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## Isothiocyanato Complexes of Nickel(II) and Copper(II)

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The preparations are described of  $[(\text{CH}_3)_4\text{N}]_4\text{Ni}(\text{NCS})_6$ ,  $[(\text{C}_2\text{H}_5)_4\text{N}]_4\text{Ni}(\text{NCS})_6$ ,  $[(\text{CH}_3)_4\text{N}]_2\text{Ni}(\text{NCS})_4$ ,  $(\text{Cat}^{2+})_2\text{M}(\text{NCS})_4$ , where  $\text{M} = \text{Co}, \text{Ni}, \text{or Cu}$ ,  $[(\text{C}_6\text{H}_5)_4\text{As}]_2\text{Ni}(\text{NCS})_4$ ,  $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{Cu}(\text{NCS})_4$ , and anhydrous  $\text{NiHg}(\text{SCN})_4$ . Two forms of  $[(\text{C}_6\text{H}_5)_4\text{As}]_2\text{Ni}(\text{NCS})_4$  were obtained, one olive-yellow and the other dark blue-green. The electronic and infrared spectra and magnetic properties of these compounds and also of  $\text{CuHg}(\text{SCN})_4$  and  $(\text{Cu,Zn})\text{Hg}(\text{SCN})_4$  are reported. The results of these physical studies point to the presence of discrete  $\text{M}(\text{NCS})_4^{2-}$  ions with distorted tetrahedral structure in  $(\text{Cat}^{2+})_2\text{M}(\text{NCS})_4$ , where  $\text{M} = \text{Ni}$  or  $\text{Cu}$ , and the blue-green form of  $[(\text{C}_6\text{H}_5)_4\text{As}]_2\text{Ni}(\text{NCS})_4$ , but show that in the olive-yellow form of  $[(\text{C}_6\text{H}_5)_4\text{As}]_2\text{Ni}(\text{NCS})_4$  and the complexes with the smaller cations the nickel(II) and copper(II) ions have a six-coordinate, tetragonal environment. The nickel(II) ion in  $\text{NiHg}(\text{SCN})_4$  is also thought to be in a tetragonal ligand field. The electronic spectra and X-ray powder patterns of the purple solids of composition  $(\text{Cu}_x\text{Zn}_{1-x})\text{Hg}(\text{SCN})_4$  show that the copper(II) ions are in a distorted tetrahedral environment of nitrogen atoms, although in the green compound  $\text{CuHg}(\text{SCN})_4$  the copper(II) ions are six-coordinate.

### Introduction

Despite recent interest<sup>2</sup> in the mode of coordination of  $\text{NCS}^-$ , there is relatively little information available concerning the complex ions  $\text{M}(\text{NCS})_x^{n-}$  or  $\text{M}(\text{SCN})_x^{n-}$  formed by some quite well-studied transition metals such as nickel or copper. Hydrated compounds of the type  $\text{M}_4\text{Ni}(\text{NCS})_6 \cdot n\text{H}_2\text{O}$  are described in the older literature,<sup>3</sup> and the potassium salt has subsequently been shown to contain discrete  $\text{Ni}(\text{NCS})_6^{4-}$  anions.<sup>4</sup> The "double salt" reported<sup>3</sup> as  $\text{Na}_2\text{Ni}(\text{NCS})_4 \cdot 8\text{H}_2\text{O}$  was later found<sup>5</sup> to be  $\text{Na}_4\text{Ni}(\text{NCS})_6 \cdot 12\text{H}_2\text{O}$ . No solid compounds of copper(II) containing  $\text{Cu}(\text{NCS})_x^{n-}$  anions appear to have been described. Accordingly, we felt it desirable to investigate the possibility of preparing copper(II) complexes of this type and to examine further the complex "thiocyanato" anions formed by nickel(II). We report here the results of these studies.

### Experimental

**Preparation of Compounds.**  $(\text{Cat}^{2+})(\text{NCS})_2^1$  and  $\text{Q}(\text{NCS})$  ( $\text{Q} = (\text{CH}_3)_4\text{N}^+$ ,  $(\text{C}_2\text{H}_5)_4\text{N}^+$ , and  $(\text{C}_6\text{H}_5)_4\text{As}^+$ ).—These were prepared metathetically from the corresponding chlorides or bromides and KNCS in ethanol or ethanol-acetone solution and were purified by recrystallization from ethanol or nitromethane.

**Solutions of nickel thiocyanate** in acetone or ethanol were prepared metathetically from nickel nitrate hexahydrate and KNCS.

$[(\text{C}_2\text{H}_5)_4\text{N}]_4\text{Ni}(\text{NCS})_6$ .—On mixing ethanolic solutions of nickel thiocyanate (1.0 g. in 10 ml.) and  $[(\text{C}_2\text{H}_5)_4\text{N}]\text{NCS}$  (2.5 g. in 10 ml.) green-blue crystals of the complex slowly separated. These were filtered off, washed with ethanol and then ether, and dried *in vacuo*; 36% yield; m.p. 176°;  $\Lambda_m$  in  $\text{C}_6\text{H}_5\text{NO}_2$  ( $10^{-3} M$ ) 95 ohm<sup>-1</sup> cm.<sup>2</sup> at 20°.

*Anal.* Calcd. for  $\text{C}_{28}\text{H}_{60}\text{N}_{10}\text{NiS}_6$ : C, 49.20; H, 8.63; N, 15.11; Ni, 6.33. Found: C, 49.43; H, 8.76; N, 15.10; Ni, 6.33.

**(Quinolinium)<sub>4</sub>Ni(NCS)<sub>6</sub>** was prepared as described by Grossmann and Hünseler.<sup>6</sup>

(1)  $\text{Cat}^{2+} = [p\text{-xylylenebis}(\text{triphenylphosphonium})]^{2+}$ .

(2) F. Basolo, W. H. Baddley, and J. L. Burmeister, *Inorg. Chem.*, **3**, 1202 (1964), and references therein.

(3) A. Rosenheim and R. Cohn, *Z. anorg. allgem. Chem.*, **27**, 280 (1901).

(4) G. S. Zhdanov, Z. V. Zvonkova, and V. P. Gluskova, *Zh. Fiz. Khim.*, **27**, 106 (1953).

(5) G. S. Zhdanov, K. I. Tobelko, and Z. V. Zvonkova, *Dokl. Akad. Nauk SSSR*, **88**, 679 (1953).

$[(\text{CH}_3)_4\text{N}]_4\text{Ni}(\text{NCS})_6$  and  $[(\text{CH}_3)_4\text{N}]_2\text{Ni}(\text{NCS})_4$ .—Both these compounds resulted from the attempt to prepare the latter complex. A hot solution of  $[(\text{CH}_3)_4\text{N}]\text{NCS}$  (4.36 g.) in nitromethane (50 ml.) was added to one of nickel thiocyanate (2.63 g.) in acetone (45 ml.). A pale blue-green solid separated. The mixture was heated to boiling and then allowed to cool to room temperature. The solid was filtered off, washed with nitromethane, and then dried *in vacuo* over  $\text{H}_2\text{SO}_4$ ; yield 4.4 g. Part (2 g.) of the solid product was dissolved in 90 ml. of boiling nitromethane, and the dark blue solution was filtered and allowed to cool to room temperature. Pale blue crystals of  $[(\text{CH}_3)_4\text{N}]_4\text{Ni}(\text{NCS})_6$  separated and were filtered off, washed with ethanol, and air-dried; yield 0.8 g.; dec. pt. ~300°.

