

been isolated in both forms.<sup>3</sup> Diphenylbenzylphosphine, however, is an exception among ligands of the type  $(C_6H_5)_2PR$  in that all three pairs of isomeric halide complexes have been isolated and it is particularly surprising that the planar chloro complex isomerizes on heating, while the iodo complex is more stable in the planar form.<sup>3</sup> Among these complexes, where the factors which determine structural type are finely balanced, it is evident that small changes may favor one isomer over the other. However, taking the broad view over the large number of related complexes which have been studied, a number of consistent factors do emerge. These may be conveniently subdivided into ligand and solubility effects.

**The Effect of Ligands on Isomer Formation.**—It has previously been suggested that effects which weaken the ligand field around the metal atom will tend to favor the paramagnetic (tetrahedral) form relative to the diamagnetic (square-planar) form.<sup>11</sup> This suggestion is consistent with the behavior of both the neutral phosphine and the anionic halide ligands. Thus, the tetrahedral structure is *increasingly* favored in the orders  $P(C_2H_5)_3 < P(C_2H_5)_2C_6H_5 < PC_2H_5(C_6H_5)_2 < P(C_6H_5)_3$  and  $SCN < Cl < Br < I$ , in each case as the crystal field strength of the ligand *decreases*. The effect of the halide ligands has been studied in solution<sup>11</sup> (by means of magnetic susceptibility measurements), and, in the present series, a similar trend is shown by the isolated solid complexes, presumably due to a similar cause. Undoubtedly, crystal packing and solubility effects are also important and may account for some apparent anomalies, for example, the unusually low stability of the planar  $[NiCl_2(P(n-C_4H_9)(C_6H_5)_2)_2]$  isomer.

The effect of the alkyl group in the diphenylalkylphosphine is small compared with that of, say, the halide ligands. However, it may be significant that, as R increases in length from methyl to *n*-amyl, corresponding ligand field absorption bands, in particular

the  ${}^3T_{1g}(F) \rightarrow {}^3A_{2g}$  band due to the tetrahedral species in the 800–1000  $m\mu$  region, tend to move to longer wave length, suggesting a weakening ligand field. It is possible that the more frequent isolation of the tetrahedral isomer as R increases in length, particularly among the chloro complexes, is due to this effect, although the existence of trends based mainly on the isolation of solid complexes must be treated with caution.

**The Effect of Solubility on Isomer Formation.**—From an experimental point of view, it was found that the square-planar isomers were more readily obtained from nonpolar solvents and at low temperatures. The effect of temperature is particularly important and had not previously been used to isolate the less stable isomers. Indeed, a number of the planar isomers, although stable in the solid state at room temperature, could only be isolated by crystallization at  $-78^\circ$ . This effect is probably mainly one of relative solubility, although it may also be that the amount of the planar isomer at equilibrium increases with decrease in temperature. The effect of solvent appears to be that the more polar solvents favor the more polar (tetrahedral) isomer and we have found that  $[NiBr_2(P(C_2H_5)(C_6H_5)_2)_2]$  has a magnetic moment of 2.5–2.6 B.M. in chloroform solution ( $7.4\text{--}31.5 \times 10^{-3} M$ ) and 1.4 B.M. in benzene solution ( $1.4 \times 10^{-3} M$ ) in agreement with these views.

**Isomerism of  $[NiI_2(PR(C_6H_5)_2)_2]$  (R = Isopropyl, *s*-Butyl).**—It is interesting to note that the unusual isomerism of the iodo complexes has been observed only when the alkyl group in the phosphine ligand is branched at the  $\alpha$  carbon atom. It had been expected that diphenyl-*t*-butylphosphine would behave similarly, but only a tetrahedral iodo complex has been isolated. In addition, solutions of this complex do not show the marked thermochroic effect characteristic of the iodo complexes of the isopropyl and *s*-butyl ligands.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,  
BEDFORD COLLEGE, REGENT'S PARK, LONDON N.W.1, ENGLAND

## Coordination of Thiocyanate and Selenocyanate in Some Diamine Complexes of Nickel(II) and Copper(II)

BY M. E. FARAGO<sup>1</sup> AND J. M. JAMES

Received April 16, 1965

Compounds of the type  $Ni(AA)_2X_2$ ,  $Ni(AA)_3X_2$ ,  $Cu(AA)_2X_2$ , and  $Cu(AA)_3X_2$ , where AA is 1,2-diaminoethane (ethylenediamine) or its C- or N-substituted derivatives and X is thiocyanate or selenocyanate, have been prepared and characterized. The infrared absorption bands due to the thiocyanate and selenocyanate groups are reported and discussed in terms of the structures of the complexes.

Two recent crystal structures of nickel(II)<sup>2a</sup> and copper(II)<sup>2b</sup> bis(ethylenediamine) thiocyanates have shown important differences between the two com-

pounds. The nickel complex is essentially octahedral with *trans* isothiocyanato groups bound to the nickel by

(1) Formerly M. E. Baldwin.

(2) (a) B. W. Brown and E. C. Lingafelter, *Acta Cryst.*, **16**, 753 (1963); (b) B. W. Brown and E. C. Lingafelter, *ibid.*, **17**, 253 (1964).

nitrogen at a distance of 2.15 Å. The copper complex, however, is tetragonal, with sulfur atoms in the axial positions. The Cu-S distance is 3.27 Å., significantly longer than the 3.0 Å. found in  $\text{Cu}(\text{py})_2(\text{NCS})_2$ , which contains bridging thiocyanate.<sup>3</sup> The latter complex is also tetragonal, the isothiocyanate groups being bonded to copper by nitrogen at a distance of 2.10 Å. and by sulfur in the axial positions at 3.0 Å. Brown and Lingafelter suggest that the long Cu-S distance in  $\text{Cu}(\text{en})_2(\text{SCN})_2$  is approximately that calculated for the sum of the square  $d_{sp^2}$  radius for copper(II) and the van der Waals radius for sulfur and that since the thiocyanate complexes of the first-row transition elements are generally nitrogen bonded,<sup>4</sup> the complex is unusual.

