in which the metal assumes a higher coördination number without an accompanying dissociation of the solvate into ions. On the other hand, the polarity of the Cd–X and Pb–X bonds decreases with the decreasing electronegativity (and increasing radius) of the halide; this makes the base displacement (eq. 7) of the halide by HOAc (or by OAc^- from the solvent) become easier with increasing atomic number of the halide. The well known order of decreasing base strength of the halides, *i.e.*, $Cl^- > Br^- > I^-$ in glacial acetic acid, makes the influence of base displacement upon the solubility the more probable mechanism.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Selenocyanate Complexes of Cobalt(II)

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The preparation and characterization of seven selenocyanate complexes of Co(II) are described. It is shown that the compounds $[(CH_3)_4N]_2[Co(NCSe)_4]$ and $[(C_6H_5)_4As]_2[Co(NCSe)_4]$ have the structures implied by the formulas as written. The $[Co(NCSe)_4]^{2-}$ ion has four N atoms tetrahedrally arranged about Co(II) and it is shown from the spectra and magnetic moments that –NCSe is very close to but slightly stronger than –NCS in the spectrochemical series. $HgCo(NCSe)_4$ is shown by X-ray study to be isomorphous with $HgCo(NCS)_4$ and it is found that the attachment of Hg to the selenium atoms has the effect of somewhat increasing the strength of the ligand field at the Co, as was the case in the analogous NCS complex. $Co[(C_6H_5)_3PO]_2(NCSe)_2$ and $Co(C_9H_7N)_2(NCSe)_2$ are also tetrahedral. With pyridine the octahedral complex $Co(py)_4(NCSe)_2$ has been obtained and is isomorphous with $Co(py)_4(NCS)_2$, which is known to have a *trans*-octahedral structure. $Co[(C_6H_5)_3P]_2(NCSe)_2$ has a magnetic moment per Co of only 3.4 B.M. and it is proposed that it has a structure containing equal numbers of octahedrally coördinated, low spin Co(II) ions and tetrahedrally coördinated, high-spin Co(II) ions. The CN stretching frequencies of these complexes also are reported. It appears that the variations parallel those known for the thiocyanate ions, $-NCSe^-$ groups absorbing in the range 2040–2080 cm.$^{-1}$ and bridging, *i.e.*, $-NCSe^-$– groups absorbing at frequencies well over 2100 cm.$^{-1}$.

Introduction

In view of the results recently reported from this Laboratory on thiocyanate complexes of cobalt(II),[2] it seemed appropriate to explore the possibility of making their selenocyanate analogs. This paper reports the preparation and properties of seven such compounds. Recently, preliminary communications from other laboratories[3] have described several compounds in this class. Turco, *et al.*, reported the isolation and partial characterization of one compound containing the $[Co(NCSe)_4]^{2-}$ ion and indicated the existence of $HgCo(NCSe)_4$. Nelson has reported the compounds $Co(py)_2(NCSe)_2$ and $Co\ (py)_4(NCSe)_2$.

Experimental

Preparation of Compounds.—Potassium selenocyanate was prepared by the method of "Inorganic Syntheses."[4]

$Co(C_5H_5N)_4(NCSe)_2$.—A solution of Co(II) selenocyanate (0.01 mole) in absolute ethanol (50 ml.) was prepared by mixing stoichiometric quantities of $Co(NO_3)_2 \cdot 6H_2O$ and KNCSe and filtering the precipitated KNO_3. This solution was treated with 3.3 ml. (3.2 g., 0.04 mole) of pyridine and the resulting tan precipitate was filtered, washed with ethyl ether, and dried *in vacuo* over silica gel; yield, 4.8 g. (82%).

$[(CH_3)_4N]_2[Co(NCSe)_4]$.—A solution of Co(II) selenocyanate (0.01 mole) was prepared as above. A solution of $[(CH_3)_4N]NCSe$ was prepared by dissolving $(CH_3)_4NCl$ (2.2 g., 0.02 mole) in 40 ml. of hot absolute ethanol, adding a solution of KNCSe (3.2 g., 0.02 mole) in 15 ml. of absolute ethanol, and filtering the warm solution. The solution of $[(CH_3)_4N](NCSe)$ was added to the cobalt selenocyanate solution and the precipitate, which appeared promptly, was filtered, washed with ethanol and

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(1) (a) Alfred P. Sloan Foundation Fellow; (b) National Science Foundation Predoctoral Fellow.

(2) F. A. Cotton, D. M. L. Goodgame, M. Goodgame, and A. Sacco, *J. Am. Chem. Soc.*, **83**, 4157 (1961).

(3) (a) A. Turco, C. Pecile, and M. Niccolini, *Proc. Chem. Soc.*, 213 (1961); (b) S. M. Nelson, *ibid.*, 372 (1961).

(4) W. C. Fernelius, Ed., "Inorganic Syntheses," Vol. 2, McGraw-Hill Book Co., New York, N. Y., 1946, p. 186.