*Anal.* Calcd. for  $\text{C}_{22}\text{H}_{48}\text{Ni}_{10}\text{S}_6$ : C, 37.54; H, 6.87; N, 19.91. Found: C, 37.09; H, 7.09; N, 19.57.

On standing in a refrigerator for 2 days the mother liquor from the above gave 0.5 g. of apple-green  $[(\text{CH}_3)_4\text{N}]_2\text{Ni}(\text{NCS})_4$ , which was filtered off, washed with nitromethane, and air-dried; m.p. 284° with frothing and decomposition.

*Anal.* Calcd. for  $\text{C}_{12}\text{H}_{24}\text{NiN}_6\text{S}_4$ : C, 32.81; H, 5.51; N, 19.13. Found: C, 32.58; H, 5.79; N, 19.07.

**$[(\text{C}_6\text{H}_5)_4\text{As}]_2\text{Ni}(\text{NCS})_4$ , Olive-Yellow Form.**—Nickel thiocyanate and  $[(\text{C}_6\text{H}_5)_4\text{As}]\text{NCS}$  were mixed in 2:1 molar ratio in acetone. Olive-yellow crystals separated from the deep blue solution. The complex was recrystallized from nitromethane and air-dried.

*Anal.* Calcd. for  $\text{C}_{52}\text{H}_{40}\text{As}_2\text{NiN}_4\text{S}_4$ : C, 59.05; H, 3.81; N, 5.30. Found: C, 58.83; H, 4.08; N, 5.62.

**Blue-Green Form.**—On heating the olive-yellow form at ~155° for 24 hr. the color changed to dark blue-green without change in weight; m.p. 219°.

**$(\text{Cat}^{2+})_2\text{Ni}(\text{NCS})_4$ .**—A solution of nickel thiocyanate (0.6 g.) in acetone was dried over molecular sieves (4A), heated to boiling, and filtered into a solution of  $(\text{Cat}^{2+})(\text{NCS})_2$  (2.6 g.) in hot nitromethane (40 ml.). Dark blue crystals separated, which were filtered off, washed with hot nitromethane and then ether, and dried *in vacuo*; 85% yield; m.p. 262–263°.

*Anal.* Calcd. for  $\text{C}_{48}\text{H}_{38}\text{N}_4\text{NiP}_2\text{S}_4$ : C, 62.67; H, 4.16; N, 6.09. Found: C, 62.10; H, 4.10; N, 6.04.

**$(\text{Cat}^{2+})_2\text{Co}(\text{NCS})_4$  and  $(\text{Cat}^{2+})_2\text{Cu}(\text{NCS})_4$**  were prepared as for the nickel(II) analog. The blue cobalt(II) complex has m.p. 270°.

*Anal.* Calcd. for  $\text{C}_{48}\text{H}_{38}\text{CoN}_4\text{P}_2\text{S}_4$ : C, 62.66; H, 4.16. Found: C, 63.13; H, 4.28.

The dark purple copper(II) complex was obtained in 32% yield; m.p. 212°.

(6) H. Grossmann and F. Hünseler, *Z. anorg. allgem. Chem.*, **46**, 361 (1905).

*Anal.* Calcd. for  $C_{48}H_{36}CuN_4P_2S_4$ : C, 62.37; H, 4.11; N, 6.06. Found: C, 61.94; H, 4.13; N, 5.88.

$[(C_2H_5)_4N]_2Cu(NCS)_4$ .—Potassium thiocyanate (1.84 g.) in acetone (25 ml.) was shaken with  $[(C_2H_5)_4N]_2CuBr_4$  (3.0 g.) for 15 min. The dark red solution was filtered into 30 ml. of ether and cooled to 0° for 6 hr. Green crystals formed and these were filtered off, recrystallized twice from nitromethane-ether, and dried *in vacuo*; 40% yield; m.p. 106°;  $\Lambda_m$  in  $C_6H_5NO_2$  ( $10^{-3}$  M) 63 ohm.<sup>-1</sup> cm.<sup>2</sup> at 25°.

*Anal.* Calcd. for  $C_{20}H_{40}CuN_6S_4$ : C, 43.20; H, 7.20; N, 15.12. Found: C, 42.87; H, 7.11; N, 15.57.

$CuHg(SCN)_4$ ,  $ZnHg(SCN)_4$ , and  $NiHg(SCN)_4 \cdot 2H_2O$  were prepared by the method of Rosenheim and Cohn.<sup>3</sup>

$NiHg(SCN)_4$ .—This yellow-green compound was obtained by heating the blue dihydrate to constant weight at 155°. Weight loss: calcd., 6.83%; found, 6.85%.

*Anal.* Calcd. for  $NiHg(SCN)_4$ : Ni, 11.94. Found: Ni, 11.88.

$(Cu,Zn)Hg(SCN)_4$ .—Purple solids containing  $Cu^{2+}$  ions doped into the  $ZnHg(SCN)_4$  lattice were prepared by adding aqueous solutions of  $(NH_4)_2Hg(SCN)_4$  to mixed aqueous solutions of zinc nitrate and copper nitrate. The mole fractions of  $Cu^{2+}$  in the products were determined by metal analysis.

**Physical Measurements.**—X-Ray powder photographs were taken with an Enraf-Nonius Guinier-De Wolff No. II camera or with a Philips Debye-Scherrer Type PW 1024 camera, using nickel-filtered copper radiation. Intensities were estimated visually. The magnetic susceptibilities of solutions were determined by the n.m.r. method<sup>7</sup> using tetramethylsilane as reference and a Willmad concentric tube. Infrared spectra were obtained with a Grubb-Parsons Spectromaster grating spectrometer. The other physical measurements were carried out as described previously.<sup>8</sup>

## Results and Discussion

**Nickel Compounds. Complexes of the Type  $(Cation)_4Ni(NCS)_6$ .**—The stoichiometries and structures of the anions  $Ni(NCS)_z^{n-}$  in the compounds we have studied depend upon the identity of the cation and the conditions of preparation. With  $(CH_3)_4N^+$ ,  $(C_2H_5)_4N^+$ , or  $(C_9H_8N)^+$  pale blue or green-blue salts of composition  $(cation)_4Ni(NCS)_6$  may be obtained in the solid state, and these are analogous to those with alkali metal cations reported by previous workers.

The electronic spectra of these compounds were measured to determine the value of  $\Delta$ , the ligand field strength parameter, for an octahedral arrangement of NCS groups around nickel(II). The band energies observed for one of them,  $[(C_2H_5)_4N]_4Ni(NCS)_6$ , are given in Table I. The spectra of the corresponding  $K^+$ ,  $(CH_3)_4N^+$ , and quinolinium salts were virtually identical with that of the tetraethylammonium compound, except that in the spectrum of the quinolinium complex the band expected at  $\sim 26,000$  cm.<sup>-1</sup> was hidden by the tail from a strong absorption band in the ultraviolet region due to the cation.

The energies of the spin-allowed transitions:  ${}^3A_{2g} \rightarrow {}^3T_{2g}$  at 9600 cm.<sup>-1</sup>,  ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$  at 15,950 cm.<sup>-1</sup>, and  ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$  at 25,800 cm.<sup>-1</sup> agree well with those predicted from the Liehr and Ballhausen energy level diagram<sup>9</sup> for nickel(II) in a ligand field of  $O_h$  symmetry with  $\Delta \approx 9600$  cm.<sup>-1</sup>. The shoulder at  $\sim 13,700$  cm.<sup>-1</sup> is probably due to  ${}^3A_{2g} \rightarrow {}^1E_g(D)$ , though, with

(7) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

(8) D. Forster and D. M. L. Goodgame, *ibid.*, 2790 (1964).