There has recently been great interest in the bonding of the thiocyanate ligand to metals. Since the observation by Turco and Pecile<sup>5</sup> that in platinum(II) and palladium(II) complexes the mode of attachment of the thiocyanate ligand depends on the nature of the other ligands, examples of M-NCS and M-SCN linkage isomerism have been reported for palladium<sup>6</sup> and manganese.<sup>7</sup>

Basolo and co-workers have discussed the importance of steric as well as electronic factors on the nature of the metal-thiocyanate linkage.<sup>8</sup> They have shown that Pd-N bonding occurs in  $[\text{Pd}((\text{C}_2\text{H}_5)_2\text{dien})\text{NCS}]^+$  rather than Pd-S bonding as in the unsubstituted  $[\text{Pd}(\text{dien})\text{SCN}]^+$ , as a result of the steric hindrance of the ethyl substituents.

The selenocyanate ligand, like thiocyanate, is also known to bond by either end; it forms selenocyanates (M-SeCN)<sup>9</sup> and isoselenocyanates (M-NCS<sub>2</sub>)<sup>10</sup> as well as acting as a bridging group.<sup>11,12</sup>

In view of the different structure of the copper and nickel bis(ethylenediamine) thiocyanates, we have investigated the infrared spectra of some copper and nickel diamine complexes containing thiocyanate and selenocyanate. We report in this paper the preparation and some of the properties of complexes of the type  $\text{Cu}(\text{AA})\text{X}_2$ ,  $\text{Cu}(\text{AA})_2\text{X}_2$ ,  $\text{Ni}(\text{AA})_2\text{X}_2$ , and  $\text{Ni}(\text{AA})_3\text{X}_2$ , where AA is: 1,2-diaminoethane (en), 1,2-diaminopropane (pn), N,N-dimethyl-1,2-diaminoethane (NN-dimeen), N,N'-dimethyl-1,2-diaminoethane (NN'-dimeen), N,N'-diethyl-1,2-diaminoethane (NN'-dieten), 2-methyl-1,2-diaminopropane (2-mepn), and meso-2,3-diaminobutane (bn).

## Experimental

**Preparation of the Complexes. Thiocyanates.**—Most of the thiocyanate complexes were prepared by the same general method, *viz.*, addition of an aqueous solution of the required amount of sodium thiocyanate to an aqueous solution of the appropriate nickel or copper diamine chlorides.

The copper monodiamine complexes prepared in this way precipitated immediately and were recrystallized from hot water. The copper bis-diamine complexes are more soluble in water. They were recrystallized in the presence of an excess of diamine.

The nickel complexes are all relatively insoluble in water; they were purified by recrystallization from aqueous ethanol.

Some complexes were not prepared by this general method. The very soluble  $\text{Cu}(\text{en})_2(\text{SCN})_2$  and  $\text{Cu}(\text{pn})_2(\text{SCN})_2$  were prepared by the method of Brown and Lingafelter.<sup>2b</sup> Bis(diamine)-copper(II) sulfate was made by the addition of the stoichiometric amount of the diamine to an aqueous solution of cupric sulfate at room temperature. The solid was filtered off, recrystallized, and dissolved in water; barium thiocyanate was added with rapid stirring and the precipitated barium sulfate was removed. The aqueous filtrate was evaporated to dryness and the resulting solid was dissolved in hot methanol. The ethylenediamine complex  $\text{Cu}(\text{en})_2(\text{SCN})_2$  was obtained by slow cooling of the methanol solution. The propylenediamine analog was precipitated from the methanol solution by the addition of one drop of the diamine followed by an excess of an acetone-ether mixture.

$\text{Cu}(\text{NN}'\text{-dieten})(\text{NCS})_2$  was prepared by the addition of sodium thiocyanate to the chloride  $\text{Cu}(\text{NN}'\text{-dieten})\text{Cl}_2$  in N,N-dimethylformamide (DMF) solution. The crystallization of the dark green complex was induced by the addition of a few drops of water. The bis complex,  $\text{Cu}(\text{NN}'\text{-dieten})_2(\text{SCN})_2$  (made by the general method above) became bright blue under vacuum at 50° and did not form the expected  $\text{Cu}(\text{NN}'\text{-dieten})(\text{NCS})_2$  by loss of amine. The blue substance is at present under investigation.

**Selenocyanates.**—The bis(diamine)copper(II) selenocyanates were prepared by the addition of potassium selenocyanate to a solution of the appropriate bis(diamine)copper(II) chloride in water, in the presence of a slight excess of the diamine. The compounds crystallized out after the mixture had been left in the cold for 2-3 days.

The bis- and tris(diamine) nickel(II) selenocyanates were prepared by the addition of potassium selenocyanate to an aqueous solution of the appropriate chloride. To prevent the formation of an oil the mixture was stirred during the addition. The compounds were recrystallized from an ethanol-water mixture.

**Spectral Measurements.**—Infrared absorption spectra from 3600 to 450  $\text{cm}^{-1}$  were measured on a Grubb Parsons GS2A double beam recording spectrophotometer. The spectra were of dispersions in Nujol (B.P. grade) or hexachlorobutadiene between potassium bromide plates. A polystyrene standard was used for calibration.