TABLE I

FORMULAS, COLORS, AND ANALYTICAL DATA[a] FOR THE NCSe⁻ COMPLEXES

			Analyses					
			C		H		N	
Compound	Color	M.p.	Calcd.	Found	Calcd.	Found	Calcd.	Found
$Co(C_5H_5N)_4(NCSe)_2$	Tan	>310	45.14	45.3	3.44	3.6	14.36	13.3
$[(CH_3)_4N]_2[Co(NCSe)_4]$	Green	~140 d	22.98	23.4	3.86	4.0	13.40	13.2
$[(C_6H_5)_4As]_2[Co(NCSe)_4]$	Green	223–224	50.14	50.8	3.24	3.4	4.50	4.2
$HgCo(NCSe)_4$	Blue-green	~150 d	7.07	7.27	0	0.2	8.25	8.1
$Co(C_9H_7N)_2(NCSe)_2$	Green	~150 d	45.56	46.5	2.68	2.8	10.63	10.6
$Co[(C_6H_5)_3PO]_2(NCSe)_2$	Blue	184 d	55.29	55.1	3.66	3.7	3.39	3.3
$Co[(C_6H_5)_3P]_2(NCSe)_2$	Green	~160 d	57.52	58.4	3.81	4.1	3.53	3.2

[a] Microanalyses by S. M. Nagy, M.I.T.; Schwarzkopf Microanalytical Laboratories, Long Island, N. Y.; and Galbraith Laboratories, Knoxville, Tennessee.

then ethyl ether, and dried *in vacuo;* yield, 3.4 g. (54%).

$[(C_6H_5)_4As]_2[Co(NCSe)_4]$.—A solution of $CoCl_2 \cdot 6H_2O$ (0.005 mole) in 25 ml. of absolute ethanol was treated with an ethanolic solution (25 ml.) of KNCSe (3.0 g., 0.01 mole) and the KCl filtered off. A solution of $[(C_6H_5)_4As]NCSe$ (0.01 mole), prepared in 80 ml. of absolute ethanol by mixing stoichiometric quantities of $(C_6H_5)_4AsCl$ and KNCSe and filtering the KCl, was added to the first solution. The resulting precipitate was filtered, slurried several times with water, washed twice with ethanol, and dried *in vacuo* over silica gel; yield, 4.0 g. (73%).

$HgCo(NCSe)_4$.—A solution of $Hg(NO_3)_2 \cdot 2H_2O$ (3.0 g., 0.01 mole) and $Co(NO_3)_2 \cdot 6H_2O$ (2.8 g., 0.01 mole) in 60 ml. of water was prepared, using a few drops of concentrated HNO_3 to aid dissolution of the $Hg(NO_3)_2 \cdot 2H_2O$. This solution was treated with KOH until a permanent turbidity developed, and filtered. A solution of KNCSe (5.4 g., 0.04 mole) in 40 ml. of water was made basic with 1.2 g. of KOH and filtered. The solution containing Hg(II) and Co(II) was added with stirring to the KNCSe solution. A tan precipitate formed immediately but rapidly turned green. (Only this tan precipitate was obtained unless base was added to the KNCSe solution. It was not further investigated.) The green precipitate was filtered, washed twice with water, twice with ethanol and once with ether, and then dried *in vacuo* over silica gel; yield, 3.6 g. (56%).

$Co(C_9H_7N)_2(NCSe)_2$.—To a solution of Co(II) selenocyanate (0.01 mole), prepared as above, was added 3 ml. (2.9 g., 0.02 mole) of quinoline and the solution placed in a refrigerator freezer compartment overnight. The resulting precipitate then was filtered, washed with ethyl ether, and dried *in vacuo* over silica gel; yield, 4.6 g. (87%).

$Co[(C_6H_5)_3PO]_2(NCSe)_2$.—A solution of Co(II) selenocyanate (0.01 mole) in absolute ethanol (25 ml.) was added to a solution of triphenylphosphine oxide (5.56 g., 0.02 mole) in ethyl acetate (35 ml.). In some instances blue crystals were obtained from this blue solution by cooling in a refrigerator for several hours. In other instances a product was obtained only on connecting the vessel to a trap cooled in liquid nitrogen and removing half or more of the solvent. The product was filtered, washed with ethyl acetate, and dried *in vacuo* over sulfuric acid; yields, 0.5–1.0 g. (~10%).

$Co[(C_6H_5)_3P]_2(NCSe)_2$.—A solution of cobalt(II) selenocyanate (0.01 mole) in absolute ethanol (40 ml.) was added to a solution of triphenylphosphine (5.24 g., 0.02 mole) in ethyl acetate (12 ml.). A green solid was immediately formed and was filtered, washed with cold ethanol, and dried *in vacuo* over sulfuric acid; yield, 7.5 g. (95%).

$Co(C_9H_7N)_2(NCS)_2$.—This compound was prepared for comparison with the corresponding selenocyanate complex. Quinoline (5 ml.) was added to a solution of cobalt(II) thiocyanate (0.02 mole, prepared from the theoretical quantities of cobalt nitrate and potassium thiocyanate and used *in situ*) in absolute ethanol (60 ml.). Blue crystals formed immediately and after 2 hr. they were filtered, washed with absolute ethanol, and dried *in vacuo* over concentrated H_2SO_4; yield, 6.55 g. (76%); m.p., 216°.

Anal. Calcd. for $C_{20}H_{14}N_4S_2Co$: C, 55.42; H, 3.26; N, 12.93. Found: C, 55.25; H, 3.23; N, 13.02.

