582. *Tetrahedral Isoselenocyanato-complexes of Cobalt*(II) *and Infrared Spectra of Inorganic Selenocyanates.*

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The preparation of complex tetraselenocyanates of the type $R_2[Co(NCSe)_4]$ where R = $[Et_4N]$ and $[Ph_4As]$ is reported. The conductivity, electronic spectra, magnetic susceptibility, and vibrational spectra of these and related compounds have been studied. The general properties of these compounds are discussed and compared with those of the corresponding thiocyanates. It is concluded that in the ion $[Co(NCSe)_4]^{2-}$ the SeCN groups are tetrahedrally co-ordinated through the nitrogen atoms.

Great interest has recently been shown in the study of the thiocyanate group in co-ordination compounds. The information generally desired relates to the manner in which the bifunctional SCN group is bound to a metal. Infrared spectroscopy and *X*-ray crystallography have given valuable help.[1,2] The bifunctional role of the thiocyanate ion is now well established, there being three ways in which this group can be attached to a metal, namely, M–SCN, M–SCN–M (or M–SCN–M′), and M–NCS. Vibrational

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[1] Turco and Pecile, *Nature*, 1961, **191**, 66, and references therein.
[2] Lewis, Nyholm, and Smith, *J.*, 1961, 4590.

spectra also suggest that a particular metal can change the co-ordination from M–S to M–N, or *vice-versa*, in complexes with SCN and suitable ligands.[1,3]

Surprisingly little work has been done on the corresponding selenocyanates. Information on the latter class of compound is limited almost wholly to compounds of metals with class (*b*) character, such as platinum, palladium, and mercury, for which there can be little doubt that co-ordination is through the selenium atom. Recently, we reported that SeCN must be co-ordinated through the nitrogen atoms when it is the sole ligand in complexes with cobalt(II).[4] Moreover, recent *X*-ray crystallographic work has established the presence of Co–NCSe–Hg bridges in the compound $Co(NCSe)_4Hg$ which has been found to be isomorphous with $Co(NCS)_4Hg$.[5,6] Very recently,[7] it was reported that the cobalt atoms are bridged by SeCN ions in the compound $[Co(py)_2(NCSe)_2]$ (py = pyridine). It thus appears that there is a close correlation between the SeCN and SCN groups with respect to their co-ordinating ability. Also the vibrational behaviour of the two triatomic groups is very similar in inorganic compounds. The types of co-ordination may be differentiated by means of infrared spectra [8] for both classes of compound.

To extend our study of the general properties of the thiocyanate ion in its co-ordination compounds, we have investigated the salts of the tetraselenocyanatocobalt(II) ion, $[Co(NCSe)_4]^{2-}$. The electronic and vibrational spectra together with the magnetic data leave little doubt that, in this anion, the cobalt must be tetrahedrally co-ordinated to the nitrogen atoms.

Bluish-green crystals, $[Ph_4As]_2[Co(NCSe)_4]$, are precipitated from ethanol solutions of cobaltous chloride containing potassium selenocyanate on addition of tetraphenylarsonium chloride. The corresponding tetraethylammonium salt can be obtained in a similar way. The molar conductivities of these compounds are given in Table 1, together with those of the corresponding thiocyanates. The conductivity data correspond well with those of similar electrolytes in the same solvent,[9] indicating that all compounds are uni-bivalent electrolytes in the solvent used.

TABLE 1.

Molar conductivities of tetraselenocyanato- and tetrathiocyanato-complexes.

		Molar conductivity at 20° in			
		$MeNO_2$		$PhNO_2$	
Compound	Colour	10^{-4}M	Λ_M	10^{-4}M	Λ_M
$[Ph_4As]_2[Co(NCSe)_4]$	Green	2·5	172	2·1	54
		5·3	168	5·4	50
		9·5	156	9·6	47
$[Ph_4As]_2[Co(NCS)_4]$	Blue	2·5	174	2·5	53
		5·5	170	5·5	50
		9·6	160	9·6	48
$[Et_4N]_2[Co(NCSe)_4]$	Green	2·7	221	2·6	64
		5·5	209	5·4	58
		10·0	190	9·4	57
$[Et_4N]_2[Co(NCS)_4]$	Blue	2·5	216	2·6	65
		5·4	204	5·5	56
		8·5	190	8·8	54