(9) A. D. Liehr and C. J. Ballhausen, *Ann. Phys.*, **6**, 134 (1959).

TABLE I

ELECTRONIC ABSORPTION SPECTRA<sup>a</sup>

Compound	Absorption max., cm. <sup>-1</sup> ( $\epsilon_{molar}$ for soln.)
$[(C_2H_5)_4N]_4Ni(NCS)_6$	25,800, $\sim 22,200$ sh, 15,950, $\sim 13,700$ sh, 9,600
$Ni(NCS)_4^{2-}$ in acetone (0.133 M + excess NCS <sup>-</sup> )	$\sim 17,700$ sh, 16,100 (287), 15,110 (260), 12,300 (17), 9,900 (60), $\sim 4,800$ br ( $\sim 65$ )
$[(CH_3)_4N]_2Ni(NCS)_4$	$\sim 20,800$ sh, <sup>b</sup> 15,750, 7,870
$[(C_2H_5)_4As]_2Ni(NCS)_4$ (olive-yellow)	23,260, $\sim 20,000$ sh, 14,030, $\sim 11,300$ sh, $\sim 9,800$ sh, 6,060 <sup>c</sup>
$[(C_2H_5)_4As]_2Ni(NCS)_4$ (blue-green)	16,100, <sup>d</sup> 14,900, <sup>d</sup> 10,000, $\sim 4,570$ v br
$(Cat^{2+})Ni(NCS)_4$ (blue)	17,800, <sup>d</sup> 15,000, <sup>d</sup> 10,050, $\sim 7,250$ sh, 4,440 v br
$NiHg(SCN)_4$	$\epsilon$ , 15,340, 9,210, $\sim 7,000$ sh
$CuHg(SCN)_4$	$\sim 23,000$ br, 15,100
$(Cu_{0.44}Zn_{0.56})Hg(SCN)_4$	$\sim 30,000$ br, 18,300, 10,500
$[(C_2H_5)_4N]_2Cu(NCS)_4$	$\sim 23,000$ br, 15,600
$(Cat^{2+})Cu(NCS)_4$	$\sim 33,000$ br, $\sim 18,600$ br, 11,100

<sup>a</sup> For solids, by reflectance, unless stated otherwise. <sup>b</sup> On side of strong absorption in the ultraviolet. <sup>c</sup> Band asymmetric to lower energy. <sup>d</sup> Maxima of broad multicomponent band. <sup>e</sup> Strong charge-transfer absorption edge  $> 19,000$  cm.<sup>-1</sup>.

the values of the interelectronic repulsion parameters chosen for the calculation of the energy level diagram in ref. 9, this would be expected at rather lower energy ( $\sim 12,500$  cm.<sup>-1</sup>). The shoulder at  $\sim 22,200$  cm.<sup>-1</sup> could be either  ${}^3A_{2g} \rightarrow {}^1A_{1g}(G)$  or  ${}^3A_{2g} \rightarrow {}^1T_{2g}(D)$ , since both of these should occur in this general energy region, but is more likely the latter alternative.

The  $\Delta$  value of  $\sim 9600$  cm.<sup>-1</sup> suggests very strongly that the NCS groups are bonded through nitrogen, since S-bonded thiocyanate lies below  $Cl^-$  in the spectrochemical series<sup>10</sup> and  $\Delta$  for an octahedral arrangement of chloride ions around nickel(II) is 6600–7200 cm.<sup>-1</sup>.<sup>11</sup> Further support for N bonding is provided by the infrared spectra of  $K_4Ni(NCS)_6 \cdot 4H_2O$ <sup>12</sup> and of the salts with organic cations (Table II).

TABLE II  
C-N AND C-S STRETCHING FREQUENCIES, CM.<sup>-1</sup>, OF THE COMPLEXES

Compound <sup>a</sup>	C-N <sup>d</sup>	C-S
$[(CH_3)_4N]_4Ni(NCS)_6$	2096	777 w
$[(C_2H_5)_4N]_4Ni(NCS)_6$	2098	775 vw, sh <sup>b</sup>
$(C_9H_8N)_4Ni(NCS)_6$	2090, 2068	<sup>c</sup>
$NiHg(SCN)_4$	2162 br	766 vw
$[(CH_3)_4N]_2Ni(NCS)_4$	2123 sh, 2114	773 m
$[(C_2H_5)_4As]_2Ni(NCS)_4$ olive-yellow	2141 m, 2096, 2079	853 vw, 813 vw, 809 vw, 790 vw
$[(C_2H_5)_4As]_2Ni(NCS)_4$ blue-green	2051	830 vw
$(Cat^{2+})Ni(NCS)_4$ blue	2070	835 w
$[(C_2H_5)_4N]_2Cu(NCS)_4$	2062	<sup>c</sup>
$(Cat^{2+})Cu(NCS)_4$	2074	835 w
$(Cat^{2+})Co(NCS)_4$	2066	836 w

<sup>a</sup> Nujol mulls. <sup>b</sup> On the side of cation absorption. <sup>c</sup> Region obscured by cation absorption. <sup>d</sup> Very strong unless stated otherwise.

The magnetic moment of  $[(C_2H_5)_4N]_4Ni(NCS)_6$ , 3.25 B.M. at room temperature, is in the range commonly found for octahedral nickel(II).

The compounds  $(cation)_4Ni(NCS)_6$  are somewhat soluble in polar, relatively noncoordinating solvents

(10) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, Oxford, London, New York, Paris, 1962, p. 109.

(11) R. W. Asmussen and O. Bostrup, *Acta Chem. Scand.*, **11**, 745 (1957); D. M. L. Goodgame, M. Goodgame, and M. J. Weeks, *J. Chem. Soc.*, 5194 (1964).

(12) J. Lewis, R. S. Nyholm, and P. W. Smith, *ibid.*, 4590 (1961).

such as nitromethane or nitrobenzene, but solution results in extensive formation of the tetrahedral  $\text{Ni}(\text{NCS})_4^{2-}$  ion (*vide infra*). This behavior parallels that found<sup>13</sup> for  $\text{Mn}(\text{NCS})_6^{4-}$ .

**Complexes of the Type  $(\text{Cation})_2\text{Ni}(\text{NCS})_4$ .**—Solutions of nickel nitrate in acetone containing excess  $\text{NCS}^-$  are deep blue. The electronic spectra of these solutions (Table I, Figure 1) are very similar, both in band position and intensity, to those of tetrahedral nickel(II) complexes and especially to that of  $\text{Ni}(\text{NCO})_4^{2-}$ . A Harvey-Manning plot<sup>14</sup> of  $\text{NCS}^-:\text{Ni}^{2+}$  against the optical density of the band maximum at  $16,100\text{ cm}^{-1}$  indicated that the blue, tetrahedral complex species present in these solutions is  $\text{Ni}(\text{NCS})_4^{2-}$ . Since the discontinuity in this plot was not absolutely sharp and occurred at  $\text{NCS}^-:\text{Ni}^{2+} = 4.15:1$ , it appears that  $\text{Ni}(\text{NCS})_4^{2-}$  is somewhat solvolyzed in acetone unless a slight excess of  $\text{NCS}^-$  is present. The tetrahalonickelate(II) anions are known<sup>15</sup> to solvolyze unless an excess of halide ions is added. The electronic spectral data given in Table I and Figure 1 for the acetone solutions of  $\text{Ni}(\text{NCS})_4^{2-}$  were obtained with well-dried solutions containing a slight excess of  $\text{NCS}^-$  to minimize solvolysis.