$Co[(C_6H_5)_3AsO]_2(NCSe)_2$ (Attempted).—This compound was not obtained in a pure state, but the following procedure and minor variations of it gave what are probably impure smples: Cobalt selenocyanate (0.005 mole, prepared as before) in absolute ethanol (17 ml.) was added to a solution of a slight excess of triphenylarsine oxide in the same solvent. A blue solid precipitated immediately; however, it was sticky and remained so after washing with absolute ethanol and it was difficult to filter; yield, 3.52 g. It is quite possible that a suitable solvent could be found for recrystallization, but this was not attempted.

Anal. Calcd. for $C_{38}H_{30}O_2N_2Se_2As_2Co$: C, 49.97; H, 3.31; N, 3.07. Found (separate preparations): C, 52.3, 53.4; H, 3.5, 3.5; N, 2.6, 2.9.

Visible Spectra.—These were measured from 400–2100 mμ using a Cary Model 14 recording spectrophotometer. Mulls in hexachlorobutadiene were prepared by hand grinding in an agate mortar.

Infrared Spectra.—These were measured in Nujol mulls using a Baird recording spectrometer equipped with a fluorite prism. Polystyrene film was used for calibration.

Magnetic Measurements.—These were made with a Gouy balance using $HgCo(NCS)_4$ for calibration as previously described.[2] Measurements were made at liquid nitrogen (~77°), Dry Ice–acetone (~195°), and room temperatures (~300°); each compound was measured with three packings of the tube. The temperature was measured to ±0.2° in each individual case. The measured molar susceptibility values were corrected for diamagnetism, using Pascal's constants, and for temperature-independent paramagnetism (TIP). The TIP was computed using the relation TIP $= 2.09/\Delta$, the Δ values being those listed in Table III. The reciprocals of the fully corrected molar susceptibility values then were plotted against temperature and from the best straight line

TABLE II

X-RAY CRYSTALLOGRAPHIC DATA FOR $HgCo(NCS)_4$ AND $HgCo(NCSe)_4$

$HgCo(NCS)_4$ Tetragonal $a = 11.09$ Å. $c = 4.37$ Å.				$HgCo(NCSe)_4$ Tetragonal $a = 11.29$ Å. $c = 4.67$ Å.			
$d_{obsd.}$[a]	Intensity	Indices	$d_{calcd.}$	$d_{obsd.}$[a]	Intensity	Indices	$d_{calcd.}$
7.84(β)	vs	110	7.84	7.97(β)	vs	110	7.98
5.55(β)	vs	200	5.55	5.65(β)	vs	200	5.65
4.09	s	101	4.07	4.32	s	101	4.32
3.94	s	220	3.94	4.00	s	220	4.00
3.50	m	310	3.51	3.57	m	310	3.57
3.29(β)	s	211	3.28	3.43(β)	vs	211	3.43
2.83	s	301	2.82	2.94	s	301	2.94
2.77	vw	400	2.77				
2.61	m	330	2.61	2.66	m	330	2.66
2.52	s	321	2.52	2.60	s	321	2.60
2.48	s	420	2.48	2.53	s	420	2.52
2.30	m	411	2.29				
2.20	w	002, 500	2.19, 2.22				
2.11	w	112	2.11	2.25	s	112	2.24
				2.22	w	421	2.22
2.04	w	202	2.03	2.16	w	202	2.16
				2.04	m	431, 501	2.04
				2.00	m	302	1.99

[a] (β) indicates CuKβ reflection also observed.

through these points the quantities μ and θ in the Curie–Weiss equation, $\mu = 2.84\ [\chi_M^{corr}\ (T - \theta)]^{1/2}$, were evaluated. In all cases the experimental points defined straight lines within the experimental uncertainties. The values of μ and θ are believed to have uncertainties of ± 0.05 B.M. and $\pm 2°$, respectively. Actual susceptibility values can be recovered from the data given by using the Curie–Weiss equation and the data in Table VI.

X-Ray Powder Diagrams.—These were obtained photographically using the standard Phillips X-ray generator and powder camera, with nickel-filtered copper radiation.

Electrolytic Conductances.—These were measured for the two ionic compounds in nitrobenzene solution (approximately 0.001 *M*) using a Serfass conductivity bridge. The results, given below, indicate that they are indeed 1:2 electrolytes on comparison with the range (38–60 ohm^{-1}) of literature values[5] for similar compounds

$[(C_6H_5)_4As]_2[Co(NCSe)_4]$: 43 ohm^{-1} mole^{-1} at 25°
$[(CH_3)_4N]_2[Co(NCSe)_4]$: 61 ohm^{-1} mole^{-1} at 26°

Discussion

X-Ray Data.—X-Ray powder diffraction patterns were recorded for all of the compounds reported here and comparisons made with analogous thiocyanate compounds.

It has been found that the two mercury compounds $HgCo(NCSe)_4$ and $HgCo(NCS)_4$ are isomorphous. The structure of $HgCo(NCS)_4$ has been determined by Jeffrey.[6] Table II gives a comparison of the powder lines for the two substances together with indices and unit cell dimensions. While the resemblance of the powder photographs of these two compounds is quite obvious, there are certain small differences in relative intensities and a few non-matching lines. Table II shows, however, that all lines observed in both patterns can be satisfactorily indexed. The increase in lattice parameters for the NCSe compound is entirely reasonable in relation to the difference in the covalent radii (~ 0.2 Å.) of S and Se.