Electronic Spectra and Magnetic Moments.—The reflectance and absorption spectra in several solvents are presented in Figs. 1—3. The general features of the bands and their extinction coefficients clearly show that the selenocyanate ion must be tetrahedrally co-ordinated to cobalt. In the tetrahedral field the ^4F ground term of the Co^{2+} ion is

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[3] Cotton, Goodgame, Goodgame, and Sacco, *J. Amer. Chem. Soc.*, 1961, **83**, 4157.
[4] Turco, Pecile, and Nicolini, *Proc. Chem. Soc.*, 1961, 213.
[5] Frasson, Turco, and Panattoni, *Gazzetta*, 1961, **91**, 750.
[6] Jeffery, *Nature*, 1947, **159**, 610.
[7] Nelson, *Proc. Chem. Soc.*, 1961, 372.
[8] Pecile, Turco, and Pizzolotto, *Ricerca Sci.*, 1961, **31** (II-A), 247.
[9] Gill and Nyholm, *J.*, 1959, 3997.

split to give the following states, listed in order of increasing energies: $^4A_2$, $^4T_2$, $^4T_1(F)$. In addition there is a $^4T_1(P)$ state originating from the ^4P term of the free ion. The separation (Δ) between the lowest states $^4A_2$ and $^4T_2$ is the modulus of the ligand field strength. The frequencies of the transitions $^4T_2 \longleftarrow {}^4A_2$, $^4T_1(F) \longleftarrow {}^4A_2$, and $^4T_1(P) \longleftarrow {}^4A_2$ are usually denoted as ν_1 (=Δ), ν_2, and ν_3, respectively.[10] The spectra in the 500—700 mμ region shown in Figs. 1—3 are those related to the last transition. The bands are broad and exhibit a great deal of fine structure as a result of splitting, probably due to spin–orbit interaction.

Comparison of the reflectance and solution spectra in Fig. 1 shows that there is no major structural change (either electronic or molecular) upon solution. Spectra in Figs. 1 and 2 indicate that solvolytic processes affecting the dissociation of the complex anion $[Co(NCSe)_4]^{2-}$ are more important in nitromethane than in dichloromethane.

The close resemblance between the spectra of the thiocyanato- and selenocyanato-compounds leaves little doubt that the cobalt atom in $[Co(NCSe)_4]^{2-}$ must be bound to nitrogen as it certainly is in the complex $[Co(NCS)_4]^{2-}$. Indeed the position of the ν_3 band is likely to be the same only if the SeCN group is linked to cobalt through the nitrogen atom. The fact that the position of ν_3 is the same does not unambiguously indicate that the ligand field strength is the same. The energy of ν_3 is determined by both the ligand field strength and by the value of the Racah parameters B, namely, by the position of the ligand in the spectrochemical series as well as in the nephelauxetic series.[10, 11] On the other hand, bonding to cobalt through the selenium atom is expected to lead to a smaller ligand field strength. In order that ν_3 shall remain constant, the value of the B' parameter should increase correspondingly. Thus the identity of the ν_3 values indicates that in both cases the bond must be through the nitrogen atom, for it is very unlikely that these two opposing effects exactly counterbalance.

It is well known that in a cubic field the magnetic moment of the spin-free Co^{2+} ion has the form $\mu_{eff} = \mu_{spin\ only}(1 - \alpha\lambda/\Delta)$; with $\alpha = 4$ (F term) and λ negative, since we are dealing with a d-shell which is more than half-filled, there is a positive orbital contribution to the magnetic moment. Inspection of Table 2 shows that the magnetic moments of corresponding selenocyanato- and thiocyanato-compounds are the same (with the exception of the tetraethylammonium salts) and well within the range of uncertainty (0·05 B.M.) which is reasonable to attribute to the determined values of μ. Therefore, the orbital contribution must be the same in the two classes of compounds. The identities of the ν_3 values and of the orbital contribution indicate beyond reasonable doubt that Δ must also have the same value. Consequently, the magnetic moments give good evidence that the cobalt atom must be tetrahedrally co-ordinated to the nitrogen ends of the SeCN groups. The above arguments also indicate that the position of the two ions SeCN and SCN in the spectrochemical series must be the same when they co-ordinate through nitrogen. The low value of the magnetic moment of $[Et_4N]_2[Co(NCSe)_4]$ is not well understood and requires some comment although we do not believe that a difference of 0·1 B.M. is necessarily significant. At least two factors can be important in explaining the scattering of the μ values for different salts of the $[Co(NCSe)_4]^{2-}$ ion. (1) It has already been pointed out [3] that magnetic moments and Δ values of a particular complex ion $[CoX_4]^{2-}$ may vary by as much as 10% from one compound to another, owing presumably to variations in compression forces in the crystal lattices. However, comparison of the reflectance spectra of the compounds $[Ph_4As]_2[Co(NCSe)_4]$ and $[Et_4N]_2[Co(NCSe)_4]$ fails to show significant changes in the absorption frequencies (Fig. 1). (2) Electrostatic perturbation or co-ordination of outer selenium atoms can influence the ligand field strength. The latter argument applies better to the compound $Co(NCSe)_4Hg$ for which a low magnetic moment is found, in agreement with the behaviour of the thiocyanato-compound.[3] A lower value