The spectrum may be assigned satisfactorily on the basis of a ligand field of  $T_d$  symmetry<sup>9</sup> with  $B = 810\text{ cm}^{-1}$ ,  $C = 3150\text{ cm}^{-1}$ ,  $\lambda = -275\text{ cm}^{-1}$ , and  $\Delta = 4900\text{ cm}^{-1}$ , as follows:  ${}^3T_1(F) \rightarrow {}^3T_2$  at  $\sim 4800\text{ cm}^{-1}$ ,  ${}^3T_1(F) \rightarrow {}^3A_2$  at  $9900\text{ cm}^{-1}$ ,  ${}^3T_1(F) \rightarrow {}^1T_2(D)$  at  $12,300\text{ cm}^{-1}$ , and  ${}^3T_1(F) \rightarrow {}^3T_1(P)$  at  $15,100, 16,100,$  and  $\sim 17,700\text{ cm}^{-1}$ . The band due to  ${}^3T_1(F) \rightarrow {}^3T_1(P)$  is rather broader than theoretically predicted,<sup>9</sup> but a similar band broadening has been observed for other tetrahedral nickel(II) complexes.<sup>16</sup> All of the band due to  ${}^3T_1(F) \rightarrow {}^3T_2$  was not observed because of the limit of the range of the spectrometer, and the band maximum could not be determined exactly owing to the presence of sharp vibrational bands in this region.

Some indication of the relative intensities of the three spin-allowed bands was obtained from the values of  $\epsilon_{\text{max}}d\nu$ , where  $d\nu$  is the band width at half-height. The ratios of these values are 0.29:0.14:1.0 for the three bands in increasing order of energy. These are in good agreement with the values obtained<sup>8</sup> for  $\text{Ni}(\text{NCO})_4^{2-}$ . The true intensity of the spin-forbidden band at  $12,300\text{ cm}^{-1}$  is probably less than the value recorded in Table I, since much of the observed intensity may be attributed to the tails of the spin-allowed bands on either side of it.

The  $\Delta$  values for the two ions  $\text{Ni}(\text{NCS})_4^{2-}$  and  $\text{Ni}(\text{NCS})_6^{4-}$  are of interest, since this represents one of the few cases where one may compare directly the field strength of a given ligand for discrete ions, or molecules, with tetrahedral and octahedral geometries. The ratio  $\Delta_{\text{tet}}/\Delta_{\text{oct}}$  in this case is 0.51, compared with 0.44 for

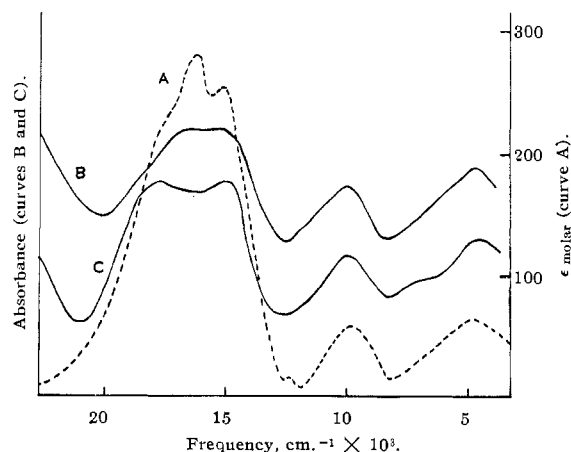


Figure 1.—Electronic absorption spectra of: A,  $\text{Ni}(\text{NCS})_4^{2-}$  0.133 M in acetone + 0.033 M  $\text{NCS}^-$ ; B, solid  $[(\text{C}_6\text{H}_5)_4\text{As}]_2\text{Ni}(\text{NCS})_4$  (blue-green form); C, solid  $(\text{Cat}^{2+})\text{Ni}(\text{NCS})_4$  (blue form).

the point charge model and 0.50 for nickel(II) in oxide ( $\text{ZnO}$  and  $\text{MgO}$ ) lattices.<sup>17</sup>

The magnetic moment of the  $\text{Ni}(\text{NCS})_4^{2-}$  ion in dry acetone was determined at room temperature by the n.m.r. method.<sup>7</sup> The value found, 3.59 B.M. at  $298^\circ\text{K}$ ., is very close to those of the solid complexes thought to contain tetrahedral  $\text{Ni}(\text{NCS})_4^{2-}$  anions (*vide infra*).

Although solutions containing tetrahedral  $\text{Ni}(\text{NCS})_4^{2-}$  may be obtained quite simply as mentioned above, the preparation of solid complexes with anions of this structure proved to be less straightforward. Compounds of composition  $(\text{cation})_2\text{Ni}(\text{NCS})_4$  could be prepared with a variety of cations but only with the very large cations  $(\text{C}_6\text{H}_5)_4\text{As}^+$  and  $(\text{Cat}^{2+})$  were complexes with tetrahedral anions obtained, and then only under certain conditions. More commonly, the complexes  $(\text{cation})_2\text{Ni}(\text{NCS})_4$  have properties consistent with the presence of six-coordinate nickel(II).

The form of  $[(\text{C}_6\text{H}_5)_4\text{As}]_2\text{Ni}(\text{NCS})_4$  isolated from solution is olive-yellow. The magnetic moment (Table III) of this compound and that of apple-green  $[(\text{CH}_3)_4\text{N}]_2\text{Ni}(\text{NCS})_4$  are in the range expected for six-coordinate, tetragonal nickel(II). Their electronic spectra (Table I, Figure 2) are also in accord with this type of structure. The presence of bridging  $\text{NCS}$  groups in these

TABLE III  
MAGNETIC DATA FOR THE COMPLEXES

Compound	$T, ^\circ\text{K}$ .	$10^3\chi_{\text{m}}^{\text{cor}}$ , c.g.s.u.	$\mu_{\text{eff}}^a$ , B.M.
$[(\text{C}_6\text{H}_5)_4\text{N}]_2\text{Ni}(\text{NCS})_4$	292.5	4480	3.25
$[(\text{CH}_3)_4\text{N}]_2\text{Ni}(\text{NCS})_4$	288	4530	3.24
$[(\text{C}_6\text{H}_5)_4\text{As}]_2\text{Ni}(\text{NCS})_4$ olive-yellow	291	4730	3.33
$[(\text{C}_6\text{H}_5)_4\text{As}]_2\text{Ni}(\text{NCS})_4$ blue-green	290	5730	3.66
$(\text{Cat}^{2+})\text{Ni}(\text{NCS})_4$ blue	295	5510	3.62
$\text{NiHg}(\text{SCN})_4$	298	4300	3.21
$\text{Ni}(\text{NCS})_4^{2-}$ in acetone	298	5360	3.59
$\text{CuHg}(\text{SCN})_4$	293	1430	1.83
$(\text{Cat}^{2+})\text{Cu}(\text{NCS})_4$	297	1400	1.83 <sup>b</sup>

<sup>a</sup> Calculated from the Curie law. <sup>b</sup> See text regarding accuracy of this value.

(13) D. Forster and D. M. L. Goodgame, *J. Chem. Soc.*, 288 (1965).

(14) A. E. Harvey and D. L. Manning, *J. Am. Chem. Soc.*, **72**, 4488 (1950).

(15) D. M. L. Goodgame, M. Goodgame, and F. A. Cotton, *ibid.*, **83**, 4161 (1961).

