butyl chloride is volatilized in the first few minutes of reaction, as with methyl chloride. However, benzyl chloride does not volatilize under the usual conditions of reaction with no application of heat but is seen from the n.m.r. spectrum to increase steadily in the reaction mixture. This shows that the condensation reaction is not driven forward by elimination of a volatile product but that formation of the alkyl chloride is thermodynamically favorable.

Reactions of Dimethyl Sulfide with Sulfur.—At temperatures below the transition (*ca.* 168°) of elemental sulfur from S_8 rings to long chains, there was no observable reaction between dimethyl sulfide and elemental sulfur held in sealed tubes over a period of several months. At higher temperatures, some reaction was observed. Thus, after 2.5 months at 190°, the mixtures were all straw to reddish colored liquids with considerable gas pressure but no solids. Upon opening the tubes, the odors of hydrogen sulfide and methyl mercaptan were very noticeable; n.m.r. study of the liquids removed from the tubes showed that only a small proportion of the reagents had undergone reaction. The n.m.r. spectra showed the presence of sulfides terminated by methyl groups and/or hydrogen atoms, as well as a group of resonance peaks in the spectral region corresponding to a methylene group with two sulfurs bonded to it. These were attributed to structures[17] based on –CH2–C– chains stemming from a reaction between sulfur and the methyl groups to give H_2S plus sulfur substitution of a methyl hydrogen.

(17) Such compounds prepared by a very different procedure have been described by F. Feher and K. Vogelbruch, *Chem. Ber.*, **91**, 996 (1958).

Discussion

The n.m.r. evidence for the existence of variously sized sulfur and selenium chain molecules *terminated with different groups at either end* opens a new vista for preparative chemists in the sulfur area. As far as we know, the previously described sulfur-based molecules having two different terminating groups are restricted to the monosulfur compounds.[2] Also of interest are our kinetic data which show that, in the absence of catalysts, the polysulfides may be kept at room temperature with inappreciable rearrangement for many months. The observation concerning precipitation of gray *vs.* red selenium may prove capable of development as a preparative method for the different allotropic forms of this element.

The attainment of a dynamic equilibrium between the variously sized dimethyl polysulfides is thought to occur because of the good stability of the C–S bond. Presumably the thermodynamic equilibrium corresponding to an infinite time for equilibration in the case of the family of dimethyl polysulfides would be simply a mixture of dimethyl monosulfide with elementary sulfur similar to the case of the hydrogen-terminated sulfur chains, as calculated from the available thermodynamic data.[18]

(18) F. Feher and J. Winkhause, *Z. anorg. allgem. Chem.*, **292**, 210 (1957).

[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORIES OF BROWN UNIVERSITY, PROVIDENCE 12, RHODE ISLAND]

Some Transition Metal Complexes of Substituted Thioureas. II. Nickel(II)[1a]

By Smith L. Holt, Jr.,[1b] and Richard L. Carlin

The preparation and properties of the crystalline compounds [Ni(naptu)4Cl2] (naptu = 1-(1-naphthyl)-2-thiourea), [Ni(naptu)2X2] (X = Br or I), Ni(etu)4X2 (X = Cl, Br, I, ClO4, or NO3; etu = ethylenethiourea), and [Ni(etu)6](ClO4)2 are described. The chloro and bromo etu complexes exist in both yellow and orange forms which are considered to be geometric isomers of octahedral nickel. [Ni(naptu)4Cl2] and [Ni(etu)6](ClO4)2 are octahedral, while [Ni(naptu)2Br2] and [Ni(naptu)2I2] are tetrahedral. The iodo etu complex is shown to be six-coordinate though diamagnetic. The compound [Ni(etu)4](ClO4)2 is square-planar as is crystalline [Ni(etu)4](NO3)2. In solution, however, all of the compounds lose ligand and retain coordinated anion. Assignment of stereochemistry is made in conjunction with spectral, magnetic, electrochemical, molecular weight, and X-ray powder data.

Systems in which nickel(II) attains a variety of stereochemical environments when coordinated to one primary donor are rare.[2] Discovery of such a system, however, gives us the opportunity of studying any one principal donor in a variety of configurations and thereby elucidating the factors which determine the stereochemistry attained by nickel. The study of such a series of compounds in which sulfur is the primary donor atom forms the basis of this report.

We report here octahedral, paramagnetic and diamagnetic tetragonal, square-planar, and tetrahedral

(1) (a) Part I: R. L. Carlin and S. L. Holt, Jr., *Inorg. Chem.*, **2**, 849 (1963); (b) further details will be found in the thesis of S. L. Holt, Jr., Brown University, June, 1965.
(2) D. M. L. Goodgame and M. Goodgame, *J. Chem. Soc.*, 207 (1963); S. Buffagni, L. M. Vallarino, and J. V. Quagliano, *Inorg. Chem.*, **3**, 480 (1964).

complexes of nickel, as well as what appear to be the first isolated isomers of octahedral nickel. The factors which govern the adoption of a particular structure by nickel are also explored.

Experimental[3]

Reagents.—Nickel nitrate, perchlorate, and chloride were reagent grade and were used without further purification. Nickel bromide and iodide were prepared from nickel carbonate and the corresponding halo acid. Ethylenethiourea was obtained from K and K Chemical and was purified by recrystallization from ethanol. Napthylthiourea was obtained from Eastman and was purified by recrystallization from 2-propanol.

Dichlorotetrakis(ethylenethiourea)nickel(II). Yellow Complex.—NiCl2·6H2O (14 g.) was dissolved in 75 ml. of absolute ethanol and was added to a hot solution of 4 g. of ethylenethiourea in ethanol. Cooling afforded yellow crystals of the compound.

These were recrystallized carefully from hot ethanol, washed with cold alcohol and ethyl ether, then dried *in vacuo* at 56°. *Anal.* Calcd. for $C_{12}H_{24}N_8S_4NiCl_2$: C, 26.81; H, 4.46; N, 20.40; Cl, 13.00. Found: C, 27.17; H, 4.14; N, 19.73; Cl, 12.73.

Orange Complex.—The yellow complex was digested in hot absolute ethanol for 48 hr. This treatment converted it to a granular orange solid. The hot mixture was then filtered rapidly and the orange material retained. This solid was ground in absolute ethanol and filtered. The final product was dried at 56° *in vacuo*. *Anal.* Calcd. for $C_{12}H_{24}N_8S_4NiCl_2$: C, 26.81; H, 4.46; N, 20.40. Found: C, 27.02; H, 4.54; N, 20.09.

Dibromotetrakis(ethylenethiourea)nickel(II). Yellow Complex.—A cold solution of 33 g. of $NiBr_2$ in ethanol was added to a hot ethanolic solution of 26 g. of ethylenethiourea. Immediately after mixing the solution was placed in an ice bath and allowed to remain there for 5 min. The reaction mixture was then filtered and the yellow crystals of the compound collected. These were dried at 56° *in vacuo*. *Anal.* Calcd. for $C_{12}H_{24}N_8S_4NiBr_2$: C, 23.00; H, 3.87; N, 17.87. Found: C, 23.17; H, 3.64; N, 17.27.

Orange Complex.—This compound was prepared by a procedure analogous to the orange chloro complex but with a digestion time of only 12 hr. *Anal.* Calcd. for $C_{12}H_{24}N_8S_4NiBr_2$: C, 23.00; H, 3.87; N, 17.87. Found: C, 22.41; H, 4.03; N, 17.24.