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[10] Cotton and Goodgame, *J. Amer. Chem. Soc.*, 1961, **83**, 1778, and references therein.

[11] Schäffer and Jorgensen, Symposium on Co-ordination Compounds, Rome, 1957; *Ricerca Sci. Suppl.*, 1958, **28**, 143.

TABLE 2.

Spectra of selenocyanato- and thiocyanato-complexes in visible region.

Compound	Medium	$\varepsilon_{max.}$	$\lambda_{max.}$ (mμ)	Concn. (M)
$[Co(NCSe)_4]^{2-}$	CH_2Cl_2	9700	358	0·00007
		70	490	0·0012
		(sh)	∼588	0·00025
		(sh)	∼615	
		1950	627	
	CH_3NO_2	5500	376	0·0001
		(sh)	∼590	0·0005
		(sh)	∼615	
		1750	627	
	CH_3NO_2 with 0·1M-KSeCN	80	493	0·001
		(sh)	∼590	0·0002
		(sh)	∼615	
		1920	628	
	$COMe_2$	8100	355	0·00007
		(sh)	∼590	0·0006
		(sh)	∼610	
		2000	627	
$[Ph_4As]_2[Co(NCSe)_4]$	Solid	w	505	
		s(sh)	∼595	
		s	∼635b	
$[Co(NCS)_4]^{2-}$	CH_2Cl_2	9900	318	0·0001
		25	498	0·013
		(sh)	∼590	0·0004
		(sh)	∼615	
		1750	626	
	CH_3NO_2	20	498	0·013
		(sh)	∼590	0·00025
		1660	625b	
	$COMe_2$	8000	330	0·0001
		1000	588	0·0004
		(sh)	∼615	
		1900	626	
$[Et_4N]_2[Co(NCS)_4]$	Solid	w	503	
		s(sh)	∼595	
		s(sh)	∼635b	
$Co(NCSe)_4Hg$	Solid	w	485	
		s(sh)	∼575	
		s	∼610b	
$Co(NCS)_4Hg$ [3]	Solid		490	
			605	

TABLE 3.

Magnetic susceptibilities of salts of the $[Co(NCSe)_4]^{2-}$ and $[Co(NCS)_4]^{2-}$ ions and their magnetic moments.

Compound	$10^6\chi_M$	Diamag., corr.	Temp. (K)	μ_{eff} (B.M.)
	(c.g.s. units)			
$[Et_4N]_2[Co(NCS)_4]$	8100	351	298·2°	4·51
$[Me_4N]_2[Co(NCS)_4]$ *	(7145)	256	297·9	4·47
$[Ph_4As]_2[Co(NCS)_4]$	7885	544	297·5	4·50
$Co(NCS)_4Hg$ †	(7611)	137	300	4·33
$[Et_4N]_2[Co(NCSe)_4]$	7694	383	298·2	4·41
$[Ph_4As]_2[Co(NCSe)_4]$	7842	576	298·2	4·50
$Co(NCSe)_4Hg$	7750	196	296·7	4·36

* Calc. from the data of Cotton *et al.*[3] by means of the expression $\mu = 2{\cdot}84(\chi T)^{\frac{1}{2}}$ and without correction for T.I.P. † Figgis and Nyholm, *J.*, 1959, 342.

of the magnetic moment is expected as a result of strong selenium–mercury interaction, and is entirely consistent with the shift to higher frequencies which occurs in going from $[Co(NCSe)_4]^{2-}$ to $Co(NCSe)_4Hg$ (Fig. 1). This shift finds its correspondence in the effect which arises when a mercury ion is bound to the free sulphur end of nitrogen-co-ordinated