(16) See, e.g., H. A. Weakliem, *J. Chem. Phys.*, **36**, 2117 (1962).

(17) R. Pappalardo, D. L. Wood, and R. C. Linares, *ibid.*, **35**, 1460 (1961).

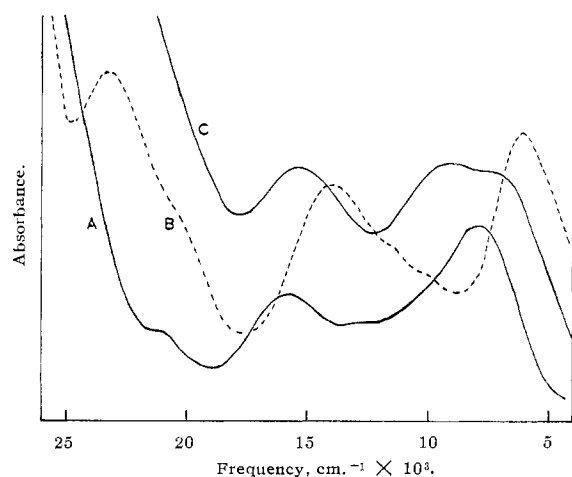


Figure 2.—Electronic absorption spectra (reflectance) of: A,  $[(\text{C}_6\text{H}_5)_4\text{N}]_2\text{Ni}(\text{NCS})_4$ ; B,  $[(\text{C}_6\text{H}_5)_4\text{As}]_2\text{Ni}(\text{NCS})_4$  (olive-yellow form); C,  $\text{NiHg}(\text{SCN})_4$ .

complexes is indicated by their infrared spectra in the C–N stretching region (Table II). The bands in the C–S stretching region are less helpful in this respect. The lower end of the range of C–S frequencies reported<sup>12,18</sup> for isothiocyanates overlaps with the region for bridging thiocyanates.<sup>15</sup> Both the  $\text{Ni}(\text{NCS})_6^{4-}$  ions and the tetragonal compounds (cation)<sub>2</sub> $\text{Ni}(\text{NCS})_4$  have bands in the region of overlap (800–770  $\text{cm}^{-1}$ ). In the case of the olive-yellow form of  $[(\text{C}_6\text{H}_5)_4\text{As}]_2\text{Ni}(\text{NCS})_4$  there is the additional complication that four bands were found in the range 855–790  $\text{cm}^{-1}$ . These do not appear to be due to  $(\text{C}_6\text{H}_5)_4\text{As}^+$ , but it is uncertain which of them may be assigned as C–S stretches.

The tetragonal ligand fields for the nickel(II) ions in these compounds presumably result from anion association, so that each metal ion is surrounded by four nitrogen atoms and two sulfur atoms, in much the same way as the copper(II) ions in  $\text{CuHg}(\text{SCN})_4$ .<sup>19</sup>

The nature of the product obtained on mixing equimolar solutions of nickel thiocyanate in acetone and  $(\text{Cat}^{2+})(\text{NCS})_2$  in nitromethane depended on the reaction temperature. When the solutions were mixed at temperatures close to their respective boiling points a blue complex,  $(\text{Cat}^{2+})\text{Ni}(\text{NCS})_4$ , crystallized out. At lower temperatures a yellow, crystalline solid was formed. The infrared spectrum of this latter compound showed the presence of nitromethane even after washing with ether and drying *in vacuo* at room temperature. However, the nitromethane could be removed on heating to  $\sim 115^\circ$  to give a complex, also yellow, analyzing approximately as  $(\text{Cat}^{2+})\text{Ni}(\text{NCS})_4$ . Repeated attempts to obtain a pure specimen of this compound were unsuccessful. However, its electronic spectrum was very similar to that of the olive-yellow form of  $[(\text{C}_6\text{H}_5)_4\text{As}]_2\text{Ni}(\text{NCS})_4$ , and this fact, and also the C–N stretching frequencies (2141 (m), 2105 (sh), and 2090 (vs)  $\text{cm}^{-1}$ ), point to the presence of six-coordinate tetragonal nickel(II) in this case also.

Several lines of evidence suggest that the anion in the blue form of  $(\text{Cat}^{2+})\text{Ni}(\text{NCS})_4$  has an essentially tetrahedral structure. The electronic spectrum of the solid compound (Table I, Figure 1) is similar to that of  $\text{Ni}(\text{NCS})_4^{2-}$  in acetone and to the solid-state spectrum of  $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{Ni}(\text{NCO})_4$ .<sup>8</sup> The magnetic moment at room temperature (3.62 B.M.) is also characteristic of essentially tetrahedral nickel(II). Moreover, the C–N and the C–S stretching frequencies are in the ranges for N-bonded rather than bridging NCS groups.

However, it is probable that the symmetry of the Ni–N<sub>4</sub> grouping in blue  $(\text{Cat}^{2+})\text{Ni}(\text{NCS})_4$  is lower than T<sub>d</sub>. The pronounced splitting observed for the band in the visible region, and the appearance of a distinct shoulder at  $\sim 7250 \text{ cm}^{-1}$ , in addition to the broad band at  $4440 \text{ cm}^{-1}$ , indicate splitting of the  ${}^3\text{T}_1(\text{P})$  and  ${}^3\text{T}_2$  levels, which would occur if the arrangement of nitrogen atoms around the nickel(II) ion is not regularly tetrahedral. Evidence for anion distortion is also provided by the splitting observed<sup>20</sup> for  $\nu_{11}$  (essentially the triply degenerate stretching mode of a tetrahedral M–N<sub>4</sub> group) in the far-infrared region, whereas the  $\nu_{11}$  band for the cobalt(II) analog is unsplit.<sup>20</sup> The cobalt(II) and nickel(II) complexes are not isomorphous, although their X-ray powder patterns are rather similar. The compounds  $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{M}(\text{NCO})_4$  (M = Co, Ni), however, are isomorphous,<sup>8</sup> and the  $\nu_{11}$  bands for these compounds are unsplit.<sup>21</sup>

Recently, Figgis, *et al.*,<sup>22</sup> have interpreted the temperature variation of the magnetic moments of several tetrahedral complexes of nickel(II) in terms of ligand field distortion, electron delocalization, and reduction in the spin-orbit coupling constant from the free-ion value. It was of interest, therefore, to see if a comparison of the temperature dependence of  $\mu_{\text{eff}}$  for the blue form of  $(\text{Cat}^{2+})\text{Ni}(\text{NCS})_4$  with that of  $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{Ni}(\text{NCO})_4$  was also indicative of greater distortion of  $\text{Ni}(\text{NCS})_4^{2-}$  than for  $\text{Ni}(\text{NCO})_4^{2-}$ .

The magnetic data for  $(\text{Cat}^{2+})\text{Ni}(\text{NCS})_4$  over the range 95–295°K. are given in Table IV; those for  $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{Ni}(\text{NCO})_4$  have been reported previously.<sup>8</sup> Using the curve-fitting procedure of Figgis, *et al.*,<sup>22</sup>

TABLE IV  
TEMPERATURE DEPENDENCE OF THE MAGNETIC MOMENT  
OF THE BLUE FORM OF  $(\text{Cat}^{2+})\text{Ni}(\text{NCS})_4$

T, °K.	$10^6 \chi_m^{\text{cor}}$ , c.g.s.u.	$\mu_{\text{eff}}$ , <sup>a</sup> B.M.
295.5	5,510	3.62
268.3	6,060	3.62
246.2	6,500	3.59
229.0	6,910	3.57
213.4	7,350	3.56
182.1	8,490	3.53
161.5	9,440	3.51
135.0	11,060	3.47
114.8	12,600	3.42
95.1	14,770	3.365

<sup>a</sup> Calculated from the Curie law.

