10^{-3}$	n-BuOH	1		.386	
Ni, Co	5 M NH$_4$SCN	.35	$.35 \times 10^{-3}$	EtOAc	1	137	.116	1180
Ni, Co	5 M NH$_4$SCN	.35	$.35 \times 10^{-3}$	MIBK	1	470	.0120	39200
Ni, Co	5 M NH$_4$SCN	.35	$.35 \times 10^{-3}$	MNAK	1	134	.0058	23100
Ni, Co	5 M NH$_4$SCN	.35	$.35 \times 10^{-3}$	BuOAc	1	6.18	.0077	803
Varying temp.								
Ni, Co	5 M NH$_4$SCN	.35	$.35 \times 10^{-3}$	MIBK	1	470	.0120	39200
Ni, Co	5 M NH$_4$SCN	.35	$.35 \times 10^{-3}$	MIBK	21	109	.0069	15800
Ni, Co	5 M NH$_4$SCN	.35	$.35 \times 10^{-3}$	MIBK	29	63.8	.0061	10470
Varying metal ion concn.								
Ni, Co	5 M NH$_4$SCN	10^{-6}	4×10^{-6}	MIBK	29	3840	.0101	390000
Ni, Co	5 M NH$_4$SCN	10^{-6}	0.35	MIBK	29	930	.0124	75000
Ni, Co	5 M NH$_4$SCN	0.35	0.35×10^{-3}	MIBK	29	470	.0120	39200
Ni, Co	5 M NH$_4$SCN	0.35	0.35	MIBK	29	223	.0206	10830
Back-extraction experiments								
Ni, Co	5 M NH$_4$SCN	0	0	MIBK	1	516	.0139	
Ni, Co	2 M NH$_4$SCN	0	0	MIBK	1	106	.0212	
Ni, Co	5 M NH$_4$SCN	0	0	MIBK	29	197	.0083	
Ni, Co	2 M NaSCN	0	0	MIBK	1	2830	.0110	

[a] The extraction is relatively insensitive to pH in the region of pH 4–6 in which the extractions were made. [b] EtOAc is ethyl acetate; MIBK is methyl isobutyl ketone (hexone); MNAK is methyl n-amyl ketone; BuOAc is butyl acetate; TBP is tributyl phosphate; Et$_2$O is ethyl ether; IAA is isoamyl alcohol; n-BuOH is n-butyl alcohol. [c] Ethyl ether forms three phases under these conditions, with the middle one rich in cobalt, the bottom one rich in nickel.

methyl n-amyl ketone and butyl acetate. These plus ethyl acetate were tried substituting the ammonium salt of thiocyanate. Little change in K_d for nickel occurred but the cobalt K_d's were two to tenfold lower. The separation factor $S = (K_d^{Co}/K_d^{Ni})$ was thus better with NaSCN. The best separation with either salt occurred with hexone.

Temperature (Table I) had a small effect on the nickel K_d but the K_d for cobalt was more than seven times as large at 0° as at 29°. Thus higher separation factors are obtainable at lower temperatures.

Increasing the cobalt ion concentration alone decreased the K_d for cobalt considerably. This was not primarily due to a K_d dependence on cobalt ion concentration directly as the K_d for cobalt changed much less when constant ionic strength of the metal ion was maintained by substituting nickel for cobalt. The variation was more likely due to lowered available thiocyanate concentration in the aqueous phase due to consumption by aqueous complexing and extraction. Similarly, the lowering of the cobalt K_d with increasing nickel concentration reflected consumption of available thiocyanate by aqueous nickel complexing. Thus the separation factor improved when the concentration of either metal ion was lowered.

The first three results under "back-extraction experiments" in Table I show the behavior on washing a freshly extracted cobalt-rich organic phase with various solutions. Hexone phases which had been previously equilibrated with an aqueous solution 0.35 M in cobalt, 0.35×10^{-3} M in nickel and 5 M in thiocyanate at 1° were washed with solutions of thiocyanate at different concentrations and temperatures. Best results were obtained by washing with a 5 M thiocyanate solution at 1°, and as in the case of the first extraction, better results were obtained with sodium than with ammonium thiocyanate.

While NaSCN gave better separation factors than NH$_4$SCN, NaSCN had the disadvantage of contaminating the purified cobalt salt with large amounts of sodium. When an aqueous phase 0.35 M in cobalt, 0.35×10^{-3} M in nickel and 5 M in Na^{22}-labeled NaSCN was extracted at 1° with hexone, 13% of the sodium extracted making the sodium concentration in the organic phase about twice that of the cobalt. This could be interpreted as meaning that the extracting species was Na$_2$Co(SCN)$_4$. While NH$_4$SCN also extracted, it could be destroyed easily by evaporating the organic phase over H$_2$SO$_4$ which decomposed both the thiocyanate and ammonium ion on fuming.

The best procedure for purifying a cobalt salt is thus to start with cobalt nitrate, extract a solution 0.35 M in cobalt and 5 M in NH_4SCN with hexone at 1°, wash this once with 5 M NH_4SCN at 1° and evaporate the organic phase to dryness over H_2SO_4. With quantitative recovery of the organic phases, this procedure will yield more than 99.5% of the original cobalt with the nickel impurity reduced by a factor of 10^4. Recycling will give higher purifications.