For the two compounds $Co(py)_4(NCS)_2$ and $Co(py)_4(NCSe)_4$ X-ray powder diagrams also show isomorphism conclusively by actual indexing of all observed lines in $Co(py)_4(NCSe)_2$ using the structural data reported by Antsyshkina and Porai-Koshits[7] for $Co(py)_4(NCS)_2$ (Table III). Thus it is established that the selenocyanate compound possesses a *trans*-octahedral structure with the NCSe groups coördinated to cobalt through the nitrogen atoms.

It also has been shown by comparison of powder patterns, but without indexing since the structures have not been reported for the NCS complexes, that $[(CH_3N)_4N]_2[Co(NCSe)_4]$, $Co(C_9H_7N)_2(NCSe)_2$, and $Co[(C_6H_5)_3PO]_2(NCSe)_2$ are isomorphous with their thiocyanate analogs. The observed *d* values are given in Table IV.

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(5) R. S. Nyholm, *et al.*, *J. Chem. Soc.*, 1767 (1951); 4375 (1956); 3997 (1959).

(6) J. W. Jeffrey, *Nature*, **159**, 610 (1947).

(7) A. S. Antsyshkina and M. A. Porai-Koshits, *Soviet Phys.-Cryst.*, **3**, 684, 694 (1959).

Table III

X-Ray Crystallographic Data for $Co(py)_4(NCSe)_2$ and $Co(py)_4(NCS)_2$

$Co(py)_4(NCS)_2$

$a = 12.44$
$b = 13.00$
$c = 16.57$ $\beta = 118°32'$

$Co(py)_4(NCSe)_2$

$a = 12.75$
$b = 13.25$
$c = 16.70$ $\beta = 120°$

$Co(py)_4(NCS)_2$				$Co(py)_4(NCSe)_2$			
$d_{obsd.}$	Intensity	Indices	$d_{calcd.}$	$d_{obsd.}$	Intensity	Indices	$d_{calcd.}$
				8.95	w	111	8.94
8.36	s	110	8.37	8.44	m	110	8.46
7.28	m	002	7.28	7.21	s	002	7.20
6.87	m	112	6.88	6.91	m	112	6.95
6.51	w	020	6.50	6.62	w	020	6.60
5.94	w	202	5.94				
5.46	w	200	5.46	5.52	w	200	5.51
				4.90	vw	022	4.87
4.49	s	221	4.48	4.56	s	221	4.56
4.39	s	222	4.39	4.44	w	222	4.47
4.08	s	131	4.07	4.15	s	131	4.14
3.96	m	223	3.96	4.01	s	223	4.03
3.85	s	311	3.84	3.89	s	311	3.90
3.62	s	004	3.64	3.64	s	004	3.60
3.39	w	133	3.41	3.44	m	133	3.44
3.15	s	041	3.17				
3.03	w	332	3.00				
				3.01	w	042	3.00

It may be noted that the essential identity of the powder pictures of the pairs of compounds is very striking when they are compared visually and there can scarcely be any doubt of the isomorphisms. Since it has been established[2] in $[(CH_3)_4N]_2[Co(NCS)_4]$ that the anions are tetrahedral with nitrogen atoms bound to the cobalt, the isomorphism shows that the selenocyanate complex contains, analogously, $[Co(NCSe)_4]^{2-}$ anions which are tetrahedral with Co–N bonds. It also has been shown by spectral and magnetic data[2] that $Co[(C_6H_5)_3PO]_2(NCS)_2$ molecules are tetrahedral with N-bonded NCS groups and therefore it may be inferred that $Co[(C_6H_5)_3PO]_2(NCSe)_2$ molecules are tetrahedral with N-bonded NCSe groups. $Co(C_9H_7N)_2(NCS)_2$ has been investigated recently in this Laboratory[8] and it has been shown that these molecules are tetrahedral with N-bonded NCS groups; hence it may be inferred that $Co(C_9H_7N)_2(NCSe)_2$ is analogously constituted.

Table IV also gives the X-ray powder data for $Co[(C_6H_5)_3P]_2(SCN)_2$ and $Co[(C_6H_5)_3P]_2(NCSe)_2$. These compounds are unquestionably not isomorphous and other data to be discussed later bear this out and provide positive clues to the structural nature of $Co[(C_6H_5)_3P]_2(NCSe)_2$.

Infrared Spectra.—It does not appear that the infrared spectra of coördinated selenocyanate ions have been reported before. Recently[9] a fairly complete spectrum of the selenocyanate ion in KNCSe has been described. The fundamentals appear at 2070 cm.$^{-1}$ (mainly CN stretching, ν_3), 558 cm.$^{-1}$ (mainly CSe stretching, ν_1), and 416, 424 cm.$^{-1}$ (slightly split components of the bending mode, ν_2, which would be doubly degenerate in the unperturbed, linear ion). It appears well established[10] that the CN stretching frequency for the SCN ion varies with its environment in the order M–NCS < M–SCN < M–NCS · · · B. For M–NCS the range appears to be about 2040–2080 cm.$^{-1}$ and for M–SCN about 2080–2120 cm.$^{-1}$. For bridging groups, M–NCS · · · B, the range is rather broad depending on the strength of the S · · · B interaction (B is a cation or other electrophilic species). For example, in $(NH_4)_2Cd(NCS)_4 \cdot 2H_2O$ and $Cu(py)_2(NCS)_2$ the C–N stretching band is found at ~2094 cm.$^{-1}$, in Ag(SCN) it is at 2149 cm.$^{-1}$, and in α-$[Pt[(C_3H_7)_3P](SCN)_2]_2$ it is as high as 2188 cm.$^{-1}$. In view of this variability in the frequency of bridging SCN with the specific nature of its environment, it seems wise to make comparisons between SCN and SeCN frequencies with pairs of compounds which are as closely analogous as

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(8) F. A. Cotton, O. D. Faut, and M. Goodgame, to be published.