(20) D. Forster and D. M. L. Goodgame, *Inorg. Chem.*, **4**, 715 (1965).

(21) D. Forster and D. M. L. Goodgame, *J. Chem. Soc.*, 262 (1965).

(22) B. N. Figgis, J. Lewis, F. Mabbs, and G. A. Webb, *Nature*, **203**, 1138 (1964).

(18) M. M. Chamberlain and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **81**, 6412 (1959).

(19) A. Korczynski, *Roczniki Chem.*, **36**, 1539 (1962).

good agreement was found between the experimental results for  $(\text{Cat}^{2+})\text{Ni}(\text{NCS})_4$  and the curve calculated with the following parameters (notation as in ref. 22):  $A = 1.5$ ,  $k = 0.8$ ,  $\lambda = -268 \text{ cm.}^{-1}$  ( $\lambda/\lambda_0 = 0.85$ ),  $\Delta = 800 \text{ cm.}^{-1}$  ( $\Delta/\lambda = -3$ ). The fit obtained for  $[(\text{C}_6\text{H}_5)_4\text{N}]_2\text{Ni}(\text{NCO})_4$  was not quite as good, but the closest set of parameters was:  $A = 1.5$ ,  $k = 0.85$ ,  $\lambda = -268 \text{ cm.}^{-1}$ , and  $\Delta = 800 \text{ cm.}^{-1}$ . It appears, therefore, that, within the errors associated with curve-fitting procedures with several variable parameters, the small differences in the magnetic behavior of the two compounds may be ascribed mainly to somewhat greater electron delocalization in the case of the isothiocyanato complex. In particular, the magnetic results suggest that distortions of the ions  $\text{Ni}(\text{NCS})_4^{2-}$  and  $\text{Ni}(\text{NCO})_4^{2-}$  are very similar, a conclusion not in accord with the infrared and electronic spectra. However, it may be noted that the treatment of Figgis, *et al.*, suggests<sup>22</sup> that the ligand field distortions of  $\text{Ni}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2\text{Cl}_2$  and  $[(\text{C}_6\text{H}_5)_3(\text{CH}_3)\text{As}]_2\text{NiCl}_4$  are also very similar, whereas X-ray structural determinations have shown that the  $\text{NiCl}_4^{2-}$  ion in the latter compound has a virtually regular tetrahedral structure,<sup>23</sup> but that the Ni-P<sub>2</sub>Cl<sub>2</sub> coordination sphere in the phosphine complex is considerably distorted.<sup>24</sup>

The solid blue form of  $(\text{Cat}^{2+})\text{Ni}(\text{NCS})_4$  is rather more resistant to decomposition by hydroxylic solvents than are most other tetrahedral complexes of nickel(II). The crystalline compound is unaffected by cold water for short periods of time, but gradually decomposes on long standing, especially in hot water.

The olive-yellow form of  $[(\text{C}_6\text{H}_5)_4\text{As}]_2\text{Ni}(\text{NCS})_4$  may be converted irreversibly to a dark blue-green isomer on heating to  $\sim 155^\circ$ . The electronic spectrum of this isomer (Table I, Figure 1) and its high magnetic moment (3.66 B.M.) at room temperature suggest that here also the anion has an essentially tetrahedral structure. The electronic bands due to  ${}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{T}_2$  and  ${}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{T}_1(\text{P})$  appear to be less split for this compound than those of the blue form of  $(\text{Cat}^{2+})\text{Ni}(\text{NCS})_4$ , and this may indicate a smaller distortion of the Ni-N<sub>4</sub> grouping in the former compound. The change from the blue color of the  $(\text{Cat}^{2+})$  salt to the green of the tetrahedral form of the tetraphenylarsonium salt may be attributed to the moving to lower energy of an electron-transfer band in the near-ultraviolet region.

**NiHg(SCN)<sub>4</sub>.**—The series of compounds  $\text{M}^{\text{II}}\text{Hg}(\text{SCN})_4$  has been known for many years.<sup>3</sup> In  $\text{CoHg}(\text{SCN})_4$  the cobalt atom is surrounded by a slightly distorted tetrahedron of nitrogen atoms,<sup>25</sup> and  $\text{ZnHg}(\text{SCN})_4$  is isomorphous with the cobalt compound.<sup>26</sup> The compound  $\text{CuHg}(\text{SCN})_4$  has a quite different structure,<sup>19</sup> in which the copper atoms are surrounded by four nitrogen atoms in a rectangle at an average distance of  $1.90 \pm 0.04 \text{ \AA}$ . and two sulfur atoms in

approximately axial positions at  $3.00 \pm 0.02 \text{ \AA}$ . The nickel(II) compound has hitherto been obtained as a dihydrate, in which the nickel atom is surrounded tetragonally by four nitrogen atoms and two oxygen atoms.<sup>27</sup> We find that the pale blue dihydrate may be dehydrated quantitatively at  $155^\circ$  to give a yellow-green, somewhat hygroscopic compound. The magnetic moment of anhydrous  $\text{NiHg}(\text{SCN})_4$ , 3.21 B.M. at room temperature, and its electronic spectrum (Table I, Figure 2) indicate tetragonal, six-coordination for nickel(II) in this compound, which may have a structure rather like that of  $\text{CuHg}(\text{SCN})_4$ , though the two compounds are not isomorphous.

**Copper(II) Complexes.**—It has long been known that if  $\text{ZnHg}(\text{SCN})_4$  is precipitated in the presence of copper(II) ions the color of the solid obtained ranges from pale pink to dark purple, depending on the relative concentrations of  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$ . The formation of this colored compound is used as a qualitative test for zinc(II).<sup>28</sup> However,  $\text{ZnHg}(\text{SCN})_4$  is white and  $\text{CuHg}(\text{SCN})_4$  is green.

We have prepared a series of the purple mixed compounds  $(\text{Cu}_x\text{Zn}_{1-x})\text{Hg}(\text{SCN})_4$  to correlate their electronic spectra with the environments of the copper atoms. In Table V are given the  $d$  values, determined from X-ray powder photographs, of two of the mixed compounds, where  $x = 0.14$  and  $0.22$ , and of  $\text{ZnHg}(\text{SCN})_4$  and  $\text{CuHg}(\text{SCN})_4$ . It can be seen that the doping of up to 22 mole% of Cu(II) into the  $\text{ZnHg}(\text{SCN})_4$  lattice causes only a slight distortion of the structure. In particular, the copper atom sites appear to be at least approximately tetrahedral,

TABLE V  
X-RAY POWDER DATA FOR  $(\text{Cu}_x\text{Zn}_{1-x})\text{Hg}(\text{SCN})_4$