**Magnetic Susceptibility Measurements.**—These measurements were made by the Gouy method over a range of field strengths. Calibrants used were  $\text{Hg}[\text{Co}(\text{SCN})_4]^{13}$  and  $[\text{Ni}(\text{en})_3]\text{S}_2\text{O}_8$ .<sup>14</sup> Diamagnetic corrections were calculated from Pascal's constants.<sup>15</sup> The correction used for  $\text{SeCN}^-$  was:  $-10^6 \chi_M = 44 \text{ c.g.s. units.}^{16}$

**Analyses.**—Microanalyses were carried out by Drs. Weiler and Strauss at Oxford, England, and by Dr. Bernhardt of Mulheim, Germany. Selenium was estimated gravimetrically after precipitation with hydrochloric acid and hydroxylammonium chloride.<sup>17</sup>

(3) M. A. Porai-Koshits and G. N. Tischenco, *Soviet Phys.-Cryst.*, **4**, 216 (1959).

(4) C. E. Shaffer, International Conference on Coordination Chemistry, The Chemical Society, London, 1959, p. 153.

(5) A. Turco and C. Pecile, *Nature*, **191**, 66 (1961).

(6) (a) F. Basolo, J. L. Burmeister, and A. J. Poe, *J. Am. Chem. Soc.*, **85**, 1700 (1963); (b) J. L. Burmeister and F. Basolo, *Inorg. Chem.*, **3**, 1587 (1964).

(7) A. Wojcicki and M. Farona, Proceedings of the 8th International Conference on Coordination Chemistry, Springer-Verlag, Vienna, 1964, p. 262.

(8) F. Basolo, W. H. Baddley, and J. L. Burmeister, *Inorg. Chem.*, **3**, 1203 (1964).

(9) C. Pecile, G. Giacometti, and A. Turco, *Atti Accad. Lincei*, **28**, 189 (1960).

(10) A. Turco, C. Pecile, and M. Nicolini, *J. Chem. Soc.*, 3008 (1962).

(11) S. M. Nelson, *Proc. Chem. Soc.*, 372 (1961).

(12) A. Turco, C. Pecile, and M. Nicolini, *ibid.*, 213 (1961).

(13) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4190 (1958).

(14) N. F. Curtis, *ibid.*, 3147 (1961).

(15) J. Lewis and R. Wilkins, Ed., "Modern Coordination Chemistry," Interscience Publishers, Inc., New York, N. Y., 1960, p. 403.

(16) C. Stephen and V. C. G. Trew, private communication.

(17) A. I. Vogel, "A Textbook of Quantitative Inorganic Analysis," 3rd Ed., Longmans, London, 1961, p. 509.

TABLE I  
 MELTING POINTS AND ANALYTICAL DATA FOR THE  $\text{Cu}(\text{AA})_2\text{X}_2$  AND  $\text{Cu}(\text{AA})_2\text{X}_2$  COMPLEXES

Compound	Color	M.p., °C.	Calcd., %			Found, %		
			C	H	N	C	H	N
$\text{Cu}(\text{en})(\text{NCS})_2^a$	Blue	150 <sup>b</sup>	20.1	3.4	<i>c</i>	20.2	3.6	<i>c</i>
$\text{Cu}(\text{pn})(\text{NCS})_2$	Blue	165 <sup>b</sup>	23.7	4.0	21.6	24.1	4.05	21.3
$\text{Cu}(2\text{-mepn})(\text{NCS})_2^d$	Green	170 <sup>b</sup>	26.9	4.5	20.9	27.4	4.8	20.4
$\text{Cu}(\text{NN-dimeen})(\text{NCS})_2$	Green	135 <sup>b</sup>	26.9	4.5	20.9	26.9	4.5	21.2
$\text{Cu}(\text{NN'-dimeen})(\text{NCS})_2$	Green	<i>b</i>	26.9	4.5	<i>c</i>	27.5	4.5	<i>c</i>
$\text{Cu}(\text{NN'-dieten})(\text{NCS})_2$	Green	130 <sup>b</sup>	32.5	5.5	18.9	32.1	5.3	19.0
$\text{Cu}(\text{en})_2(\text{SCN})_2$	Purple	140	24.0	5.4	28.0	24.4	5.4	28.1
$\text{Cu}(\text{pn})_2(\text{SCN})_2$	Purple	117	29.3	6.1	25.6	29.4	6.5	25.7
$\text{Cu}(\text{NN-dimeen})_2(\text{SCN})_2^e$	Purple	<i>c</i>	24.0	6.8	<i>c</i>	33.6	6.8	<i>c</i>
$\text{Cu}(\text{NN'-dimeen})_2(\text{SCN})_2 \cdot 2\text{H}_2\text{O}$	Blue	72	30.6	6.9	21.5	31.1	6.5	21.7
$\text{Cu}(\text{NN'-dieten})_2(\text{SCN})_2 \cdot 2\text{H}_2\text{O}$	Purple	60	37.5	8.0	18.7	38.0	7.9	19.0
$\text{Cu}(\text{en})_2(\text{SeCN})_2$	Purple	<i>f</i>	18.3	4.1	21.9	18.2	4.3	21.0
$\text{Cu}(\text{pn})_2(\text{SeCN})_2$	Purple	<i>f</i>	22.8	4.8	19.7	22.7	4.9	20.1
$\text{Cu}(\text{NN-dimeen})_2(\text{SeCN})_2$	Blue	<i>f</i>	27.0	5.4	18.7	26.6	5.6	18.7
$\text{Cu}(\text{NN'-dimeen})_2(\text{SeCN})_2$	Blue	<i>f</i>	27.0	5.4	18.7	27.0	5.5	18.7
$\text{Cu}(\text{NN'-dieten})_2(\text{SeCN})_2 \cdot 2\text{H}_2\text{O}$	Purple	<i>f</i>	32.1	6.5	16.1	32.2	6.5	16.9

<sup>a</sup> Sulfur analysis: calcd. 26.7, found 26.4. <sup>b</sup> With decomposition. <sup>c</sup> Not measured. <sup>d</sup> Sulfur analysis: calcd. 23.9, found 23.5. <sup>e</sup> Sulfur analysis: calcd. 17.9, found, 17.8. <sup>f</sup> Decomposes on heating.