(9) H. W. Morgan, *J. Inorg. Nucl. Chem.*, **61**, 367 (1961).

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

TABLE IV

INTERPLANAR SPACINGS IN SEVERAL ANALOGOUS SeCN AND SCN COMPLEXES

$[(CH_3)_4N]_2$-$Co(NCS)_4$	$[(CH_3)_4N]_2$-$Co(NCSe)_4$	$(quin)_2$-$Co(NCS)_2$	$(quin)_2$-$Co(NCSe)_2$	$[(C_6H_5)_3P]_2$-$Co(NCS)_2$	$[(C_6H_5)_3P]_2$-$Co(NCSe)_2$	$[(C_6H_5)_3PO]_2$-$Co(NCS)_2$	$[(C_6H_5)_3PO]_2$-$Co(NCSe)_2$
10.81	11.00	7.73	7.93	9.82	8.86	10.38	10.50
7.88	7.99	7.38		8.99	7.40	8.74	8.78
	6.36	6.98	7.09	7.57	6.63		7.00
5.53	5.55	6.71		6.05	6.31	6.70	6.72
4.95	4.97		5.83	5.66	5.46		5.83
4.49	4.56	5.37	5.57	5.09	4.68		5.48
	4.29		5.35	4.56	4.45		5.25
3.88	3.92		5.10	4.43	4.37		4.86
3.67		4.25	4.34	4.27	4.24	4.56	4.58
2.68	2.81	4.09	4.19	4.12	4.00		4.42
2.53	2.51	3.95		3.77	3.69	4.29	4.30
2.25	2.27	3.85	3.97	3.61	3.56	4.04	4.08
		3.68		3.47	3.45	3.52	3.55
		3.47	3.54	3.26	3.34		3.44
		3.34	3.45	2.79	3.24	3.31	3.33
		3.22	3.34	2.49	3.08	3.24	3.26
		3.16			3.03	3.16	3.18
			3.00		2.94		2.90
		2.73	2.82		2.70		2.81
					2.55		
					2.32		

TABLE V

CN STRETCHING FREQUENCIES[a] OF SOME $NCSe^-$ AND NCS^- COMPLEXES OF Co(II)

$NCSe^-$ Complexes		CNS^- Complexes	
Compound	Cm.$^{-1}$	Compound	Cm.$^{-1}$
$[(CH_3)_4N]_2[Co(NCSe)_4]$	2075	$[(CH_3)_4N]_2[Co(NCS)_4]$	2075
$[(C_6H_5)_4As]_2[Co(NCSe)_4]$	2062	$K_2[Co(NCS)_4]$	2066
$Co(C_9H_7N)_2(NCSe)_2$	2070, 2037	$Co(C_9H_7N)_2(NCS)_2$	2062, 2045
$Co[(C_6H_5)_3PO]_2(NCSe)_2$	2066	$Co[(C_6H_5)_3AsO]_2(NCS)_2$	2070
$Co(C_5H_5N)_4(NCSe)_2$	2073	$Co(C_5H_5N)_4(NCS)_2$	2072
$HgCo(NCSe)_4$	2146	$HgCo(NCS)_4$	2141
$Co[(C_6H_5)_3P]_2(NCSe)_2$	2165, 2137, ~2070sh	$Co[(C_6H_5)_3P]_2(NCS)_2$	2040

[a] All data reported here were obtained on Nujol mulls of the solid compounds using a spectrometer equipped with a fluorite prism.

possible although we might expect a fairly general parallel for the two series.

Table V lists the observed CN frequencies of the SeCN complexes of cobalt(II) which we have studied together with data for some analogous or similar SCN compounds. It can be seen that the variation in the CN frequencies follows a similar pattern in the two groups of compounds. The CN frequencies for compounds in which it is believed that the selenocyanate ions are N-bonded and non-bridging are all within ±10 cm.$^{-1}$ of those in analogous or similarly constituted thiocyanate complexes. On the basis of the X-ray data discussed above the compounds in this category are the two salts of $[Co(NCSe)_4]^{2-}$, $Co(C_9H_7N)_2(NCSe)_2$, $Co[(C_6H_5)_3PO]_2(NCSe)_2$, and $Co(C_5H_5N)_4(NCSe)_2$.

For $HgCo(NCSe)_4$ the CN stretching frequency is quite high and nearly the same as that in $HgCo(NCS)_4$. Since these two compounds are isomorphous and contain bridging NCSe and NCS units, these data suggest that bridging NCSe groups, like bridging NCS groups, tend to have much higher CN stretching frequencies than non-bridging, N-bonded groups.