Diiodotetrakis(ethylenethiourea)nickel(II).—NiI_2 (18 g.) in 160 ml. of 3:1 butanol–ethanol mixture was added to 7 g. of ethylenethiourea in 175 ml. of hot butanol. Upon standing overnight black crystals precipitated. These were collected, washed with ethanol and ether, and dried at 56° *in vacuo*. *Anal.* Calcd. for $C_{12}H_{24}N_8S_4NiI_2$: C, 19.98; H, 3.33; N, 15.50; I, 35.23. Found: C, 20.10; H, 3.49; N, 15.50; I, 35.32.—

Hexakis(ethylenethiourea)nickel(II) Perchlorate.—A warm solution of 8 g. of $Ni(ClO_4)_2 \cdot 6H_2O$ in 100 ml. of butanol was mixed with a hot solution of 4 g. of ethylenethiourea in 100 ml. of butanol. After standing 3 hr., yellow-bronze crystals were collected by filtration. These were washed with absolute ethanol and ethyl ether, then dried at 56° *in vacuo*. *Anal.* Calcd. for $C_{18}H_{36}N_{12}S_6NiCl_2O_8$: C, 24.80; H, 4.17; N, 19.20; Cl, 8.10. Found: C, 25.26; H, 4.45; N, 19.18; Cl, 8.30.

Tetrakis(ethylenethiourea)nickel(II) Perchlorate.—$Ni(ClO_4)_2 \cdot 6H_2O$ (20 g.) in 100 ml. of butanol was added to 0.5 g. of ethylenethiourea in 25 ml. of butanol. This solution was evaporated by boiling to approximately one-third the original volume and then allowed to stand. After 12 hr. the blue-black crystals were collected, washed with absolute ethanol and ether, and dried at 56° *in vacuo*. *Anal.* Calcd. for $C_{12}H_{24}N_8S_4NiCl_2O_8$: C, 21.65; H, 3.62; N, 16.85. Found: C, 21.99; H, 3.75; N, 16.53.

Tetrakis(ethylenethiourea)nickel(II) Nitrate.—$Ni(NO_3)_2 \cdot 6H_2O$ (15 g.) was added to 3 g. of ethylenethiourea in 50 ml. of 1-butanol. This mixture was heated until all solid had dissolved and then allowed to stand; after 30 min. black crystals began to precipitate. These were collected, washed with ethanol, and dried *in vacuo* at 80°. *Anal.* Calcd. for $C_{12}H_{24}N_{10}S_4O_6Ni$: C, 23.55; H, 3.92; N, 22.90. Found: C, 24.14; H, 4.16; N, 23.34.

Tetrakis(naphthylthiourea)nickel(II) Chloride.—Recrystallized 1-(1-naphthyl)-2-thiourea (10 g.) was dissolved in hot 1-butanol. To this was added, with vigorous stirring, 20 g. of finely ground $NiCl_2 \cdot 6H_2O$. The solution was allowed to boil for 5 min. and then was filtered to remove any undissolved $NiCl_2$. The filtrate was allowed to stand yielding yellow plates on cooling. These were recrystallized from warm 1-butanol and dried at 80° *in vacuo*. *Anal.* Calcd. for $C_{44}H_{40}N_8S_4NiCl_2$: C, 56.40; H, 4.30; N, 11.92. Found: C, 56.68; H, 4.27; N, 10.73.

Dibromobis(naphthylthiourea)nickel(II).—Recrystallized naphthylthiourea (10 g.) was dissolved in a minimum of hot 1-butanol. To this was added 20 g. of $NiBr_2 \cdot 6H_2O$. Green crystals began to precipitate immediately. These crystals were collected, washed with 2-propanol and ether, then dried at 100° *in vacuo*. Attempts to recrystallize the compound were unsuccessful. *Anal.* Calcd. for $C_{22}H_{20}N_4S_2NiBr_2$: C, 42.50; H, 3.22; N, 9.02. Found: C, 42.88; H, 3.21; N, 8.94.

Diiodobis(naphthylthiourea)nickel(II).—Naphthylthiourea (10 g.) was dissolved in a minimum of hot 1-butanol. To this was added 15 g. of hydrated NiI_2. The solution immediately turned brown and brown crystals began to precipitate. These crystals were collected while the solution was still warm, washed with 2-propanol, and dried at 80° *in vacuo*. Recrystallization attempts were not successful. *Anal.* Calcd. for $C_{22}H_{20}N_4S_2NiI_2$:

C, 36.79; H, 2.81; N, 7.82. Found: C, 36.34; H, 2.77; N, 7.41.

Spectral Measurements.—A Cary 14 recording spectrophotometer was used for all measurements. Solid-phase spectra of all complexes were recorded on the reflectance attachment with $MgCO_3$ as the standard. Supplementary studies of the ultraviolet region for all ethylenethiourea complexes were conducted using NaCl pellets.

Solution spectra were obtained in acetone with supplementary studies, where feasible, in absolute ethanol, chloroform, and benzene.

Magnetic Measurements.—These were made with a Gouy balance of standard design. The calibrant was $HgCo(NCS)_4$. A standard double-walled dewar served for the low temperature measurements. The n.m.r. method of Evans[4] was used for several solution measurements.

Electrolytic Conductance.—This was measured as previously.[1] Replicate measurements were made on solutions 10^{-3}–10^{-5} M. Where only a single value is reported, it corresponds to the most dilute solution measured.

Conductometric titrations were made using a Wheatstone bridge consisting of decade box resistors, an oscilloscope for use as a null point indicator, and a sine wave generator as a current source.

Molecular Weight Determinations.—All molecular weights were determined ebullioscopically in acetone. A Cottrell apparatus of local fabrication and a Beckmann thermometer graduated to 0.01° were used for the determinations.

X-Ray Patterns.—X-Ray powder patterns were obtained by standard techniques using $CuK\alpha$ radiation.

Results

Only those solid-phase data for $[Ni(detu)_4X_2]$ (detu is N,N'-diethylthiourea; X = Cl, Br, or I) which are necessary for comparison are given here as the physical properties of these compounds in the crystalline phase have been discussed in a previous communication.[5] It is sufficient to repeat here that these complexes are six-coordinate and tetragonal in nature. The solution chemistry of these compounds has not been touched upon, however,[5] and will be dealt with here.

Only in the case of $[Ni(naptu)_2Br_2]$ and $[Ni(naptu)_2I_2]$ can information about the compounds in the solid state be obtained from solution measurements, since all other compounds undergo a marked change on dissolution. The magnetic susceptibilities of all crystalline ethylenethiourea and diethylthiourea compounds reported have been measured at three temperatures (80, 195, 300°K.) on several different samples of each. For the naphthylthiourea compounds the susceptibility has been determined at room temperature only. All susceptibilities were corrected for diamagnetism to provide the molar susceptibilities, χ_M^{cor}, which are listed together with the corrections in Table I. Reciprocals of these molar susceptibilities were plotted against temperature and from the resulting straight lines, the magnitudes of μ and θ were obtained. The resulting moments may be considered accurate to ±0.05 B.M. We use the equation $\chi = C/(T - \theta)$.