 TABLE II  
 MELTING POINTS AND ANALYTICAL DATA FOR THE  $\text{Ni}(\text{AA})_2\text{X}_2$  AND  $\text{Ni}(\text{AA})_2\text{X}_2$  COMPLEXES

Compound	Color	M.p., °C.	Calcd., %			Found, %		
			C	H	N	C	H	N
$[\text{Ni}(\text{en})_2(\text{NCS})_2]$	Purple	226	24.4	5.5	28.5	24.3	5.5	28.5
$[\text{Ni}(\text{pn})_2(\text{NCS})_2]$	Violet	192	29.7	6.2	<i>a</i>	29.7	6.2	<i>a</i>
$[\text{Ni}(2\text{-mepn})_2(\text{NCS})_2]$	Violet	236	34.3	6.8	23.8	34.4	7.1	23.5
$[\text{Ni}(\text{bn})_2(\text{NCS})_2]$	Violet	182	34.3	6.8	23.8	34.4	6.65	23.4
$[\text{Ni}(\text{NN'-dimeen})_2(\text{NCS})_2]$	Purple	232	34.3	6.8	23.8	34.3	6.5	23.4
$[\text{Ni}(\text{NN'-dieten})_2(\text{NCS})_2] \cdot 2\text{H}_2\text{O}$	Purple	181	38.0	8.1	<i>a</i>	37.9	7.8	<i>a</i>
$[\text{Ni}(\text{en})_3(\text{SCN})_2]$	Violet	228 <sup>b</sup>	27.0	6.8	<i>a</i>	26.8	6.9	<i>a</i>
$[\text{Ni}(\text{pn})_3(\text{SCN})_2]$	Violet	201	33.3	7.6	<i>a</i>	33.3	7.8	<i>a</i>
$[\text{Ni}(\text{en})_2(\text{NCSe})_2]$	Blue	<i>d</i>	18.5	4.2	21.7	18.6	4.3	21.7
$[\text{Ni}(\text{pn})_2(\text{NCSe})_2]$	Violet	<i>d</i>	23.0	4.8	20.2	22.7	4.3	20.3
$[\text{Ni}(\text{bn})_2(\text{NCSe})_2]$	Violet	<i>d</i>	27.0	5.7	18.9	27.3	5.7	18.0
$[\text{Ni}(\text{NN'-dimeen})_2(\text{NCSe})_2] \cdot \text{H}_2\text{O}$	Purple	<i>d</i>	26.0	5.6	18.2	26.1	5.6	18.3
$[\text{Ni}(\text{NN'-dieten})_2(\text{NCSe})_2] \cdot 2\text{H}_2\text{O}$	Purple	<i>d</i>	31.4	6.35	15.7	31.3	6.5	15.1
$[\text{Ni}(\text{pn})_3(\text{SeCN})_2]$	Violet	<i>d</i>	26.9	6.2	22.8	27.3	6.2	23.0

<sup>a</sup> Not measured. <sup>b</sup> With decomposition. <sup>c</sup> Selenium analysis: calcd. 40.7, found 40.8. <sup>d</sup> Decomposes on heating.

## Results

The compounds studied are presented in Tables I and II. Some of these compounds have been reported previously in the literature.

The type of bonding in the thiocyanate and selenocyanate complexes was determined by the positions of the bands due to these ligands in their infrared absorption spectra. The bands were assigned in all the copper and in the tris(diamine)nickel complexes by comparison with the corresponding chlorides. However, it has been shown that bis(ethylenediamine)nickel chloride and bromide complexes exist as dimers, with ethylenediamine molecules in the *cis* positions and with chloride bridges.<sup>18</sup>

This *cis* dimerization produces a symmetry different from that of the *trans* thiocyanates and selenocyanates. The positions of the bands due to SCN and SeCN in the  $\text{Ni}(\text{AA})_2\text{X}_2$  complexes could not therefore be deduced by comparison of their spectra with those of the

chlorides. They were, however, assigned by comparing the spectra of one with that of the other.

The infrared spectrum of the thiocyanate ion is characterized by three fundamental modes, the C-N stretch  $\nu_1$  which occurs near 2050  $\text{cm}^{-1}$ , the doubly degenerate bending mode  $\nu_2$  near 480  $\text{cm}^{-1}$ , and the C-S stretch  $\nu_3$  at about 750  $\text{cm}^{-1}$ .<sup>19</sup>

The position of the C-S stretching frequency,  $\nu_3$ , has been found to be a useful guide to the mode of bonding of the thiocyanate ligand.<sup>5,6b,20</sup> Relative to that in ionic thiocyanate the C-S stretching frequency increases in isothiocyanato complexes (M-NCS) to the region 780–860  $\text{cm}^{-1}$  and drops in thiocyanato complexes (M-SCN) to 690–720  $\text{cm}^{-1}$ .

It was noted by Turco<sup>10</sup> and Cotton<sup>21</sup> and further by

(19) L. H. Jones, *J. Chem. Phys.*, **25**, 1069 (1956).