It already has been mentioned that the X-ray powder pattern for $Co[(C_6H_5)_3P]_2(NCSe)_2$ shows that it is not isostructural with the stoichiometrically analogous thiocyanate compound. That the difference is more fundamental than a mere difference in packing of molecules in the crystal is shown by the marked dissimilarity in the infrared spectra of the two compounds. The selenocyanate complex has two pronounced bands at high frequencies, suggesting that bridging NCSe groups are present, and a small but real shoulder at ~2070 cm.$^{-1}$, which probably implies that non-bridging groups are present. These conclusions will be further analyzed when the magnetic and spectroscopic data are considered.

Magnetic and Spectral Data.—The data for all of the compounds considered to contain tetrahedral cobalt(II) are collected in Table VI, and some representative spectra are shown in Fig. 1.

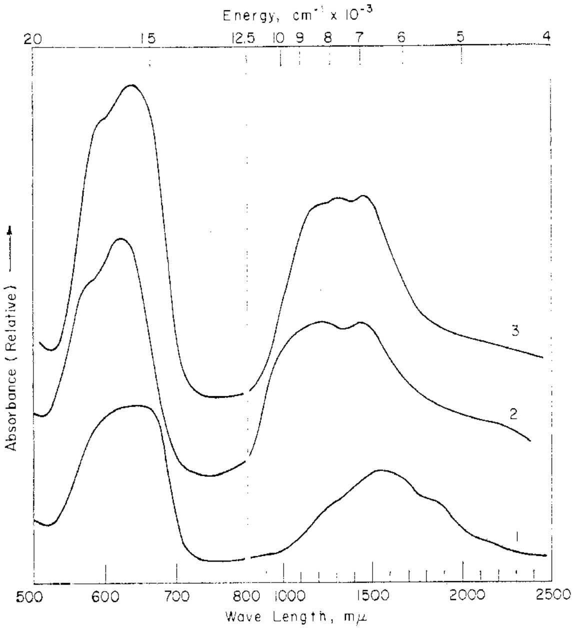

Fig. 1.—Some representative electronic absorption spectra. Those shown are all taken on the solid compounds mulled in hexachlorobutadiene: (1) $Co[(C_6H_5)_3PO]_2(NCSe)_2$; (2) $HgCo(NCSe)_4$; (3) $[(C_6H_5)_4As]_2[Co(NCSe)_4]$.

The general appearance of the spectra of all of the compounds in Table VI was quite similar to that of other tetrahedral Co(II) complexes[2, 11] in regard to band positions, band shapes, and, where solution measurements could be made, band intensities. For $[Co[(C_6H_5)_3P]_2(NCSe)_2]$ there was very strong absorption rising into the ultraviolet, with the bands cited in Table VI situated on this steeply rising edge. Using the Tanabe and Sugano equations as before,[12] the crystal field parameters, Δ, were calculated from the energies of ν_2 and ν_3 given in Table VI and are listed there also.

We turn first to the three compounds containing $[Co(NCSe)_4]$ groups. The spectra alone strongly indicate that the selenocyanate ions are N-bonded, in agreement with the X-ray work. The Δ value obtained from the spectra of the two ionic $[Co(NCSe)_4]^{2-}$ compounds, 4710–4720 cm.$^{-1}$, may be compared with the Δ value of 4550 cm.$^{-1}$ previously reported[2] for $[Co(NCS)_4]^{-2}$. It thus appears that under comparable conditions N-bonded selenocyanate ion makes a slightly greater contribution to the ligand field, that is lies a little more toward the strong end of the spectrochemical series, than does N-bonded NCS. For $HgCo(NCSe)_4$, Δ is about 6% greater than for the two ionic compounds in which the selenium atoms are essentially free. This is quite analogous to what was found for the corresponding thiocyanate compounds,[2] namely, that the attachment of the sulfur atom to the mercury atoms significantly enhances the strength of the ligand field produced by the nitrogen atoms at the cobalt.

For $Co(C_9H_7N)_2(NCSe)_2$ the X-ray work has shown that it is isomorphous with the corresponding thiocyanate compound, which has been shown to contain cobalt tetrahedrally coördinated by the two quinoline nitrogens and by two N-bonded NCS groups.[8] The magnetic moment and Δ value for $Co(C_9H_7N)_2(NCSe)_2$ are entirely consistent with its having a similar structure, since the position of $-NCSe^-$ has been shown to be slightly higher in the spectrochemical series than that of $-NCS^-$.

Similarly, $Co[(C_6H_5)_3PO]_2(NCSe)_2$ is found from the X-ray work to be isomorphous with $Co[(C_6H_5)_3PO]_2(NCS)_2$ and magnetic and spectral data already have been reported[2] to show that the latter compound has a tetrahedral structure with N-bonded thiocyanate ions. The Δ values for the NCSe and NCS compounds, 4120 and 4030 cm.$^{-1}$, are consistent with the location of $-NCSe^-$ a little higher than $-NCS^-$ in the spectrochemical series. We also may invoke the average ligand field concept and compare the Δ value of 4120 cm.$^{-1}$ in $Co[(C_6H_5)_3PO]_2(NCSe)_2$ with the average of the Δ values[11] in $[Co[(C_6H_5)_3PO]_4]^{2+}$, 3680 cm.$^{-1}$, and $[Co(NCSe)_4]^{2-}$, 4715 cm.$^{-1}$, which is 4200 cm.$^{-1}$.