Solution measurements (Table II) were made at ambient temperature using boiled, distilled water as a calibrant ($\chi_g = 0.720 \times 10^{-6}$). These may be considered accurate to ±0.10 B.M.

A compilation of reflectance spectra collected in this work is presented in Table III, some solution spectra are recorded in Table IV, and further details will be found in ref. 1b. The selection of the position of the

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

(5) S. L. Holt, Jr., R. J. Bouchard, and R. L. Carlin, *J. Am. Chem. Soc.*, **86**, 519 (1964).

TABLE I

MAGNETIC PROPERTIES OF SOLID Ni–S COMPLEXES AT 298°K.

Compound	Dia. cor. $\times 10^6$	$\chi_M{}^{cor} \times 10^6$, c.g.s.u.	μ, B.M.	θ, °K.
[Ni(etu)$_4$Cl$_2$] (yellow)	−292	4310	3.29	−15
[Ni(etu)$_4$Cl$_2$] (orange)	−292	4430	3.33	−13
[Ni(etu)$_4$Br$_2$] (yellow)	−313	4320	3.30	−15
[Ni(etu)$_4$Br$_2$] (orange)	−313	4280	3.28	−15
[Ni(etu)$_4$I$_2$]		Diamagnetic		
[Ni(etu)$_4$](ClO$_4$)$_2$		Diamagnetic		
[Ni(etu)$_6$](ClO$_4$)$_2$	−432	4350	3.24	− 2
[Ni(etu)$_4$](NO$_3$)$_2$		Diamagnetic		
[Ni(detu)$_4$Br$_2$]		Diamagnetic		
[Ni(detu)$_4$I$_2$]		Diamagnetic		
[Ni(detu)$_6$](ClO$_4$)$_2$	−625	4180	3.17	
[Ni(naptu)$_4$Cl$_2$]	−377	3480	2.89	
[Ni(naptu)$_2$Br$_2$]	−318	4560	3.32	
[Ni(naptu)$_2$I$_2$]	−328	4910	3.44	

TABLE II

MAGNETIC PROPERTIES OF Ni–S COMPLEXES IN ACETONE[a] AT ROOM TEMPERATURE

Compound	Concn., $M \times 10^2$	Dia. cor. $\times 10^6$	$\chi_M{}^{cor} \times 10^6$, c.g.s.u.	μ, B.M.
[Ni(etu)$_4$I$_2$]	0.82	−341	3950	3.07[b]
	1.13	−341	4210	3.17[b]
	2.03	−341	3860	3.05
	2.40	−341	4070	3.12
[Ni(detu)$_4$Cl$_2$]	2.08	−412	5000	3.45
	2.36	−412	5040	3.46
[Ni(detu)$_4$Br$_2$]	1.36	−447	4530	3.27
[Ni(detu)$_4$I$_2$]	4.98	−479	4320	3.21
	5.20	−479	4260	3.20
[Ni(detu)$_6$](ClO$_4$)$_2$	1.58	−625	1710	2.02
	4.61	−625	1650	1.99

[a] Calculated assuming no ligand dissociation.   [b] Determined by the method of Evans.[4]

Fig. 1.—Molar conductance in acetone of [Ni(etu)$_4$](ClO$_4$)$_2$, upper curve; [Ni(etu)$_4$I$_2$], lower curve.

tions, is essentially a nonelectrolyte at concentrations above 2×10^{-3} M. This same behavior is observed for [Ni(detu)$_4$I$_2$] and to a much lesser extent for the other halo complexes of diethylthiourea and ethylenethiourea. A complete compilation of conductivity data is found in Table VI.

Marked color changes accompany dissolution of almost all the compounds reported here. The molecular weight data (Table VII) together with the conductivities indicate *dissociation of ligand and retention of anion* in solution in all cases except for [Ni(naptu)$_2$I$_2$], [Ni(naptu)$_2$Br$_2$], and the perchlorates. In the case of [Ni(etu)$_4$Cl$_2$] a very low solubility precluded determination of its molecular weight. All molecular weights were determined ebullioscopically as the low solubilities of these compounds did not allow a cryoscopic determination.

TABLE III

REFLECTANCE SPECTRA FOR Ni(II) COMPLEXES

Compound	ν_3, cm.$^{-1}$	ν_2, cm.$^{-1}$	ν_1, cm.$^{-1}$
[Ni(etu)$_4$Cl$_2$] (yellow)	21,300 (sh)	13,250, 11,500 (sh)	7,820
[Ni(etu)$_4$Cl$_2$] (orange)	21,300	12,600, 11,200 (sh)	7,700
[Ni(etu)$_4$Br$_2$] (yellow)	20,400 (sh)	12,840, 10,820 (sh)	7,600
[Ni(etu)$_4$Br$_2$] (orange)	20,000	11,550	7,520
[Ni(etu)$_6$](ClO$_4$)$_2$	19,100 (sh)	13,500	8,000
[Ni(etu)$_4$](ClO$_4$)$_2$			16,500
[Ni(etu)$_4$](NO$_3$)$_2$			17,000
[Ni(etu)$_4$I$_2$]			16,400, 14,200
[Ni(detu)$_6$](ClO$_4$)$_2$	20,000 (sh)	13,700	8,060
[Ni(detu)$_4$Br$_2$]			15,600
[Ni(detu)$_4$I$_2$]			15,400
[Ni(naptu)$_4$Cl$_2$]	20,800 (sh)	13,000, 10,300 (sh)	7,750
[Ni(naptu)$_2$Br$_2$]	14,900, 14,100	10,100, 9,000	5,400, 4,800 (?)
[Ni(naptu)$_2$I$_2$]	13,300	9,750, 8,200	5,400, 4,800 (?)

absorption maxima is necessarily arbitrary for the broad bands we have observed, and may be considered accurate to only ±100 cm.$^{-1}$. This problem is accentuated in the assignment of ν_1 for the octahedral complexes reported here for not only is ν_1 itself very broad but a broad shoulder (6300 cm.$^{-1}$) occurs on the low frequency side of this band. This is thought to be due to the ligand and as such is ignored for the purposes of deriving the various electronic parameters displayed in Table V.

The conductivity data displayed in Fig. 1 indicate that [Ni(etu)$_4$](ClO$_4$)$_2$ is correctly viewed as a 1:2 electrolyte. It will be noted, however, that the iodo compound, while a strong electrolyte at low concentra-

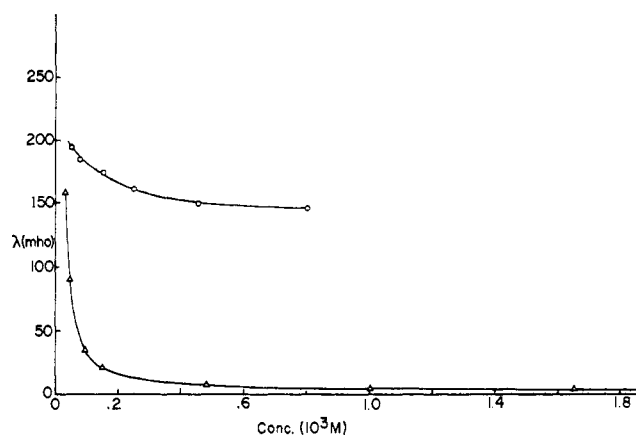X-Ray powder data (d-spacings) for the orange and yellow forms of [Ni(etu)$_4$Cl$_2$] are collected in ref. 1b. The compounds are not isomorphous.