(20) (a) M. M. Chamberlain and J. C. Bailar, *J. Am. Chem. Soc.*, **81**, 6412 (1959); (b) M. E. Baldwin, *J. Chem. Soc.*, 471 (1961); (c) J. Lewis, R. S. Nyholm, and P. W. Smith, *ibid.*, 4590 (1961); (d) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, p. 175.

(21) F. A. Cotton, D. M. L. Goodgame, M. Goodgame, and T. E. Haas, *Inorg. Chem.*, **1**, 565 (1962); K. Michelsen, *Acta Chem. Scand.*, **17**, 1811 (1963).

TABLE III  
FREQUENCIES (CM.<sup>-1</sup>) OF BANDS DUE TO THIOCYANATE IN COPPER  
DIAMINE COMPLEXES<sup>a</sup>

Complex	$\nu_1(\text{SCN})$	$\nu_2(\text{SCN})$
Cu(en)(NCS) <sub>2</sub>	2137 s 2110 s	794 m
Cu(pn)(NCS) <sub>2</sub>	2119 s 2080 s	800 w 811 w
Cu(2-mepn)(NCS) <sub>2</sub>	2141 s 2070 s	805 m
Cu(NN'-dimeen)(NCS) <sub>2</sub>	2141 s 2075 s	784 m
Cu(NN'-dieten)(NCS) <sub>2</sub>	2121 s 2075 s	786 m
Cu(NN'-dieten)(NCS) <sub>2</sub>	2119 s 2070 s	817 m
Cu(en) <sub>2</sub> (SCN) <sub>2</sub>	2020 s	730 m
Cu(pn) <sub>2</sub> (SCN) <sub>2</sub>	2063 s	736 m
Cu(NN'-dimeen) <sub>2</sub> (SCN) <sub>2</sub>	2075 s 2070 s 2065 s	740 m
Cu(NN'-dimeen) <sub>2</sub> (SCN) <sub>2</sub> · 2H <sub>2</sub> O	2062 s	746 m
Cu(NN'-dieten) <sub>2</sub> (SCN) <sub>2</sub> · 2H <sub>2</sub> O	2117 sh 2079 s 2012 sh	748 m

<sup>a</sup> s, strong, sharp band; m, medium band; w, weak band; sh, shoulder.

TABLE IV  
FREQUENCIES (CM.<sup>-1</sup>) OF BANDS DUE TO THE SELENOCYANATE  
GROUP IN COPPER DIAMINE COMPLEXES

Complex	$\nu_1(\text{SeCN})$	$\nu_2(\text{SeCN})$
Cu(en) <sub>2</sub> (SeCN) <sub>2</sub>	2055 s 2008 sh	a
Cu(pn) <sub>2</sub> (SeCN) <sub>2</sub>	2053 s 2028 sh	a
Cu(NN'-dimeen) <sub>2</sub> (SeCN) <sub>2</sub>	2074 s 2024 sh	560 m
Cu(NN'-dieten) <sub>2</sub> (SeCN) <sub>2</sub>	2072 s	530 m

<sup>a</sup> Region obscured by amine band. For other notes see Table III.

TABLE V  
FREQUENCIES (CM.<sup>-1</sup>) OF BANDS DUE TO THIOCYANATE IN NICKEL  
DIAMINE COMPLEXES

Complex	$\nu_1(\text{SCN})$	$\nu_2(\text{SCN})$
[Ni(en) <sub>2</sub> (NCS) <sub>2</sub> ]	2110 sh 2060 s	769 m
[Ni(pn) <sub>2</sub> (NCS) <sub>2</sub> ]	2092 s 2050 sh	775 m
[Ni(2-mepm)(NCS) <sub>2</sub> ]	2096 s	770 m
[Ni(bn) <sub>2</sub> (NCS) <sub>2</sub> ]	2096 s 2050 sh	775 m
[Ni(NN'-dimeen) <sub>2</sub> (NCS) <sub>2</sub> ] <sup>a</sup>	2092 s 2050 sh	790 m
[Ni(NN'-dieten) <sub>2</sub> (NCS) <sub>2</sub> ]	2101 sh 2062 s	780 m
[Ni(NN'-dieten) <sub>2</sub> (NCS) <sub>2</sub> ] · 2H <sub>2</sub> O	2070 s 2020 sh	775 m
[Ni(en) <sub>3</sub> ](SCN) <sub>2</sub>	2065 s 2055 s	740 m
[Ni(pn) <sub>3</sub> ](SCN) <sub>2</sub>	2061 s 2051 s	740 m
[Ni(bn) <sub>3</sub> ](SCN) <sub>2</sub>	2083 sh 2062 s	738 m

<sup>a</sup> Data from ref. 23; for other notes see Table III.

Michelson<sup>21</sup> that there is a parallel behavior between the corresponding thiocyanate and selenocyanate complexes with respect to the variation of the C-Se stretching frequency.

TABLE VI  
FREQUENCIES (CM.<sup>-1</sup>) OF BANDS DUE TO SELENOCYANATE IN  
NICKEL DIAMINE COMPLEXES

Complex	$\nu_1(\text{SeCN})$	$\nu_2(\text{SeCN})$
[Ni(en) <sub>2</sub> (NCSe) <sub>2</sub> ]	2070 s	a
[Ni(pn) <sub>2</sub> (NCSe) <sub>2</sub> ]	2024 w, sh 2096 sh 2083 s	692 w ?
[Ni(bn) <sub>2</sub> (NCSe) <sub>2</sub> ]	2101 s 2058 sh	
[Ni(NN'-dimeen) <sub>2</sub> (NCSe) <sub>2</sub> ]	2096 s	
[Ni(NN'-dieten) <sub>2</sub> (NCSe) <sub>2</sub> ] · 2H <sub>2</sub> O	2081 s 2037 sh	
[Ni(pn) <sub>3</sub> ](SeCN) <sub>2</sub>	2069 s 2052 s	520 w

<sup>a</sup> For notes see Tables III and IV.