$\text{ZnHg}(\text{SCN})_4^a$		$x = 0.14$		$x = 0.22$		$\text{CuHg}(\text{SCN})_4^b$	
$d$ , Å.	In- tensity	$d$ , Å.	In- tensity	$d$ , Å.	In- tensity	$d$ , Å.	In- tensity
7.80	vs	7.80	vs	7.88	vs	7.53	m
5.53	vs	5.57	vs	5.57	vs	5.86	m
4.12	s	4.09	s	4.05	s	5.48	vw
3.89	s	3.92	s	3.93	s	4.62	vs
3.51	w	3.52	w	3.52	w	4.52	vw
3.30	vs	3.28	vs	3.26	s	3.79	m
2.84	s	2.84	s	2.82	s	3.23	w
2.78	vw					2.88	m
2.61	w	2.62	w	2.63	w	2.72	m
2.52	s	2.52	s			2.63	m
				2.49 <sup>c</sup>	s		
2.47	s	2.48	s			2.52	m
2.29	m	2.29	m	2.28	m	2.42	w
2.13	vw					2.32	s
2.05	vw					2.28	w
1.99	m	1.98	m	1.99	m	2.20	w
1.96	w	1.92	vw	1.92	vw	1.95	w
1.88	s	1.86	s	1.86	m	1.88	w
1.76	m	1.76	m	1.76	w	1.77	vw
1.69	m	1.69	m	1.69	w	1.74	w
1.61	m	1.61	m	1.61	m	1.71	w

<sup>a</sup> Tetragonal;  $a = 11.06$ ,  $c = 4.43 \text{ \AA}$ . <sup>b</sup> Orthorhombic;  $a = 7.65$ ,  $b = 9.02$ ,  $c = 15.17 \text{ \AA}$ . <sup>c</sup> Broad line.

(23) P. Pauling, personal communication.

(24) G. Garton, D. E. Henn, H. M. Powell, and L. M. Venanzi, *J. Chem. Soc.*, 3625 (1963).

(25) J. W. Jeffery, *Nature*, **159**, 610 (1947); *Acta Cryst.*, *Suppl.*, A66, abstract 6.6 (1963).

(26) W. Stahl and M. Straumanis, *Z. physik. Chem.*, **193**, 121 (1943).

(27) M. A. Poraj-Kosic, *Acta Cryst.*, *Suppl.*, A42, abstract 4.72 (1963).

(28) A. I. Vogel, "Macro and Semimicro Qualitative Inorganic Analysis," 4th Ed., Longmans, Green and Co., London, New York, Toronto, 1954, p. 228.

although the lattice might tolerate *somewhat* lower site symmetry for  $\text{Cu}^{2+}$  than for  $\text{Zn}^{2+}$  without any great change in the over-all structure.

The reflectance spectra of  $\text{CuHg}(\text{SCN})_4$  and  $(\text{Cu}_{0.14}\text{Zn}_{0.86})\text{Hg}(\text{SCN})_4$  are shown in Figure 3. The band at

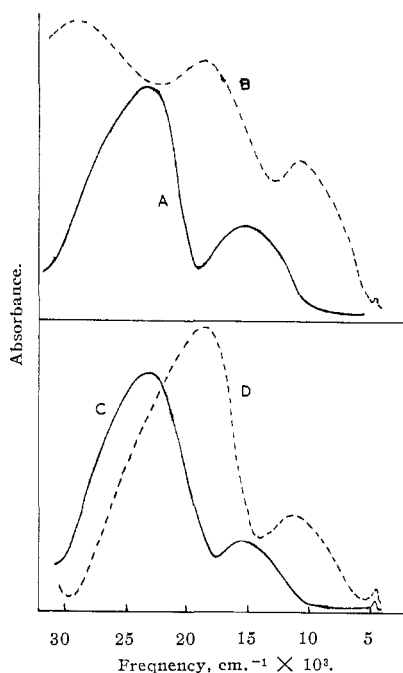


Figure 3.—Electronic absorption spectra (reflectance) of: A,  $\text{CuHg}(\text{SCN})_4$ ; B,  $(\text{Cu}_x\text{Zn}_{1-x})\text{Hg}(\text{SCN})_4$ ; C,  $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{Cu}(\text{NCS})_4$ ; D,  $(\text{Cat}^{2+})\text{Cu}(\text{NCS})_4$ .

$15,100\text{ cm}^{-1}$  for  $\text{CuHg}(\text{SCN})_4$  may be assigned either as  ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$  with the other expected transitions, to the upper states  ${}^2\text{B}_{2g}$  and  ${}^2\text{E}_g$ , lying under the charge-transfer band at  $\sim 23,000\text{ cm}^{-1}$  or as more than one of these three transitions, since they are often observed as one rather broad band.

The band at  $10,500\text{ cm}^{-1}$  in the spectrum of  $(\text{Cu}_{0.14}\text{Zn}_{0.86})\text{Hg}(\text{SCN})_4$  may be assigned as  ${}^2\text{B}_2 \rightarrow {}^2\text{A}_1$  for a distorted tetrahedral ( $\text{D}_{2d}$ ) ligand field of nitrogen atoms around copper(II), or as  ${}^2\text{A}' \rightarrow {}^2\text{A}' + {}^2\text{A}''$  if the site symmetry is  $\text{C}_s$ . The corresponding bands for other distorted tetrahedral  $\text{CuX}_4$  systems are:  $\text{CuBr}_4^{2-}$ ,  $8000$  and  $7570\text{ cm}^{-1}$  (polarized crystal spectrum),<sup>29</sup>  $\text{CuCl}_4^{2-}$ ,  $9050$  and  $7900\text{ cm}^{-1}$  (polarized crystal spectrum),<sup>30</sup> and  $\text{Cu}(\text{NCO})_4^{2-}$ ,  $11,500\text{ cm}^{-1}$  (reflectance spectrum).<sup>8</sup> One puzzling feature of the spectra of both  $(\text{Cu}_x\text{Zn}_{1-x})\text{Hg}(\text{SCN})_4$  and  $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{Cu}(\text{NCS})_4$  is the absence of any bands assignable as  ${}^2\text{B}_2 \rightarrow {}^2\text{E}$ . Between the bands discussed above and the limit of our measurements ( $4000\text{ cm}^{-1}$ ) only the weak, sharp vibrational bands due to NCO or NCS were found, whereas the  ${}^2\text{B}_2 \rightarrow {}^2\text{E}$  transitions for  $\text{CuCl}_4^{2-}$  and  $\text{CuBr}_4^{2-}$  are reported to be at  $\sim 5200$  and  $4650\text{ cm}^{-1}$ , respectively.<sup>30,31</sup> It is, of course, possible that the  ${}^2\text{B}_2 \rightarrow {}^2\text{E}$  transition contributes to the bands assigned solely as  ${}^2\text{B}_2 \rightarrow {}^2\text{A}_1$  above, since these are

broad and may not be sufficiently resolved by our room-temperature reflectance measurements, or that it lies below  $4000\text{ cm}^{-1}$  if the distortions from  $\text{T}_d$  symmetry are small.

The purple color of  $(\text{Cu}_x\text{Zn}_{1-x})\text{Hg}(\text{SCN})_4$  is caused by the intense electron-transfer bands at  $18,300$  and  $\sim 30,000\text{ cm}^{-1}$ , analogous to those observed<sup>30,32</sup> for the  $\text{CuCl}_4^{2-}$  and  $\text{CuBr}_4^{2-}$  ions.

The compound  $\text{CuHg}(\text{SCN})_4$  obeys the Curie-Weiss law over the range  $113$ – $293^\circ\text{K}$ ., and the small value of the Weiss constant,  $-8^\circ$ , suggests that there is little magnetic ordering, despite the polymeric structure.