Infrared spectra pertinent to the state of the nitrate groups in [Ni(etu)$_4$(NO$_3$)$_2$] both in the solid and in solution have been examined but the data are inconclusive at best.

Discussion

Structure in the Solid State.—The yellow isomer of [Ni(etu)$_4$Cl$_2$], the first product of the reaction of nickel chloride in solution with ethylenethiourea, is analogous to the octahedral yellow compound dichlorotetrakis-(thiourea)nickel(II). This compound was reported

TABLE IV

SOLUTION SPECTRA OF SUBSTITUTED Ni–THIOUREA COMPLEXES[a]

Compound	Phase	Concn., $M \times 10^4$	ν_3, cm.$^{-1}$	ν_2, cm.$^{-1}$	ν_1, cm.$^{-1}$
[Ni(etu)₆](ClO₄)₂	Acetone	26.7			21,600 (180)
	Acetone + etu	26.7 + excess etu			16,260 (158)
[Ni(etu)₄](ClO₄)₂	Acetone	36.7		26,300 (~90)	19,950 (13)
	Acetone	123.6			16,150 (91)
[Ni(etu)₄Br₂] (yellow)	Nitroethane	Satd. soln.		15,000, 14,300	10,100, 9,700, 9,100
[Ni(etu)₄Br₂] (orange)	Nitroethane	Satd. soln.		15,000, 14,300	10,100, 9,700, 9,100
[Ni(etu)₄Br₂] (yellow)	Acetone	Satd. soln.		15,000, 14,400	10,100, 9,700, 9,100
[Ni(etu)₄I₂]	Nitroethane	36.5		13,500 (342)	9,530 (58), 8,510 (33)
	Acetone	85.4		~13,500 (?), 10,200 (19)	9,530 (68), 8,400 (27)
[Ni(tu)₆](NO₃)₂	Acetone	163	23,000 (61)	13,600 (28)	8,000 (11), 6,700 (10)
[Ni(etu)₄](NO₃)₂	Acetone	236	22,500 (61)	13,700 (28), 11,700 (sh)	7,800 (13)
[Ni(detu)₄Cl₂]	Acetone	56.9		15,650 (187), 14,600 (182)	10,500 (27), 10,100 (28), 9,300 (41)
	Acetone + detu	58.9 + 620		15,400 (190)	10,500 (33), 10,100 (34), 9,300 (46)
[Ni(detu)₄Br₂]	Acetone	35.7		14,800 (308)	10,100 (45), 9,700 (41), 9,100 (49)
	Acetone + detu	72.8 + 584		15,000 (279)	10,100 (53), 9,700 (44), 9,100 (56)
[Ni(detu)₄I₂]	Acetone	24.3		13,600 (474)	9,500 (70), 8,400 (39)
	CHCl₃	Satd. soln.		13,700	9,500, 8,700
	Nitroethane	40.1		13,700 (379)	9,800 (82), 8,400 (52)
[Ni(naptu)₄Cl₂]	Acetone	40.0		15,800 (161), 15,100 (161)	10,600 (32), 10,100 (33), 9,620 (40), 9,300 (41)
[Ni(naptu)₄Cl₂]	Acetone	80.0		15,700 (159), 15,200 (157)	10,600 (31), 10,100 (32), 9,600 (39), 9,300 (40)
[Ni(naptu)₂Br₂]	Acetone	62.4		14,800 (270)	11,700 (sh), 10,100 (52), 9,700 (48), 9,100 (55)
[Ni(naptu)₂I₂]	Acetone	57.5		14,100 (sh), 13,600 (431)	9,700 108), 8,420 (sh)

[a] Molar extinction coefficient in parentheses.

TABLE V

DERIVED ELECTRONIC STRUCTURE PARAMETERS FOR OCTAHEDRAL Ni(II) COMPLEXES

Compound	Dq, cm.$^{-1}$	B', cm.$^{-1}$ [a]	β [b]
[Ni(etu)₄Cl₂] (yellow)	782	679	0.66
[Ni(etu)₄Cl₂] (orange)	770	660	.64
[Ni(etu)₄Br₂] (yellow)	760	613	.60
[Ni(etu)₄Br₂] (orange)	752	599	.58
[Ni(etu)₆](ClO₄)₂	800	573	.56

[a] B' determined by assuming $\nu_1 = 10Dq$ and solving equation $B' = (\nu_2 + \nu_3 - 30Dq)/15$. [b] B is taken to be 1030 cm.$^{-1}$ for the free Ni(II) ion.

TABLE VI

ELECTROLYTIC CONDUCTIVITIES AT 25° [a]

Compound	Solvent	Concn., $M \times 10^5$	Molar conductance, ohm^{-1}
[Ni(etu)₄Cl₂] (orange)	Acetone	28	9
[Ni(etu)₄Br₂] (orange)	Acetone	8	31
[Ni(etu)₄I₂]	Acetone	2	156
	Acetone	15	23
	Acetone	48	6
	Acetone	105	3
[Ni(etu)₄](ClO₄)₂	Acetone	5	197
	Acetone	9	185
	Acetone	26	162
[Ni(etu)₆](ClO₄)₂	Acetone	9	278
[Ni(etu)₄](NO₃)₂	Acetone	14	19
[Ni(detu)₄Cl₂]	Acetone	7	16
[Ni(detu)₄Br₂]	Acetone	6	29
[Ni(detu)₄I₂]	Acetone	3	202
	Acetone	9	100
	Acetone	50	21
[Ni(detu)₆](ClO₄)₂	Acetone	2	331
[Ni(tu)₆](NO₃)₂	Acetone	15	25
[Ni(naptu)₄Cl₂]	Acetone	5	15
[Ni(naptu)₂Br₂]	Acetone	13	27
[Ni(naptu)₂I₂]	Acetone	8	111
	Acetone	24	70
	Acetone	77	31
[Ni(detu)₄Cl₂]	Nitroethane	6	9
[Ni(detu)₆](ClO₄)₂	Nitroethane	15	138
[Ni(detu)₄Br₂]	Nitroethane	5	14
[Ni(detu)₄I₂]	Nitroethane	4	23
	Nitroethane	16	12
	Nitroethane	27	10
	Nitroethane	46	7
[Ni(etu)₄](NO₃)₂	Nitroethane	24	5
[Ni(naptu)₂I₂]	Nitroethane	20	10

[a] A 1:1 electrolyte in acetone has a molar conductance of approximately 120 ohm^{-1} mole^{-1}.

by Nardelli, Chierici, and Braibanti[6] to consist of a trans-NiS₄Cl₂ coordination sphere. The crystal structure was studied in greater detail recently by Lopez-Castro and Truter[7] and therefore their data are quoted. The space group is I4 and the unit cell contains two hexacoordinated nickel units in which four sulfur atoms are in a plane about the nickel atom at 2.46 Å, while the two axial positions are filled (nonequivalently) by the two chlorine atoms at 2.40 and 2.52 Å. The gross features of the environment must be very similar to those in yellow [Ni(etu)₄Cl₂] (the colors and resulting spectra and magnetism are very similar, though not identical) and we therefore take the yellow [Ni(etu)₄Cl₂] as trans octahedral. The yellow bromo compound is assigned similarly, as is yellow [Ni-(naptu)₄Cl₂].