TABLE VII  
MAGNETIC MOMENTS (B.M.) OF M(AA)<sub>2</sub>X<sub>2</sub> COMPLEXES IN THE  
SOLID STATE

Complex	Temp., °C.	$\mu_{\text{eff}}$
Ni(en) <sub>2</sub> (NCSe) <sub>2</sub>	20	3.24
Cu(en) <sub>2</sub> (SCN) <sub>2</sub>	21	1.81
Cu(en) <sub>2</sub> (SeCN) <sub>2</sub>	24	1.79

The positions of the bands in solid KSeCN<sup>22</sup> are:  $\nu_1$  2070 cm.<sup>-1</sup>,  $\nu_2$  424, 416 cm.<sup>-1</sup>, and  $\nu_3$  558 cm.<sup>-1</sup>. Turco<sup>10</sup> and Cotton<sup>21</sup> suggest the region around 650 (600–700) cm.<sup>-1</sup> for M–NCSe bonding and that around 550 (500–600) cm.<sup>-1</sup> for M–SeCN bonding.

The bands assigned to thiocyanate and selenocyanate are shown in Tables III–VI.

**Magnetic Measurements.**—The magnetic moments of some of the complexes are reported in Table VII. The values are normal, and that of the nickel compound agrees well with those found for complexes of nickel(II) with N,N-diethyl-1,2-diaminoethane.<sup>23</sup>

## Discussion

**Complexes of the Type Cu(AA)<sub>2</sub>X<sub>2</sub>.**—The infrared results also indicate ionic or weakly sulfur-bonded thiocyanate, in agreement with the conclusion from X-ray investigations.<sup>2b</sup> The Cu–S stretching frequency for Cu(en)<sub>2</sub>(SCN)<sub>2</sub> is 730 cm.<sup>-1</sup>, as compared with ~750 cm.<sup>-1</sup> for ionic thiocyanate and 690–720 cm.<sup>-1</sup> for sulfur–metal bonding. The Cu–S stretching rises to the "ionic" value with substitution on the diamine (see Table III).

Preliminary X-ray investigation of Cu(en)<sub>2</sub>(SeCN)<sub>2</sub> has shown<sup>24</sup> that this compound is probably isostructural with the thiocyanate analog. Bands at 560 and 530 cm.<sup>-1</sup> in the copper diamine selenocyanates can be assigned to ionic or selenium bonded selenocyanate.<sup>22</sup>

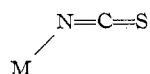
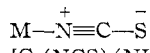
**Compounds of the Type Cu(AA)(NCS)<sub>2</sub>.**—The mono-diamine copper complexes all contain nitrogen-bonded isothiocyanate, the C–S stretching frequencies falling in the range 790–810 cm.<sup>-1</sup> (see Table III). The high C–N stretching frequencies indicate that the thiocyanate group is most probably bridging<sup>20c</sup> as in Cu(py)<sub>2</sub>(NCS)<sub>2</sub> with sulfur atoms in the axial positions.<sup>3</sup> Alterna-

(22) H. W. Morgan, *J. Inorg. Nucl. Chem.*, **16**, 367 (1961).

(23) D. M. L. Goodgame and L. M. Venanzi, *J. Chem. Soc.*, 616 (1961); *ibid.*, 5909 (1963).

(24) E. C. Lingafelter, private communication.

TABLE VIII  
 BOND DISTANCES AND BOND ANGLES IN SOME ISOTHIOCYANATO COMPLEXES

	N-C, Å.	C-S, Å.	N-S, Å.	∠MNC, deg.	Ref.
	N=C 1.26	C=S 1.60	2.86	<180	25
	N≡C 1.15	C-S 1.77	2.92	180	25
1 [Cr(NCS) <sub>4</sub> (NH <sub>3</sub> ) <sub>2</sub> ]NH <sub>4</sub>	1.14	1.80	2.94	180	b
2 [Cr(NCS) <sub>4</sub> (NH <sub>3</sub> ) <sub>2</sub> ]C <sub>5</sub> H <sub>5</sub> NH	1.15	1.76	2.91	180	b
3 [Cr(NCS) <sub>4</sub> (NH <sub>3</sub> ) <sub>2</sub> ]C <sub>5</sub> H <sub>13</sub> NOH	1.27	1.64	2.91	155	b
4 K <sub>2</sub> [Co(NCS) <sub>4</sub> ]·4H <sub>2</sub> O	1.23	1.59	2.82	111	c
5 Hg[Co(NCS) <sub>4</sub> ]	a	a	a	180	d
6 [Ni(en) <sub>2</sub> (NCS) <sub>2</sub> ]	1.20	1.64	2.84	140	2a
7 [Ni(NH <sub>3</sub> ) <sub>4</sub> (NCS) <sub>2</sub> ]	1.20	1.61	2.81	180	25

<sup>a</sup> No bond lengths reported in the literature. <sup>b</sup> Y. Takeuchi and Y. Saito, *Bull. Chem. Soc. Japan*, **30**, 319 (1957). <sup>c</sup> G. S. Zhdanov and Z. V. Zvonkova, *Zh. Fiz. Khim.*, **24**, 1338 (1950). <sup>d</sup> J. W. Jeffrey, *Nature*, **159**, 610 (1947).

tively, the compounds may be square-planar with *cis* isothiocyanate groups. A structure of the latter type might produce the splitting of the C-N stretching bands into two sharp peaks, although Burmeister and Basolo<sup>6b</sup> noted that there was no such splitting in the *cis* isothiocyanato complexes of Pt(II) and Pd(II) which they investigated. Further work on this group of compounds and the selenocyanate analogs is in progress.