NCS^-.[12] Recent *X*-ray crystallographic work [5] has shown that the mercury and cobalt atoms are linked by Hg–SeCN–Co bridges in $Co(NCSe)_4Hg$, the structure of this compound being similar to that of the "bridged" $Co(NCS)_4Hg$. The hypsochromic effect which arises in going from $[Co(NCS)_4]^{2-}$ to $Co(NCS)_4Hg$ has been shown to be due to enhancement of the ligand field around the cobalt atom.[3] The shift to higher energy is of the same order of magnitude in the two cases (500—600 cm.$^{-1}$), suggesting that electronic effects caused by attachment to the Hg^{2+} ion are transmitted with roughly the same intensity along NCS and NCSe, respectively.

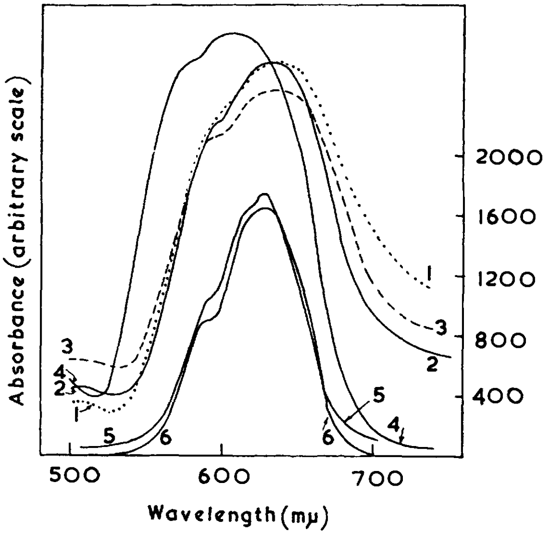

FIG. 1. Visible reflectance spectra of:
(1) $[Et_4N]_2[Co(NCSe)_4]$; (2) $[Ph_4As]_2[Co(NCSe)_4]$; (3) $[Et_4N]_2[Co(NCS)_4]$; (4) $Co(NCSe)_4Hg$.
Visible absorption spectra in CH_3NO_2 of:
(5) $[Ph_4As]_2[Co(NCSe)_4]$; (6) $[Et_4N]_2[Co(NCS)_4]$.

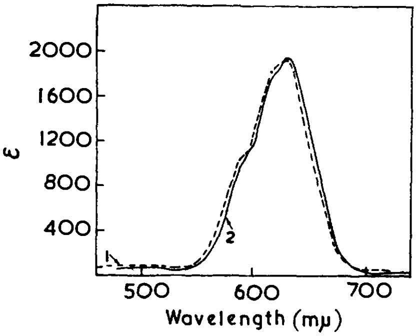

FIG. 2. Visible absorption spectra of:
(1) $[Et_4N]_2[Co(NCSe)_4]$ in CH_3NO_2, with added 0·1M-KSeCN; (2) $[Et_4N]_2[Co(NCSe)_4]$ in CH_2Cl_2.

Finally with regard to the near-ultraviolet spectra, Fig. 3 shows that the first charge-transfer band of the $[Co(NCSe)_4]^{2-}$ ion occurs at longer wavelengths than those of $[Co(NCS)_4]^{2-}$ in the same solvent. It largely overlaps the first visible band, accounting thus for the different colours of the two complex ions.

Infrared Spectra.—Infrared spectroscopy has provided a very useful method of structural investigation of inorganic thiocyanates. No work has been done on the corresponding selenocyanates; only very recently in a preliminary publication we presented results suggesting a close correlation between the vibrational behaviour of the SeCN and SCN groups in inorganic compounds.[8]

In thiocyanates the frequencies of the two fundamental stretching modes of the tri-atomic SCN group correlate well with the type of co-ordination and are diagnostic of M–NCS, M–NCS–M, and M–SCN bonds. A comparison of the vibrational behaviour of thiocyanates and selenocyanates was of obvious interest and we have extended to the latter class of compound our previous infrared investigation of thiocyanates.