The magnetic behavior of the chloro and bromo compounds is normal. That is, the measured magnetic moments fall in the range (2.80–3.40 B.M.) generally accepted for octahedral nickel(II). It is of interest to note that there is only a small variation in the magnetic moment among the several halide compounds.

It will be noted (Fig. 2) that while the gross spectral features of the orange [Ni(etu)₄Cl₂] complex are similar to those of the yellow form, differences in detail exist. While the yellow compound shows only a shoulder on the charge-transfer band, the orange complex shows a distinct peak. Also the ν_2 band (~13,000 cm.$^{-1}$) of the yellow form exhibits a distinct splitting while for the orange complex only a broaden-

(6) M. Nardelli, I. Chierici, and A. Braibanti, Gazz. chim. ital., **88**, 37 (1958).

(7) A. Lopez-Castro and M. R. Truter, J. Chem. Soc., 1309 (1963).

ing occurs. It can also be seen that the yellow compound absorbs at slightly higher frequencies than does the orange. Since the yellow chloro (and bromo) forms differ from the corresponding orange forms in spectral details and X-ray powder patterns[1b] and since both sets of compounds are octahedral (cf. spectra, magnetism, stoichiometry), these compounds are assigned as cis-trans isomers.

TABLE VII

EBULLIOSCOPIC MOLECULAR WEIGHT DETERMINATION DATA[a]

| Compound | Found mol. wt. | Expected mol. wt. for | | | |
		1 particle	2 particles	3 particles	4 particles
[Ni(etu)₄](ClO₄)₂	295	666	333	111	
[Ni(etu)₆](ClO₄)₂	251	871	436	290	218
[Ni(etu)₄](NO₃)₂	217	613	307	204	
[Ni(etu)₄Br₂] (orange)	235[b]	627	319	209	
[Ni(etu)₄I₂]	260	721	361	240	
[Ni(detu)₆](ClO₄)₂	337	1057	529	352	264
[Ni(detu)₄Cl₂]	211	663	332	221	
[Ni(detu)₄I₂]	288[c]	845	423	282	
[Ni(naptu)₂Br₂]	636	623			
[Ni(naptu)₂I₂]	718	718			
[Ni(tu)₆](NO₃)₂	158	640	320	219	160
Thiourea	80	76			

[a] Acetone was used as the solvent ($K_b = 1.72$). [b] Very low solubility. [c] The molecular weight of [Ni(detu)₄I₂] was also determined in CHCl₃. Erratic results were obtained however, apparently due to formation of an oil.

Further support for this postulate is afforded by the assignment of a specific configuration to both the yellow and orange forms. It has been predicted theoretically[8] and borne out experimentally[9,10] that for *cis-trans* isomers the lowering of symmetry due to a tetragonal distortion should produce a splitting of the spectral bands of the *trans* isomer that is twice that observed in the spectrum of the corresponding *cis* compound. It would appear therefore that the yellow chloro and bromo complexes have a *trans* configuration while the orange have a *cis* configuration.[11] This assign-ment assumes that the spin–orbit coupling remains fairly constant in the two sets of isomers. A rationali-zation of the shoulders at 6300 cm.⁻¹ in the spectra of all four complexes is not so easily obtained. It is probable that this perturbation of the band shape is due to a ligand vibrational mode even though such a mode is not in evidence in any of the spectra of square-planar complexes of Ni(II) and ethylenethiourea.

No such isomers of [Ni(tu)₄Cl₂] (where tu is thiourea) have been reported by previous workers nor have we been able to prepare such isomers.

[Ni(etu)₆](ClO₄)₂, [Ni(detu)₆](ClO₄)₂, and [Ni-(naptu)₄Cl₂] can similarly each be assigned an octa-hedral configuration. On the basis of its single spectral band at 16,500 cm.⁻¹ and its diamagnetism [Ni-(etu)₄](ClO₄)₂ is viewed as having a square-planar structure; similar reasoning leads to the same assign-ment for [Ni(etu)₄](NO₃)₂.

We propose that the diamagnetic [Ni(etu)₄I₂], which is a nonelectrolyte at concentrations greater than 10^{-3} M, is a distorted octahedral (tetragonal) molecule similar to the diamagnetic [Ni(diarsine)₂I₂].[12] This molecule has recently been shown[13] to be *trans* octahedral with a short (3.21 Å.) Ni–I bond distance.

(8) C. J. Ballhausen and C. K. Jørgensen, *Kgl. Danske Videnskab. Selskab. Mat. fys. Medd.*, **29**, No. 14 (1955).

(9) M. Linhard and M. Weigel, *Z. anorg. allgem. Chem.*, **264**, 321 (1952).

(10) F. Basolo, C. J. Ballhausen, and J. Bjerrum, *Acta Chem. Scand.*, **9**, 810 (1955).

(11) This is not, of course, proof that the orange compounds are in fact the *cis* isomers. Such definitive proof must await X-ray crystallographic structure analysis. Since, however, the orange and yellow modifications have the same stoichiometry, we shall for convenience call them *cis-trans* isomers. Linkage isomerism (coordination through N instead of S) is ruled out by infrared spectra.

(12) C. M. Harris, R. S. Nyholm, and D. J. Phillips, *J. Chem. Soc.*, 4379 (1960).

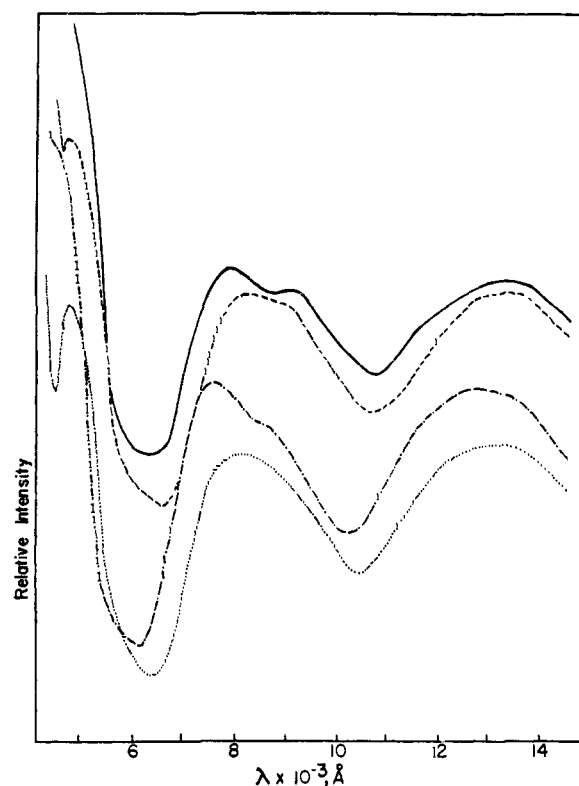(13) N. C. Stephenson and G. A. Jeffrey, *Proc. Chem. Soc.*, 173 (1963).

Fig. 2.—Reflectance spectra of yellow [Ni(etu)₄Cl₂], – · – · – ·; orange [Ni(etu)₄Cl₂], · · · · · · ; yellow [Ni(etu)₄Br₂], ———; orange [Ni(etu)₄Br₂], - - - - - - - .