**Compounds of the Type Ni(AA)<sub>2</sub>X<sub>2</sub>.**—The tris(diamine)nickel(II) thiocyanates show bands which are usual for ionic thiocyanate. The C-N stretching bands show splitting of a type previously reported for tris(ethylenediamine)cobalt(III) thiocyanate in the solid state.<sup>20b</sup> A similar splitting occurs in the tris(propylenediamine)nickel(II) selenocyanate (Table VI). This last compound has a band at 520 cm.<sup>-1</sup> which can be assigned to ionic selenocyanate.

**Compounds of the Type Ni(AA)<sub>2</sub>X<sub>2</sub>.**—Bis(ethylenediamine)nickel(II) isothiocyanate has been shown<sup>1</sup> to be octahedral with nitrogen-bonded isothiocyanate in the *trans* positions, and a preliminary X-ray investigation<sup>24</sup> of [Ni(en)<sub>2</sub>(NCSe)<sub>2</sub>] indicates that the two compounds are isostructural.

The MNC bond angle in [Ni(en)<sub>2</sub>(NCS)<sub>2</sub>] is 140°, in contrast to that in [Ni(NH<sub>3</sub>)<sub>4</sub>(NCS)<sub>2</sub>] which, although similarly *trans* bonded, has collinear M-N-C-S.<sup>25</sup>

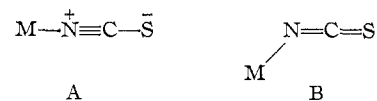
There are such wide variations in the C-N stretching frequencies reported in the literature that to obtain meaningful correlations between the position of this band and the bonding of the thiocyanate ligand it appears necessary to compare stretching frequencies, bond lengths, and bond angles in complexes which contain thiocyanate attached to the same metal in the same oxidation state. Some data on bond distances and bond angles for complexes of Cr(III), Co(II), and Ni(II) are collected in Table VIII.

Comparing compounds 1 and 3 in Table VIII, the ammonium and choline reineckates, it appears that the bonding of the isothiocyanate in these two complexes approximates to A and B, respectively.<sup>26</sup>

On going from a structure of type B to that of type A the C-N bond goes from approximately C≡N to

(25) M. A. Porai-Koshits, E. K. Inkhno, A. S. Antsyshkina, and L. M. Dikareva, *Soviet Phys.-Cryst.*, **2**, 366 (1957).

(26) J. Fujita, K. Nakamoto, and M. Koboyashi, *J. Am. Chem. Soc.*, **78**, 3295 (1956).



C≡N, and this should be accompanied by a decrease in the covalent character of the coordinated bond, with a corresponding increase in the C-N stretching frequency. The C-N stretch of 3, the choline salt, is at 2081 cm.<sup>-1</sup>,<sup>20c</sup> and that of compound 1, the ammonium salt, is at 2120 (s), 2056 (sh) cm.<sup>-1</sup>,<sup>20c</sup>

The two cobalt complexes may also be compared. In compound 4, the bonding about cobalt approximates to B, while that in compound 5 corresponds to A, with a further interaction between the sulfur and mercury atoms. The C-N stretching frequencies for these compounds are: compound 4 2093–2095 (s), 2065 (sh) cm.<sup>-1</sup>; compound 5 2144 cm.<sup>-1</sup>,<sup>20c</sup>

Thus in both cases the compound with bonding type A has a higher C-N stretching frequency than that with bonding type B. Considering the nickel(II) complexes, compound 6 has type B structure and compound 7 has type A structure; the C-N stretching frequencies are 2060 (s), 2110 (sh),<sup>27</sup> and 2096 cm.<sup>-1</sup>,<sup>28</sup> respectively.

Substitution of bulky groups on the diamine might be expected to result in considerable steric strain with angular M-NCS bonding, particularly if the substitution is at one or both of the carbon atoms of the diamine.<sup>29</sup>

The main C-N stretching bands, given in Table V, show that the frequencies fall in the order: en < NN'-dimeen < NN'-dieten < NN-dimeen < pn < bn ~ 2-mepn. Thus it is expected that substituents on the carbon atoms of the diamine make bonding of type B unlikely on steric grounds and that the higher frequencies found in the carbon-substituted compounds are indicative of bonding which tends toward type A.

The C-N stretching frequencies of the selenocyanates follow a similar order: en < NN'-dieten < NN'-dimeen < pn < bn.

In only one compound could a band be assigned to the isoselenocyanate C-Se stretch. A band was found

(27) This work.

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

(29) See ref. 2a, Figure 3 (001 projection).