The lack of structural information on selenocyanates [only a preliminary *X*-ray structure determination on $Se(CN)_2$ has been reported [13]] made it difficult to correlate the

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[12] Schäffer, Abstracts, Conference on Co-ordination Chemistry, London, 1959.
[13] Aksnes and Foss, *Acta Chem. Scand.*, 1954, **8**, 1787.

shifts of the assigned vibrational frequencies with the structural properties of the compounds under investigation. We have made the assumption that the nature of the co-ordination in selenocyanates must be similar to that of the corresponding thiocyanato-derivatives. Thus the compounds $K_2[Hg(SeCN)_4]$ and $K_2[Pt(SeCN)_6]$ have been taken as examples of selenium-bonded mononuclear selenocyanates. The cobalt complexes discussed above were taken as representative of mononuclear compounds in which SeCN binds through nitrogen. As an example of bridging SeCN groups we took $Co(NCSe)_4Hg$.

TABLE 4.

Infrared absorption bands assigned to the stretching vibrations of the SeCN group in inorganic compounds (cm.$^{-1}$).

Compound (X = Se or S)	ν_3(SeCN)	ν_1(SeCN)	ν_3 (SCN)	ν_1(SCN)	Ref.
KXCN	2070s *	560w *	2053s	749m	15
$K_2[Hg(XCN)_4]$	2098s, b	543w	2115s	716w	1
$K_2[Pt(XCN)_6]$	2124s 2080w	520w	$\left.\begin{matrix}2125\\2115\end{matrix}\right\}$ s, b	649w	14*c*
$[Ph_4As]_2[Co(NCX)_4]$	2060s, b	—	2067s, b	840vw 836vw	
$[Et_4N]_2[Co(NCX)_4]$	2053s, b	672m	2053s, b	840w	
$Co(NCX)_4Hg$	2135s	639m	2145s	795w	
AgXCN	2142s 2098sh	580w	2145s 2096sh	749sh 742w	14*a*

* The frequencies of KSeCN recorded by us and reported in Tables 4 and 5 are in good agreement with those recently reported by Morgan.[16]

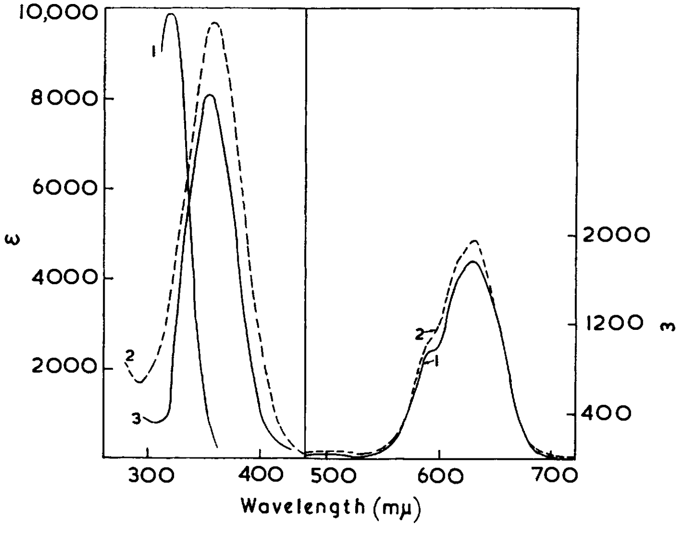

FIG. 3. Near-ultraviolet and visible absorption spectra of: (1) $[Et_4N]_2[Co(NCS)_4]$ and (2) $[Et_4N]_2[Co(NCSe)_4]$ in CH_2Cl_2; (3) $[Et_4N]_2[Co(NCSe)_4]$ in acetone.

The absorption frequencies assigned to the fundamental stretching modes of co-ordinated SeCN are collected in Table 4. We denote the stretching modes approximating to CN

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[14] (*a*) Pecile, Giacometti, and Turco, *Atti Accad. Lincei*, 1960, **28**, 189; (*b*) Pecile and Turco, unpublished results; (*c*) Chamberlain and Bailar, *J. Amer. Chem. Soc.*, 1959, **81**, 6412; (*d*) Baldwin, *J.*, 1961, 471.

[15] Jones, *J. Chem. Phys.*, 1956, **25**, 1069.

[16] Morgan, *J. Inorg. Nuclear Chem.*, 1961, **16**, 369.

and CS stretching as ν_3(SeCN) and ν_1(SeCN), respectively. The characteristic frequencies of the related thiocyanates are also given for comparison.