These iodo complexes are, to our knowledge, the only six-coordinate complexes of nickel with a singlet ground state.[14] The one broad spectral band is also indicative of a strong tetragonal field.

[Ni(naptu)₂Br₂] and [Ni(naptu)₂I₂] appear to exhibit yet another type of structure. The absorption bands at 14,000 and 9700 cm.⁻¹ (*cf.* Fig. 3) as well as magnetic moments of 3.32 and 3.44 B.M., re-spectively, are indicative of tetrahedral coordina-tion.[15-17] The compounds retain their structure in solution, and conductance and molecular weight measurements as well as solution spectra confirm this assertion.

In tetrahedral symmetry, the bands at 14,000 cm.⁻¹ may be assigned to the ³T₁g(F) → ³T₁g(P) transition, while those at 9700 cm.⁻¹ may be assigned to ³T₁g(F) → ³A₂g(F). The splitting of this band cannot readily be explained, since the excited state is an orbital singlet. We have been unable to invent an acceptable alternative assignment. A broad structured band appears for both the bromide and iodide complexes in the 5000 cm.⁻¹ region. While this band may be the ³T₁g(F) → ³T₂g(F) transition, its position in the near-infrared does not allow unambiguous assignment; ligand vibrations may be involved here. An attempt to fit these data to an energy level diagram was not successful; we ascribe this difficulty to the low value of B for thiourea ligands.[1a]

Solution Behavior.—As was noted above, in general information about the solid state structure of these compounds cannot be related to solution measurements

(14) But see ref. 5.

(15) N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 3997 (1959).

(16) L. M. Venanzi, *ibid.*, 719 (1958).

(17) D. M. L. Goodgame, M. Goodgame, and F. A. Cotton, *J. Am. Chem. Soc.*, **83**, 4161 (1961).
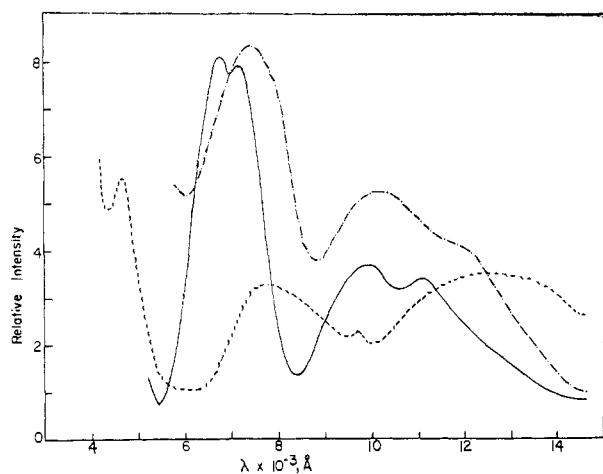
Fig. 3.—Reflectance spectra of [Ni(naptu)₄Cl₂], ·········; [Ni-(naptu)₂Br₂], ———; [Ni(naptu)₂I₂], —·—·—·.

as reaction occurs upon dissolution. This reaction is however of an unusual type. Whereas it is not unusual for a compound which is four-coordinate in the solid to become six-coordinate in solution, either by addition of solvent molecules[18,19] or by solute association,[20] it appears that for a nickel compound which is six-coordinate in the solid phase to become four-coordinate in solution is not so common. When compounds of the type [NiS₄I₂] (S = etu or detu, X = Cl, Br, or I; S = naptu, X = Cl) are dissolved in acetone *or nitroethane* a change in both spectral and magnetic properties occurs. Whereas [Ni(detu)₄X₂] and [Ni-(etu)₄I₂] exhibit a single band at about 15,500 cm.⁻¹ in the solid phase, when dissolved in acetone they exhibit a new band of high intensity whose position varies from 13,500 to 15,000 cm.⁻¹, depending on the compound, and a lower intensity band at 9500 cm.⁻¹ (*cf.* Fig. 4). When the compounds [Ni(etu)₄X₂] (X = Cl or Br) and [Ni(naptu)₄Cl₂], which are all octahedral in the solid phase and possess a yellow or orange color, are dissolved in acetone or nitroethane they yield blue-green solutions whose spectra are almost identical with those of the corresponding diethylthiourea complexes. All of those compounds which are soluble enough to yield solution moments show paramagnetism which is of the order of 3.0–3.4 B.M. None of these compounds obeys Beer's law.

Molecular weight measurements indicate the presence of three particles in solution instead of the one expected in the case of no dissociation, while conductance measurements indicate coordination of the halide ions.[21]

Comparing the spectra in Fig. 4 with those in Fig. 3 it is immediately apparent that we find tetrahedral entities in solution, formed by loss of thiourea ligand. Certainly the magnetism, molecular weight, and conductance data bear this out. From these data we postulate the presence of species of the type [NiS₂X₂].

(18) J. B. Willis and D. P. Mellor, *J. Am. Chem. Soc.*, **69**, 1237 (1947).
(19) F. Basolo and W. R. Matoush, *ibid.*, **75**, 5663 (1953).
(20) R. H. Holm, *ibid.*, **83**, 4683 (1961).
(21) A qualification is necessary in the case of [Ni(etu)₄I₂] and in general for all the iodides. In dilute solution, 10⁻⁵ *M*, these compounds are all strong electrolytes in acetone and moderate electrolytes in nitroethane. However in the concentration region in which all spectral and magnetic studies were carried out the iodo complexes are nonconductors. As a further check on this a conductometric titration was carried out in acetone between [Ni(etu)₄](ClO₄)₂ and KI. A break occurred in the curve at 2 equiv. of KI added indicating coordination of the iodides.
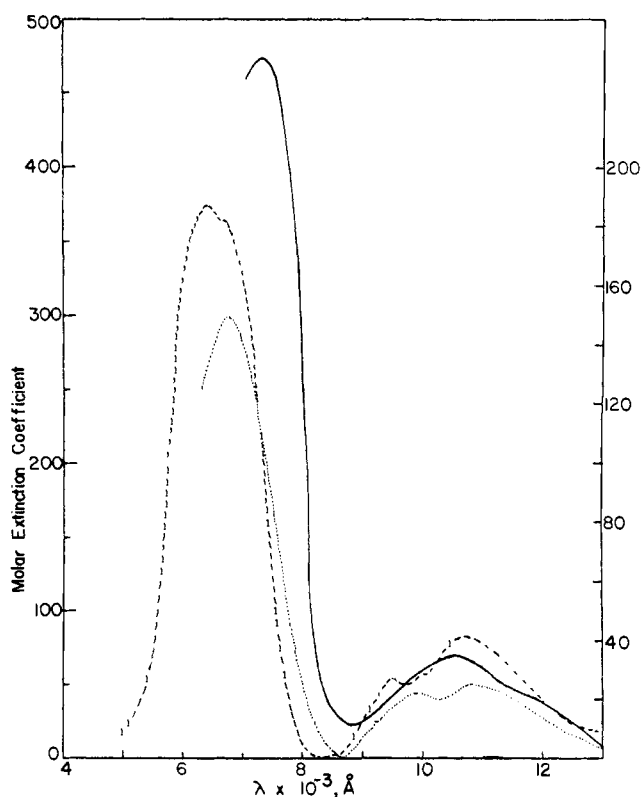
Fig. 4.—Spectra in acetone of [Ni(detu)₄Cl₂], ········· (right-hand ordinate); [Ni(detu)₄Br₂], ······ (left-hand ordinate); [Ni(detu)₄I₂], ——— (left-hand ordinate).