The magnetic moment of the $[Co(NCSe)_4]^{2-}$ ion is 4.45 and 4.55 B.M. in the two compounds studied. The average of these, 4.50 B.M., is 0.1 B.M. higher than the moment reported[2] for the $[Co(NCS)_4]^{2-}$ ion. Similarly, the moment for $Co[(C_6H_5)_3PO]_2(NCSe)_2$, 4.57 B.M., is about 0.1 B.M. higher than that reported[2] for its NCS analog, 4.46 B.M. These differences are about equal to the total estimated experimental errors,

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[11] F. A. Cotton, D. M. L. Goodgame, and M. Goodgame, *J. Am. Chem. Soc.*, **83**, 4690 (1961), and prior references cited therein.

[12] F. A. Cotton and M. Goodgame, *ibid.*, **83**, 1777 (1961).

TABLE VI

SPECTROSCOPIC AND MAGNETIC DATA AND LIGAND FIELD STRENGTH PARAMETERS FOR SELENOCYANATE COMPLEXES OF Co(II)

		Spectral data					Magnetic data		
		ν_3		ν_2					
Compound	Medium	Cm.$^{-1}$	ϵ	Cm.$^{-1}$	ϵ	Δ, cm.$^{-1}$	μ, B.M.	θ, °K.	λ, cm.$^{-1}$
$[(CH_3)_4N]_2[Co(NCSe)_4]$	C_4Cl_6 mull	15,900	...	8000	...	4710			
	CH_3NO_2 soln.	16,000	1970	7840	290	...	4.45	−8	169
$[(C_6H_5)_4As]_2[Co(NCSe)_4]$	C_4Cl_6 mull	15,670	...	8000	...	4720			
	CH_3NO_2 soln.	16,000	1950	7840	290	...	4.55	−9	200
$HgCo(NCSe)_4$	C_4Cl_6 mull	16,000	...	8400	...	4980	4.34	−5	144
$Co(C_9H_7N)_2(NCSe)_2$	C_4Cl_6 mull	16,290	...	9340	...	5610			
	CH_3CN soln.	16,000	410	8330	62	...	4.39	−7	180
$Co[(C_6H_5)_3PO]_2(NCSe)_2$	C_4Cl_6 mull	16,150	...	6510	...	4120	4.57	−8	180
$Co[(C_6H_5)_3P]_2(NCSe)_2$	C_4Cl_6 mull	16,750	...	8800	...	5150	3.40	−27	...

viz., about 0.05 B.M. in each moment, so that it is possible that they are not significant. However, the fact that the differences are consistently in the same direction would suggest that they perhaps are not entirely due to accumulated random errors. When the moments and Δ values recorded in Table VI are used to calculate[2,11] the effective spin-orbit coupling constant, λ', values for this constant in the range 180 ± 20 cm.$^{-1}$ are obtained. In previous studies it has been found that λ' values in tetrahedral Co(II) complexes are anywhere from 10 to 50 cm.$^{-1}$ below the free ion value ($\sim$ 180 cm.$^{-1}$) and this apparently is true for complexed metal ions in general.[13] We are unable to offer any firm explanation for the apparently anomalous results found in this study. It is hoped that electron spin resonance studies of these and other tetrahedral Co(II) complexes, which will not be subject to various errors which may be incurred in bulk susceptibility measurements, will provide more accurate and reliable values of the magnetic moments and hence a check on the authenticity of these seemingly overlarge λ' values. For the present we believe that they should be viewed with reservations, although the replicated measurements from which they are derived have been made carefully and appear to be trustworthy.

The magnetic moment, 4.34 B.M., for $HgCo(NCSe)_4$ is significantly lower than the mean of the moments, 4.50 B.M., for the compounds containing $[Co(NCSe)_4]^{2-}$ ions with essentially uncoördinated selenium atoms, and nearly the same as the moment for $HgCo(NCS)_4$,[2] 4.32 B.M. This result corroborates the inference from the Δ values that the effect of binding the selenium atoms is to enhance the ligand field provided by the N-coördinated NCSe ions, in complete analogy with the previously reported behavior of the comparable thiocyanate complexes.

The apparent magnetic moment for $Co[(C_6H_5)_3P]_2(NCSe)_2$ provides the most direct indication that this compound has an entirely different constitution from the stoichiometrically analogous thiocyanate compound. The most obvious way to explain the observed moment, 3.40 B.M. (and almost certainly the correct one) is to postulate that the crystalline compound contains both low-spin octahedral and high-spin tetrahedral Co(II). A similar proposal has been made to explain apparent magnetic moments of anomalous magnitude found in some complexes of the type $Co(CNR)_2X_2$[14] and although this proposal was later questioned as to the detailed nature of the non-tetrahedral species,[15] recent work has established its essential correctness.[16] In the present case the nature of the two (at least) species cannot be deduced with much certainty, but the visible and infrared spectra provide some clues. The Δ value shows that the ligands bound to the tetrahedrally coördinated cobalt provide a fairly strong ligand field, somewhat stronger than that provided by four –NCSe groups. Since it has been found previously[17] that triphenylphosphine has a position in the spectrochemical series not much different from though perhaps a bit below that of –NCS, the Δ value for the tetrahedral species in this compound would seem to imply that the coördination sphere of this Co(II) ion must contain three or four –NCSe ions which are bridging to the cobalt in the octahedral species. Such a postulate is in accord with three other

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[13] J. Owen, *Proc. Roy. Soc.* (London), **A227**, 183 (1955); T. M. Dunn, *J. Chem. Soc.*, 623 (1959).