In addition to these frequencies the infrared spectrum in the 2—30 μ region shows important features at 370—430 and 750—850 cm.$^{-1}$ due to the co-ordinate SeCN group. In the former region is localised the doubly degenerate bending frequency ν_2 of the triatomic ion $SeCN^-$ and in the latter region the corresponding first harmonic $2 \times \nu_2$. In solid KSeCN we find two absorption bands in both regions, the degeneracy of ν_2 being presumably removed for the ion in the crystal lattice. In Table 5 we denote the observed frequencies, grouped very roughly relative to KSeCN, as ν_2(SeCN) and ν_2 overtones, respectively. A close resemblance can be observed with the behaviour of the corresponding thiocyanates in the ranges 420—480 and 850—970 cm.$^{-1}$ where the ν_2 and $2 \times \nu_2$ frequencies of the thiocyanate ion occur.[14]

TABLE 5.

Infrared frequencies of co-ordinate SeCN group in the regions 370—430 and 750—850 cm.$^{-1}$.

Compound	ν_2 (SeCN)			ν_2 overtones			
KSeCN	425m	418m		847w	832w		
$K_2[Hg(SeCN)_4]$	407w	389w		812w	794vw	779w, b	
$K_2[Pt(SeCN)_6]$	392m	379w	370m	782w	762w	755w	742w
$[Et_4N]_2[Co(NCSe)_4]$	433m	417m		861w			
$Co(NCSe)_4Hg$	417w	403w		833w	817vw	805w, b	
AgSeCN	393m	381sh	377m	788w	762w		

There can be little doubt that in $K_2[Hg(SeCN)_4]$ and $K_2[Pt(SeCN)_6]$ the metal atom must be bound to selenium, the larger polarisability of the selenium than of the sulphur atom being the factor which favours a metal–nitrogen bond. The frequency shifts of the stretching vibrations, relative to the SeCN ion in KSeCN, occur in the order observed in the corresponding thiocyanates. The stretching frequencies ν_3 increase; the stretching frequencies ν_1 decrease.

The infrared behaviour of $Co(NCSe)_4Hg$ is closely similar to that of $Co(NCS)_4Hg$. The stretching frequencies ν_3 and ν_1 increase, relative to $K_2[Hg(SeCN)_4]$. In thiocyanates this is a typical effect indicating that bridging SCN groups are present. The infrared results are therefore in agreement with the conclusion of the *X*-ray crystallographic work.[5] The data in Table 4 suggest that the same type of co-ordination must occur in AgSeCN. It is known that AgSCN has a polymeric structure based upon Ag–SCN–Ag bridges.

Identification of the ν_1 stretching band in $[Ph_4As]_2[Co(NCSe)_4]$ is complicated by the occurrence of the intense benzene bands of the cation. The compound $[Et_4N]_2[Co(NCSe)_4]$ shows a band at 672 cm.$^{-1}$ which we attributed to SeCN stretch by comparing the spectrum of this compound with those of $[Et_4N]Cl$ and $[Et_4N]_2[Co(NCS)_4]$. Here again one finds the same kind of shift of the stretching frequencies as occurs in the corresponding thiocyanates. The increase, relative to the ion, of the ν_1 stretching is particularly remarkable.

The results presented here clearly indicate that the vibrational behaviour of the SeCN and SCN groups is very similar in all investigated compounds. It appears that in both cases the type of co-ordination can be differentiated on the basis of the infrared spectra.

EXPERIMENTAL

Magnetic Measurements.—The magnetic susceptibilities were measured at 25° by using a Gouy balance. The Gouy tube was calibrated with aqueous nickel chloride. The calibration was checked with $CuSO_4,5H_2O$ for which a value of $\chi_g = 6{\cdot}04 \times 10^{-6}$ c.g.s. units was assumed [average of the most reliable values given in the literature:[17] (*a*) $5{\cdot}95 \times 10^{-6}$; (*b*) $6{\cdot}01 \times 10^{-6}$;

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[17] (*a*) Gorter and de Haas, *Comm. Kammerlingh Onnes Lab.*, Leiden, 1930, No. 210 *d*; (*b*) ref. 10; (*c*) Figgis and Nyholm, *J.*, 1959, 331; (*d*) Sugden, *J.*, 1932, 161.

(*c*) $6{\cdot}05 \times 10^{-6}$; (*d*) $6{\cdot}14 \times 10^{-6}$]. The two values of the β constant agreed within 0·15%. The magnetic moment was calculated[18] by means of the expression $\mu_{\text{eff}} = 2{\cdot}84(\chi_M T)^{\frac{1}{2}}$. Diamagnetic corrections were calculated by using Pascal constants or were measured experimentally.