Whether any of the parent octahedral [NiS₄X₂] exists in equilibrium in solution is difficult to say; any spectral bands which might arise from such species are completely masked by the more intense tetrahedral bands.[22]

[Ni(etu)₄](ClO₄)₂, [Ni(etu)₆](ClO₄)₂, and [Ni(detu)₆]-(ClO₄)₂ exhibit a common solution behavior. Typical solution spectra are displayed in Fig. 5. The spectra at higher concentrations are reminiscent of the spectra of solid square-planar [Ni(etu)₄](ClO₄)₂. Electrolytic conductivities indicate noncoordination of the perchlorate groups in all three compounds. Molecular weight determinations indicate coordination of at least four sulfur donors per nickel atom in all three cases. It appears from this that there occurs an equilibrium of the type

$$NiS_6^{+2} \rightleftharpoons NiS_4^{+2} + 2S$$

where NiS_4^{+2} is square-planar and NiS_6^{+2} is octahedral. This postulate is justified by two further observations: (1) A depressed magnetic moment (of ~2.0 B.M.) is found for [Ni(detu)₆](ClO₄)₂ in acetone, and (2) the fact that no bands other than the one attributable to the square-planar species are observed in solution. If the equilibria were square-planar ⇌ tetrahedral we would expect to see the intense tetrahedral bands, especially since ~¹/₃ of the species in solution should be tetrahedral (based on observed and predicted magnetic moments). On the other hand, octahedral compounds possess bands of low extinction coefficient which would not be observed in the presence of strong d–d and charge-transfer bands of the square-planar species. The independent preparation of planar [Ni(etu)₄]-

(22) It is of interest to note that we have observed that [Ni(tu)₄Cl₂] is probably also tetrahedral in solution.

($ClO_4)_2$ lends strength to the argument that the species can exist in solution.

In solution the compound [Ni(etu)$_4$](NO$_3$)$_2$ exhibits another type of behavior. Its visible spectrum and its diamagnetism in the solid indicate a square-planar configuration, while solution-phase data are indicative of octahedral coordination with coordinated nitrate groups. The compound is a nonelectrolyte in acetone and nitroethane, yet its molecular weight is one-third that anticipated for a compound of the constitution [Ni(etu)$_4$(NO$_3$)$_2$] and its spectrum, which exhibits bands at 22,500 cm.$^{-1}$ (ϵ 61), 13,700 (28), 11,700 (sh), and 7800 (13), is typical of an octahedral species. Infrared data[1] also tend to support coordination of nitrate groups in solution, but say little about their solid state behavior. This then indicates the loss of two ethylenethiourea groups on dissolution accompanied by coordination of the nitrate groups. Whether these groups occupy four coordination positions in a bidentate manner or are accompanied in the coordination sphere by two molecules of acetone is hard to say. The fact that this phenomenon also occurs in nitroethane lends credence to a bidentate function. Analogous behavior is observed with [Ni(tu)$_6$](NO$_3$)$_2$. Cotton, et al.,[23] prepared the latter compound in order to compare its infrared spectrum with that of [Co(tu)$_4$(NO$_3$)$_2$]. It was assumed that the nickel compound in solution had all six thiourea groups coordinated, with the nitrates ionic. Support for the octahedral character of the compound was obtained from spectra in acetone solution. As may be seen from Tables VI and VII, however, this compound, while octahedral in solution, obtains this configuration only by coordination of the nitrate groups in a manner similar to that of Ni(etu)$_4$-(NO$_3$)$_2$.[24]

Electronic Spectra.—We take the reflectance spectra of the complexes as the true spectra. Unfortunately these procedures do not allow us to measure extinction coefficients, thereby making spectral assignments difficult.

The spectra of [Ni(etu)$_6$](ClO$_4$)$_2$, both isomers of [Ni(etu)$_4$Cl$_2$], and both isomers of [Ni(etu)$_4$Br$_2$] are readily interpreted in terms of octahedral symmetry.[25] If we assign the broad band occurring at about 8000 cm.$^{-1}$ in the spectrum of [Ni(etu)$_6$](ClO$_4$)$_2$ to the $^3A_{2g} \rightarrow$ $^3T_{2g}$ transition and the band occurring at 13,500 cm.$^{-1}$ to the $^3A_{2g} \rightarrow$ $^3T_{1g}$ ($t_{2g}e_g$) transition we obtain immediately a value of Dq for this compound of 800 cm.$^{-1}$.

Since the band is broad and asymmetric, we have made an arbitrary choice of the band maximum; perhaps it is more appropriate to put Dq in the range 750–800 cm.$^{-1}$. This may be compared with the recent assignment of an average Dq of 798 cm.$^{-1}$ to [Ni(tu)$_4$Cl$_2$],[26] as well as that of 1060 cm.$^{-1}$ for 1,2-dimethylmercaptoethane, another sulfur donor, coordinated to Ni^{+2}.[27]

The assignment of the shoulder at 19,100 cm.$^{-1}$ (on the charge-transfer band) is then difficult. If we assign it to $^3T_{1g}(P)$ we find a very low value of β. However, assignment to the $^3T_{1g}(P)$ level does involve a term
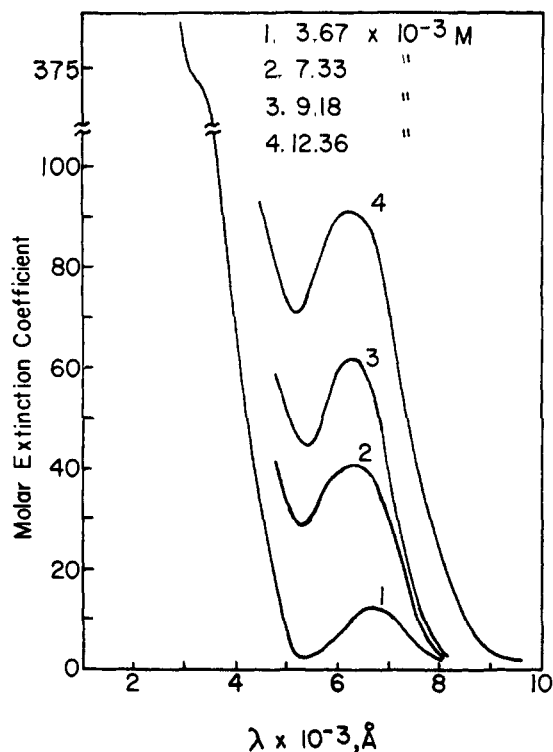
(23) F. A. Cotton, O. D. Faut, and J. T. Mague, *Inorg. Chem.*, **3**, 17 (1964).

(24) Professor Cotton, in a private communication, agrees that [Ni-(tu)$_6$](NO$_3$) is actually a nonelectrolyte in acetone.

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

(26) C. R. Hare and C. J. Ballhausen, *J. Chem. Phys.*, **40**, 788 (1964).

(27) R. L. Carlin and E. Weissberger, *Inorg. Chem.*, **3**, 611 (1964).