The thiocyanate–hexone extraction has also been used in this Laboratory for the separation of carrier-free Ni^{57} tracer from proton-bombarded cobalt. Very high specific activity can be obtained if the cobalt target is first purified of nickel as described above.

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Infrared Absorption Spectra of Inorganic Coordination Complexes. VI. The Molecular Structure of 1,2-Dimethylmercaptoethane and its Metal Chelate Compounds[1]

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1,2-Dimethylmercaptoethane, $H_3CSCH_2CH_2$-SCH_3, has several axes of internal rotation and, therefore, may exist in several molecular forms in the liquid state.[3] However, this molecule cannot exist in the extended form as a chelate ligand in coordination compounds. Therefore, marked differences in the absorption spectra are to be expected for the free organic compound and for the ligand in its metal complexes.

This study was carried out to investigate spectral differences between the free molecule and the molecule coördinated about a metal ion in order to contribute to the knowledge of the geometrical role of chelated ligands, having internal rotation axes, in metal complexes.

Experimental

Preparation of Compounds. 1,2-Dimethylmercaptoethane.—This compound was prepared according to the method of Morgan and Ledbury.[4] The product was a colorless liquid boiling at 181°, at atmospheric pressure.

Anal. Calcd. for $C_4H_{10}S_2$: S, 52.46; C, 39.29; H, 8.24. Found: S, 52.47; C, 39.11; H, 8.21.

Dichloro-(1,2-dimethylmercaptoethane)-platinum (II).—This compound was prepared according to the method of Tschugaeff.[5] The bright yellow product was recrystallized from hot water.

Anal. Calcd. for $Pt(C_4H_{10}S_2)Cl_2$: C, 12.39; H, 2.54; Cl, 18.25. Found: C, 12.43; H, 2.85; Cl, 18.05.

Dichloro-(1,2-dimethylmercaptoethane)-palladium (II).—This compound was prepared according to the directions of Morgan and Ledbury.[4] The dark orange product was recrystallized from hot water.

Anal. Calcd. for $Pd(C_4H_{10}S_2)Cl_2$: C, 16.02; H, 3.36; Cl, 23.65. Found: C, 16.13; H, 3.53; Cl, 23.54.

Dichloro-(1,2-dimethylmercaptoethane)-copper (II).—This compound was prepared according to the directions of Morgan and Ledbury.[4] The dark green product was recrystallized from hot alcohol as fine needles.

Anal. Calcd. for $Cu(C_4H_{10}S_2)Cl_2$: C, 18.71; H, 3.93; Cl, 27.63. Found: C, 18.76; H, 3.92; Cl, 27.68.

Dichloro-(1,2-dimethylmercaptoethane)-mercury (II).—This compound was prepared according to the directions of Morgan and Ledbury.[4] The white crystalline powder was recrystallized from hot alcohol in the form of white needles.

Anal. Calcd. for $Hg(C_4H_{10}S_2)Cl_2$: C, 12.20; H, 2.56; Cl, 18.01. Found: C, 12.48; H, 2.76; Cl, 18.41.

Diiodo-(dimethylmercaptoethane)-cadmium (II).—This compound was prepared according to the directions of Morgan and Ledbury.[4] The white product recrystallized from hot alcohol in the form of colorless prisms.

Anal. Calcd. for $Cd(C_4H_{10}S_2)I_2$: C, 9.85; H, 2.06; I, 51.96. Found: C, 10.15; H, 2.28; I, 52.39.

Bis-(1,2-dimethylmercaptoethane)-nickel(II) Thiocyanate.—This compound was prepared according to the directions of Tschugaeff.[6]

Anal. Calcd. for $[Ni(C_4H_{10}S_2)_2](SCN)_2$: C, 28.57; H, 4.80; N, 6.67. Found: C, 28.72; H, 4.94; N, 6.77.

Apparatus and Procedure.—All spectra were obtained by means of Perkin–Elmer model 21 recording infrared spectrophotometer, employing a NaCl prism. The liquid and solid state spectra of 1,2-dimethylmercaptoethane were obtained from thin films of the compound contained in a low temperature cell similar to that described by Wagner and Horning.[7] The spectra of the solid complexes were obtained by means of the KBr disk technique[8] and checked by measurements in nujol mulls.

Experimental Results

The infrared frequencies of both the liquid and the solid states of 1,2-dimethylmercaptoethane are shown in Table I.

TABLE I[a]

INFRARED FREQUENCIES IN CM.$^{-1}$ OF 1,2-DIMETHYLMERCAPTOETHANE

Solid state	Liquid state	Solid state	Liquid state
2910 s	2925 s	. .	1010 m sh
2300 vw	2350 vw	964 vs	958 vs
2010 vw	1970 vw	. .	900 w
1430 vs	1430 vs	. .	840 m
1320 m	1323 m	735 vs	736 vs
. .	1270 s	728 vs sh	. .
1210 vs	1203 vs	678 vs	682 vs
1137 s	1136 s		

^{a} Abbreviations: s = strong; m = medium; w = weak; v = very; sh = shoulder.

The infrared frequencies of metal complexes containing 1,2-dimethylmercaptoethane as a ligand are shown in Table II.

Discussion of Results

A comparison of the spectra of 1,2-dimethylmercaptoethane in the liquid state with the solid state shows that the former has more absorption peaks. The number of peaks observed in the spectrum of the ligand in the solid state are not so numerous as to be incapable of assignment upon the basis of a single molecular form. This form is probably the extended form.[3]

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