Spectra.—Electronic spectra were measured on a Beckman D.U. spectrophotometer for solutions and the same apparatus equipped with the standard reflectance attachment for powders. Infrared spectra were recorded for Nujol mulls on a Perkin–Elmer model 21 spectrometer with a sodium chloride prism and a Perkin–Elmer model 112 spectrometer with calcium fluoride and cæsium bromide prisms.

Preparations.—*Potassium selenocyanate.* Commercial material ("Reagent" grade) was dissolved in acetone. The solution was filtered and treated with pure ether. The resulting white crystalline precipitate was filtered off and dried (Found: Se, 54·3. Calc. for KSeCN: Se, 54·8%).

Potassium tetraselenocyanatomercurate(II). Mercuric chloride (1·55 g.) was dissolved in anhydrous ethanol (16 ml.), and solid potassium selenocyanate (3·3 g.) was added. The mixture was stirred until all the potassium chloride had been precipitated. The solution was filtered and the filtrate was treated with ether. After a few minutes, white crystals were filtered off, washed with alcohol and ether, and dried (P_2O_5) {Found: Se, 44·5. Calc. for $K_2[Hg(C_4N_4Se_4)]$: Se, 45·2%}. Rosenheim and Pitzer[19] made this compound but we found their method less satisfactory.

The corresponding *thiocyanate* was prepared in a similar manner {Found: C, 9·30; N, 11·1. $K_2[Hg(C_4N_4S_4)]$ requires C, 9·40; N, 10·95%}.

Tetraselenocyanatocobalt(II)*mercury*(II) (cf. ref. 19). Mercuric chloride (1·19 g.) was dissolved in water (15 ml.), and a solution of potassium selenocyanate (2·54 g.) in water (5 ml.) was added. This mixture was immediately treated with cobaltous chloride hexahydrate (1·06 g.) in water (5 ml.). A dark-green precipitate was formed which was filtered off, washed with water, ethanol, and acetone, and dried (P_2O_5) {Found: Se, 45·4. Calc. for $CoHg(C_4N_4Se_4)$: Se, 46·5%}.

Bis(*tetraethylammonium*)*tetraselenocyanatocobaltate*(II). Tetraethylammonium bromide (2·28 g.) in ethanol (10 ml.) was added to a mixture of cobalt(II) chloride (0·7 g.) and potassium selenocyanate (3·12 g.) in ethanol (25 ml.). The mixture was stirred for a few minutes, and a green precipitate was filtered off. The dried *product* was treated with acetone (15 ml.), and the filtered solution was treated with ether (40 ml.) to give green crystals (2·0 g., 50%) {Found: N, 11·3; C, 32·45; H, 5·6; Co, 7·95; Se, 42·2. $[C_{16}H_{40}N_2][Co(N_4C_4Se_4)]$ requires N, 11·35; C, 32·5; H, 5·45; Co, 8·0; Se, 42·7%}.

The corresponding *thiocyanate* was prepared by an analogous method {Found: N, 15·0; C, 42·8; H, 7·5. $[C_{16}H_{40}N_2][Co(N_4C_4S_4)]$ requires N, 15·2; C, 43·5; H, 7·3%}.

Bis(*tetraphenylarsonium*)*tetraselenocyanatocobaltate*(II). A mixture of cobalt(II) chloride (0·3 g.) and potassium selenocyanate (1·8 g.) was stirred in ethanol. Tetraphenylarsonium chloride (2·1 g.) in ethanol (50 ml.) was slowly added. A green precipitate was immediately formed. After a few minutes' stirring, the crude product, contaminated with potassium chloride, was filtered off. The *compound* was obtained free from by-products by washing with water. The green crystalline powder was washed with ethanol, dried with ether, and stored in desiccator (P_2O_5) (yield 2·3 g., 80%) {Found: Co, 4·7; N, 4·5; Se, 25·25. $[C_{48}H_{40}As_2][Co(N_4C_4Se_4)]$ requires Co, 4·7; N, 4·5; Se, 25·4%}.

The corresponding *thiocyanate* was prepared in a similar manner {Found: N, 5·3. $[C_{48}H_{40}As_2][Co(N_4C_4S_4)]$ requires N, 5·3%}.

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[18] Figgis, *Trans. Faraday Soc.*, 1960, **56**, 1554; Figgis and Nyholm, *J.*, 1959, 331.

[19] Rosenheim and Pitzer, *Z. anorg. Chem.*, 1909, **63**, 277.