Fig. 5.—Spectrum in acetone of [Ni(etu)$_4$](ClO$_4$)$_2$ as a function of concentration.

lowering of over 3000 cm.$^{-1}$. While it might then not be unreasonable to associate this transition with the $^1T_{2g}(D)$ level, in the absence of extinction coefficients we feel that the transition is best assigned to the triplet state and that the low value of β is real. The large nephelauxetic effect of substituted thioureas has been pointed out previously.[1]

Comparing the spectra of the two chloro and two bromo complexes, we see that they exhibit, in large measure, similar spectra, and a similar assignment is made. The bands at 21,300 cm.$^{-1}$ for the chloro isomers are also assigned as transitions to $^3T_1(P)$. It is important to note that the spectra of each isomeric pair are similar in broad outline but differ somewhat in detail.

The diamagnetic compound [Ni(etu)$_4$](ClO$_4$)$_2$ exhibits, in the reflectance spectrum, a broad band with a maximum at 16,500 cm.$^{-1}$. In acetone solution, a band occurs in a similar position, but the behavior of the compound is not straightforward. Thus, at a concentration of 3.67 $\times$ 10^{-3} M, the band maximum occurs at 14,950 cm.$^{-1}$, and the molar extinction coefficient is 13. With increasing concentration, the band shifts regularly to higher energy (16,150 cm.$^{-1}$ at 12.36 $\times$ 10^{-3} M) and becomes more intense (molar extinction, 91). While the position and intensity of this band are characteristic of square-planar nickel complexes,[28] we are unable to explain why Beer's law is not obeyed for this compound other than to require solvolysis.

Stereochemistry of Nickel(II).—In recent years there have been many studies of nickel(II) complexes, in order to determine the criteria for the three main stereochemical arrangements, octahedral, tetrahedral, and planar, and to identify the factors influencing their adoption. While magnetic and spectral data, usually used in conjunction with ligand field theory, have

(28) G. Maki, *J. Chem. Phys.*, **29**, 1129 (1958).

enabled such structures to be determined with fair certainty, much less is known about the reasons for the adoption of a particular structure.[2] We believe that this work on complexes of nickel with substituted thioureas has perhaps raised more questions than provided answers in this respect.

Why, for example, do the octahedral compounds [NiS₄X₂] change to the less common tetrahedral structure in solution? A similar equilibrium has recently been shown to occur with several cobalt complexes[29]; cobalt is, of course, well known to frequently favor a tetrahedral structure. These authors indicate that they also have evidence for a simple tetrahedral–octahedral configuration equilibrium for nickel in solution, and are investigating the thermodynamics of the equilibrium.

It would be useful if we could sort out the steric factor from the polarizability of the ligands in determining stereochemistry, but this is very difficult. Thus, the fact that both [Ni(naptu)₂Br₂] and [Ni(naptu)₂I₂] are tetrahedral rather than octahedral like the chloride complex formed by naphthylthiourea could be ascribed to steric factors (the larger size of bromide and iodide vs. chloride), or perhaps the larger polarizability, and presumably more covalency, helps to favor the tetrahedral structure. Other factors, such as the relative stability of the solid phases, may of course also be important.

On the other hand, the donor atom in ethylenethiourea is really about as polarizable as iodide, or at least the two ligands neighbor each other in the nephelauxetic series,[1] yet the regular octahedral [Ni(etu)₆]-(ClO₄)₂ is formed. This suggests that highly polarizable ligands alone cannot force nickel to attain a tetrahedral structure, and that steric factors may be more important.

That the situation is not straightforward is readily realized when we try to account for the fact that nickel may also attain a planar geometry. Thus, while both [Ni(naptu)₂Br₂] and [Ni(quinoline)₂Br₂] are tetrahedral, we find [Ni(naptu)₂I₂] is tetrahedral while [Ni(quinoline)₂I₂] is planar.[2] That the factors which determine square-planar vs. tetrahedral stereochemistry are finely balanced is evidenced by several recent expositions of solution equilibria between the two structures.[30]

We believe that ethylenethiourea is the first ligand which has been shown to be capable of forming either planar, [Ni(etu)₄](ClO₄)₂, or octahedral, [Ni(etu)₆]-(ClO₄)₂, structures. We see no ready explanation for the formation of both of these.

That [Ni(etu)₄I₂] is tetragonal (diamagnetic) while [Ni(etu)₄X₂] (X = Cl, Br) are octahedral can probably be explained by a consideration of the position of the ligands in the spectrochemical series. Since ethylenethiourea is closest to chloride in this series,[1] the average ligand field is nearest to octahedral in [Ni(etu)₄Cl₂], while the average ligand field approximation is probably poor in the case of the iodide.

Lastly, why is [Ni(etu)₄Cl₂] (yellow) a normal octahedral molecule while [Ni(detu)₄Cl₂] exhibits a weak tetragonal field?[5] Electronically, the constriction of tying back the ethyl groups (in ethylenethiourea) is only a second-order effect at the donor sulfur atom, and we think that this does not cause the change in electronic structure (crystalline field) at the nickel. Rather, we think the important factor may be that of steric crowding among the diethylthiourea molecules. Complete crystal structure analyses of these two compounds should prove to be very interesting.

(29) H. C. A. King, E. Körös, and S. M. Nelson, *J. Chem. Soc.*, 5449 (1963).

(30) D. R. Eaton, W. D. Phillips, and D. J. Caldwell, *J. Am. Chem. Soc.*, **85**, 397 (1963); R. H. Holm and K. Swaminathan, *Inorg. Chem.*, **2**, 181 (1963).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE 39, MASSACHUSETTS]

The Crystal, Molecular, and Electronic Structures of a Binuclear Oxomolybdenum(V) Xanthate Complex[1]

BY A. B. BLAKE, F. A. COTTON,[2] AND J. S. WOOD

The crystal and molecular structures of [(C₂H₅OCS₂)₂MoO]₂O, a binuclear, oxo-bridged complex of molybdenum(V), have been determined by single crystal X-ray diffraction methods, including least-squares refinement of atomic positional parameters and isotropic thermal vibration parameters. The space group is P2₁, Z = 2, and the unit cell dimensions are $a = 10.72 \pm 0.03$, $b = 13.57 \pm 0.03$, $c = 10.86 \pm 0.03$ Å., $\beta = 123.5 \pm 0.5°$. The electronic structure of this molecule as a function of the internal angle of twist has been investigated by the Hückel LCAO–MO method and it is shown that the diamagnetism can be accounted for. It is also shown that this treatment leads to a possible explanation for the reported existence of both diamagnetic and paramagnetic dimeric Mo(V) species in HCl solutions of Mo(V).

Introduction

In 1939, Malatesta[3] reported a molybdenum complex of ethyl xanthate with the formula Mo₂O₃(S₂COC₂H₅)₄. The structure of this compound appeared to us to be worthy of investigation for many reasons, including

(1) Supported by the National Institutes of Health.
(2) Fellow of the Alfred P. Sloan Foundation.
(3) L. Malatesta, *Gazz. chim. ital.*, **69**, 408 (1939).

(1) the probable presence of both Mo—O and Mo=O bonds; (2) the probable presence of an Mo—O—Mo group, the linearity of which is of interest; (3) the need of knowing the molecular structure and orientation in order to interpret the electronic structure of the compound, which is diamagnetic; (4) the importance of structural information on Mo(V) and Mo(VI) complexes in understanding the behavior of molybdenum