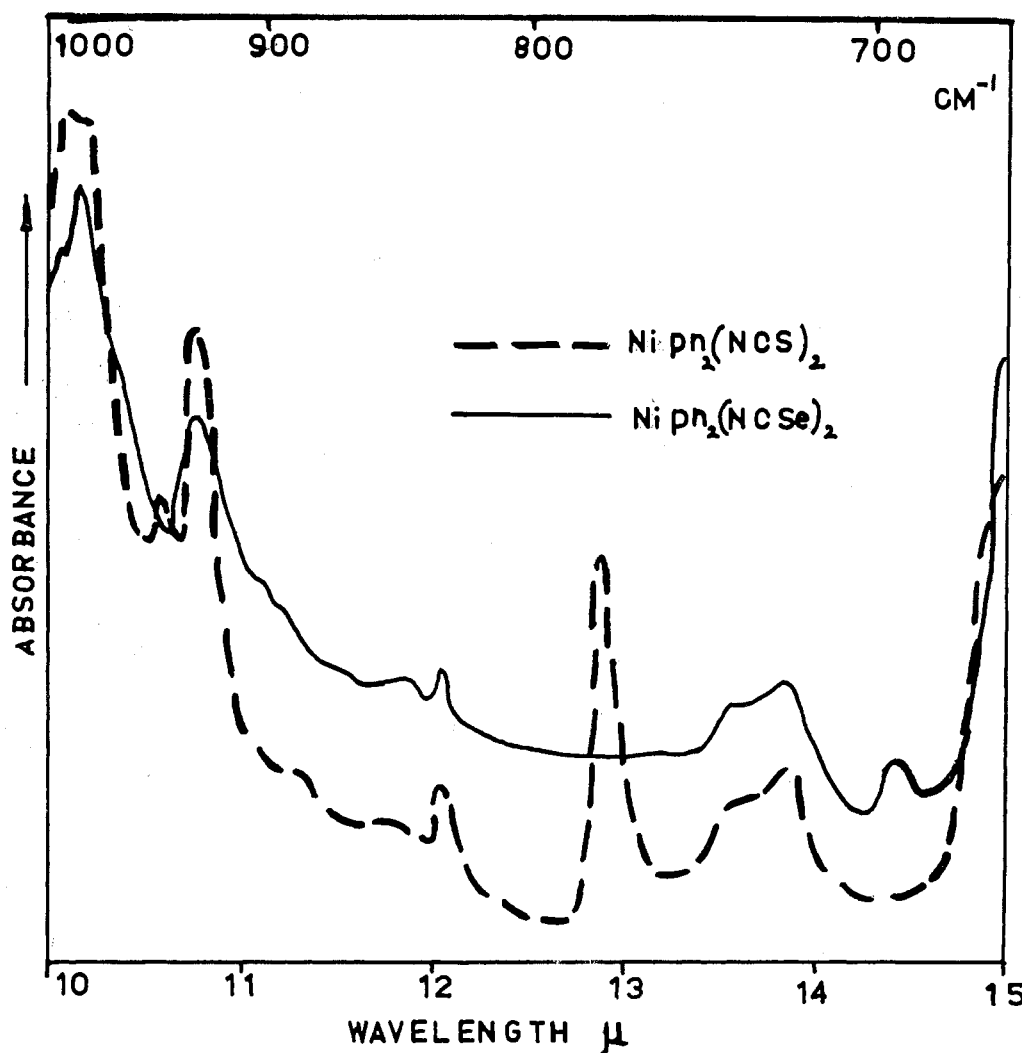


Figure 1.—Infrared spectra from 10 to 15  $\mu$  of  $\text{Ni}(\text{pn})_2(\text{NCS})_2$  and  $\text{Ni}(\text{pn})_2(\text{NCSe})_2$ .

at  $692\text{ cm}^{-1}$  in  $[\text{Ni}(\text{pn})_2(\text{NCSe})_2]$  which was not present in the isothiocyanato complex (see Figure 1).

**Water in the Compounds  $[\text{Ni}(\text{NN}'\text{-dieten})_2\text{X}_2] \cdot 2\text{H}_2\text{O}$ .**—Both the complexes where X is thiocyanate and where X is selenocyanate contain two molecules of water. That the thiocyanate is not  $[\text{Ni}(\text{NN}'\text{-dieten})_2(\text{OH}_2)_2](\text{SCN})_2$  is shown by the C-S stretch at  $775\text{ cm}^{-1}$  and the absence of any band which could be assigned to the C-S stretching frequency of ionic thiocyanate.

There are very sharp bands in the region of the O-H stretch ( $3500\text{--}3400\text{ cm}^{-1}$ ) and in the  $\text{OH}_2$  deformation region ( $1610\text{ cm}^{-1}$ ). The bands are:  $3567$  (sh),  $3497$  (s),  $3448$  (sh),  $3284$  (s),  $3245$  (s), and  $1612\text{ cm}^{-1}$ . The spectrum of the selenocyanate complex is negligibly different from that of the thiocyanate in these regions and it is concluded that they have similar structures.

The bands at  $3284$  and  $3245\text{ cm}^{-1}$  are in the position expected for the N-H stretching frequency of coordinated amine.<sup>30</sup> However, only one band would be expected in this region in the complex of the N,N'-

disubstituted amine, and it is therefore possible that one of these two sharp bands is either  $\nu_1$  or  $\nu_3$  of water.<sup>31</sup>

The bands in the  $3400\text{ cm}^{-1}$  region are much sharper than those in  $[\text{Ni}(\text{NN}'\text{-dieten})_2(\text{OH}_2)_2]\text{Cl}_2$ , which has a broad absorption covering the O-H and N-H stretching regions.<sup>32</sup>

Heating the thiocyanato complex at  $90^\circ$  for 3 hr. produced no visible change in the infrared spectrum. It seems possible that the water is held in the complex by hydrogen bonding similar to that discussed by Goodgame and Venanzi for the nickel N,N-diethylethylenediamine fluoro, chloro, and sulfato complexes.<sup>23</sup>

**Acknowledgments.**—The authors wish to thank Dr. V. C. G. Trew for help and discussions and Professor E. C. Lingafelter for crystallographic results. A studentship from the University of London (to J. M. J.) is gratefully acknowledged.

(30) M. E. Baldwin, *J. Chem. Soc.*, 4369 (1960); D. B. Powell and N. Sheppard, *Spectrochim. Acta*, **17**, 68 (1961).

(31) Reference 20d, p. 83.

(32) M. E. Farago and J. M. James, unpublished results.