Two types of compound  $(\text{cation})_2\text{Cu}(\text{NCS})_4$  were obtained; the complex  $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{Cu}(\text{NCS})_4$  is green, but  $(\text{Cat}^{2+})\text{Cu}(\text{NCS})_4$  is dark purple. The reflectance spectrum of the tetraethylammonium salt (Table I, Figure 3) is very similar to that of  $\text{CuHg}(\text{SCN})_4$ , but that of  $(\text{Cat}^{2+})\text{Cu}(\text{NCS})_4$  is quite different and in the visible and near-infrared region closely resembles the spectrum of  $(\text{Cu}_x\text{Zn}_{1-x})\text{Hg}(\text{SCN})_4$ . The electron-transfer band which occurs at  $\sim 30,000\text{ cm}^{-1}$  for  $(\text{Cu}_x\text{Zn}_{1-x})\text{Hg}(\text{SCN})_4$  moves  $\sim 3000\text{ cm}^{-1}$  to higher energy for the  $\text{Cat}^{2+}$  salt.

These spectra suggest that in  $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{Cu}(\text{NCS})_4$  the copper(II) ion is in a tetragonal ligand field whereas in the  $\text{Cat}^{2+}$  salt the  $\text{Cu}(\text{NCS})_4^{2-}$  anions have a distorted tetrahedral structure. It is possible that in the solid tetraethylammonium salt there is association of the complex anions so that each copper atom is surrounded by four nitrogen and two sulfur atoms, as in  $\text{CuHg}(\text{SCN})_4$ . The larger cation  $\text{Cat}^{2+}$  would tend to favor the formation of discrete  $\text{Cu}(\text{NCS})_4^{2-}$  anions. The large cation  $(\text{C}_6\text{H}_5)_4\text{As}^+$  also gives a purple cupric thiocyanate complex with an electronic spectrum similar to that of the  $\text{Cat}^{2+}$  salt, but we could not obtain it in a pure state. Moreover, when  $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{Cu}(\text{NCS})_4$  is dissolved in acetone or nitromethane (a process which would also tend to break up any associated units), the solutions produced are blood-red in color and have electronic spectra more closely resembling those of the solid purple compounds than that of the original solid; there is an electron-transfer band at  $\sim 20,000\text{ cm}^{-1}$  and a much weaker band ( $\epsilon_{\text{molar}} \sim 150$ ) at  $\sim 12,000\text{ cm}^{-1}$ . However, any copper-sulfur bonding in the solid tetraethylammonium salt must be weaker than in the tetragonal nickel complexes since the infrared spectrum of this compound (Table II) provides no indication of the presence of strongly bridging NCS groups.

The magnetic moment (1.83 B.M.) of  $(\text{Cat}^{2+})\text{Cu}(\text{NCS})_4$  at room temperature is lower than those found for other tetrahedral  $\text{CuX}_4^{2-}$  ions ( $\text{CuCl}_4^{2-}$ , 2.00 B.M.<sup>33</sup>;  $\text{Cu}(\text{NCO})_4^{2-}$ , 1.98 B.M.<sup>8</sup>), but this must be regarded as only an approximate value ( $\pm 0.1$  B.M.) since the high molecular weight and large diamagnetic

(29) A. G. Karipides and T. S. Piper, *Inorg. Chem.*, **1**, 970 (1962).

(30) J. Ferguson, *J. Chem. Phys.*, **40**, 3406 (1964).

(31) P. Day, *Proc. Chem. Soc.*, 18 (1964).

(32) C. Furlani and G. Morpurgo, *Theoret. chim. Acta*, **1**, 102 (1963); P. S. Braterman, *Inorg. Chem.*, **2**, 448 (1963).

(33) B. N. Figgis and C. M. Harris, *J. Chem. Soc.*, 855 (1959).

contributions lead to relatively small weight differences in the Gouy method.

**General Conclusions.**—Our studies suggest that an important factor in the coordination behavior of  $\text{NCS}^-$  toward nickel(II) is the tendency of this metal ion to adopt six-coordination in the solid state. This is shown by the formation of  $\text{Ni}(\text{NCS})_6^{4-}$  ions (a property in which Ni(II) resembles Mn(II) and Fe(II)) and by the tetragonal, six-coordination of nickel(II) in anhydrous  $\text{NiHg}(\text{SCN})_4$  and in many of the solid compounds  $(\text{cation})_2\text{Ni}(\text{NCS})_4$ , where the bridging ability of the NCS group permits association of the anions, especially when the cation is relatively small. In the analogous isocyanate complexes there is no evidence of such association, the anion in, e.g.,  $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{Ni}(\text{NCO})_4$  having a tetrahedral structure.<sup>8</sup>

As expected, the tendency toward six-coordination is less pronounced for copper(II). No complexes of the type  $\text{Cu}(\text{NCS})_6^{4-}$  were isolated and, although in some compounds of composition  $(\text{cation})_2\text{Cu}(\text{NCS})_4$  the metal ions have tetragonal environments due to anion association, it is probable that the Cu-S bonding is weaker than the analogous Ni-S bonding. Moreover,

some cations, e.g.,  $(\text{C}_6\text{H}_5)_4\text{As}^+$  and  $\text{Cat}^{2+}$ , which gave tetragonal complexes for nickel(II) did not do so for copper(II).

The existence of the six-coordinate complexes discussed above is confined predominantly, if not entirely, to the solid state, since solution of  $(\text{cation})_4\text{Ni}(\text{NCS})_6$  and the tetragonal forms of  $(\text{cation})_2\text{M}(\text{NCS})_4$  in polar, relatively noncoordinating solvents results in the formation of tetrahedral  $\text{M}(\text{NCS})_4^{2-}$  ions. The formation of solid compounds with tetrahedral anions  $\text{M}(\text{NCS})_4^{2-}$  is favored by higher temperatures and the use of very large cations, as both these factors tend to reduce opportunities for M-NCS-M bridging. However, it appears that the discrete anions so formed are distorted from a regularly tetrahedral structure.

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## Inner Complexes. V. Copper(II) and Nickel(II) Chelates of N-Alkylthiopicolinamides

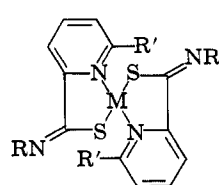
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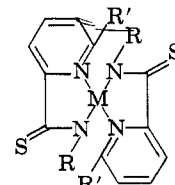
The copper(II) and nickel(II) chelates of a number of N-alkylthiopicolinamides were prepared. These inner complexes are coordinated through the pyridine nitrogen and the thioamide sulfur with a *trans* square-planar configuration around the central metal atom. N-n-Butyl-6-methylthiopicolinamide reacts with copper (II) to give a copper(I) chelate.

In the course of studies on mixed chelates we have prepared a number of N-alkylthiopicolinamides and converted these to their copper(II) and nickel(II) inner complexes. As these chelates can have the ligand structure shown in  $A_1$  or  $A_2$  or be a mixture of both ligand structures and each of these can exist in various geometrical configurations around the central metal atom some of which involve aggregation, an effort was made to determine the structure of these materials. Previously, chelates of N-arylthiopicolinamides were prepared and assigned the ligand structure shown in formula  $A_1$ .<sup>2</sup> The nickel chelate of N,N'-4,4'-biphenylenebisthiopicolinamide, an insoluble infusible polymer, was assigned a tetrahedral configuration on the basis

of its magnetic moment (2.76 B.M.).<sup>3</sup> Octahedral ionic complexes have also been studied and the nickel chelate tentatively assigned nitrogen-sulfur coordination.<sup>4</sup> The present work indicates that the copper(II) and nickel(II) inner complexes of N-alkylthiopicolinamides have the square-planar *trans* structure  $A_1$ .



$A_1$  (M,R,R')



$A_2$  (M,R,R')

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