[14] A. Sacco and M. Freni, *Gazz. chim. ital.*, **89**, 1800 (1959).

[15] F. A. Cotton and R. H. Holm, *J. Am. Chem. Soc.*, **82**, 2983 (1960).

[16] A. Sacco and F. A. Cotton, *ibid.*, **84**, 2043 (1962).

[17] F. A. Cotton, O. D. Faut, D. M. L. Goodgame, and R. H. Holm, *ibid.*, **83**, 1780 (1961).

lines of reasoning. First, the infrared spectrum strongly indicates that most if not all selenocyanate ions are bridging. Second, only by use of the NCSe ions as bridges can a sufficient number of coördinate bonds be formed to provide octahedral coördination of some Co(II) ions. Third, unless the coördination of the low-spin Co(II) ions is octahedral rather than planar, the average of the moments, assuming a 1:1 ratio of the two types of Co(II), would significantly exceed the observed value.[18] The high negative θ is similar to those found in the isonitrile complexes mentioned earlier. Thus reasonable suppositions as to the species present in this compound would be $[Co[(C_6H_5)_3P](NCSe)_3]$ or $[Co(NCSe)_4]$ for the tetrahedral species and $[Co[(C_6H_5)_3P]_3(SeCN)_3]$ or $[Co[(C_6H_5)_3P]_4(SeCN)_2]$ for the octahedral species.

The X-ray data have shown that $Co(py)_4(NCSe)_2$ is *trans*-octahedral. It has a magnetic moment, μ_{eff}, at 301°K. of 5.06 B.M. When examined in a hexachlorobutadiene mull, it exhibited strong absorption rising into the ultraviolet. A shoulder was observed at $\sim$20,000 cm.$^{-1}$ and a well defined absorption band was found at 9090 cm.$^{-1}$. These observations are consistent with the presence of Co(II) in an octahedral field with a Δ of $\sim$9700 cm.$^{-1}$. Nelson[3b] also has reported the preparation and a magnetic moment (5.1 B.M. at 18°) of this compound and concluded that it is octahedral. He also found that it loses 2py at 70° *in vacuo* to give $Co(py)_2(NCSe)_2$, for which he suggests a polymeric octahedral structure. From the spectrum of the blue-green solution of $Co(py)_2(NCSe)_2$ in nitromethane solution he postulates the presence there of tetrahedral $Co(py)_2(NCSe)_2$ molecules. We would observe, however, that this conclusion is not entirely certain. It has been shown that Co(*p*-toluidine)$_2$(NCS)$_2$ gives a solution in acetonitrile which apparently contains tetrahedral molecules but that in dimethylformamide there is disproportionation to produce $[Co(NCS)_4]^{2-}$ and octahedrally coördinated cations.[19] Thus the mere observation of bands assignable to a tetrahedrally coördinated Co(II) species on the basis of intensity and position does not necessarily identify the tetrahedral species present. It is of course quite possible that Nelson's suggestion is correct.

We find that $Co(py)_4(NCSe)_2$ dissolves in acetonitrile to give a blue-green solution having the following absorption bands (cm.$^{-1}$): $\sim$17,400 sh, 16,160 ($\epsilon = 235$), 8700 ($\epsilon \sim 60$). These data suggest that there is disproportionation or other rearrangement of the molecule to give tetrahedral species. However, the band positions do not agree well with those for $[Co(NCSe)_4]^{2-}$ and the intensities are far too low for the disproportionation.

$$2[Co(py)_4(NCSe)_2] + 2CH_3CN = [Co(py)_4(CH_3CN)_2]^+[Co(NCSe)_4]^{2-}$$

There is, however, a fair resemblance of the spectrum to that of $Co(C_9H_7N)_2(NCSe)_2$, which would suggest that in the acetonitrile solution the following dissociation reaction proceeds appreciably to the right

$$[Co(py)_4(NCSe)_2] = [Co(py)_2(NCSe)_2] + 2py$$

Katzin[20] recently has reported a detailed study of an analogous equilibrium between $Co(py)_2Cl_2$ and $Co(py)_4Cl_2$ in pyridine.

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[18] From the work of B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 12 (1954), it appears that octahedral, low-spin Co(II) ions have moments of 1.8–2.0 B.M. while planar, low-spin Co(II) ions have moments around 2.5 B.M. Assuming a moment of $\sim$4.4 B.M. for the tetrahedrally coördinated cobalt, the apparent moments expected for mixed compounds of the octahedral–tetrahedral and planar–tetrahedral types would be 3.4 and 3.6 B.M., respectively. For the compound $\{Co[(C_2H_5)_2PCH_2CH_2(C_2H_5)_2]\}[CoBr_4]$, E. M. Wymore and J. C. Bailar, *J. Inorg. Nucl. Chem.*, **14**, 42 (1960), report a magnetic moment of 3.7 B.M. at room temperature, consistent with the presence of the planar four-coördinate cation with a magnetic moment of $\sim$2.2 B.M.

[19] F. A. Cotton and R. H. Holm, *J. Am. Chem. Soc.*, **82**, 2983 (1960).

[20] L. I. Katzin, *J. Chem. Phys.*, **35**, 467 (1961).