CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF CALIFORNIA, DAVIS, CALIFORNIA 95616

Medium-Ring Complexes. V. Nickel(II) Complexes of Cyclic Dithioethers, 1,4-Dithiacycloheptane and 1,5-Dithiacyclooctane

BY W. K. MUSKER*[1] AND N. L. HILL

Received April 30, 1971

Complexes of the seven- and eight-membered ring dithioethers 1,4-dithiacycloheptane (dtch) and 1,5-dithiacyclooctane (dtco) with nickel perchlorate, tetrafluoroborate, chloride, bromide, and iodide have been investigated. The structures of the solid complexes have been assigned by analysis of their spectral and magnetic properties. The diamagnetic perchlorate and tetrafluoroborate salts are planar. $Ni(dtco)_2Cl_2$ is octahedral but polymeric (crystal structure determination); however, $Ni(dtch)_2Cl_2$ could not be isolated. The stoichiometry of the bromide salts is unusual, $Ni_2(dithioether)_3Br_4$. $Ni_2(dtco)_3Br_4$ appears to contain two tetrahedral nickel ions with one bridging and two monodentate dithioether ligands; $Ni_2(dtch)_3Br_4$ appears to have two trigonal-bipyramidal nickel ions with one bridging and two chelated dithioether ligands although a polymeric structure cannot be ruled out. Three iodide complexes were obtained: $Ni(dtco)_2I_2$, $Ni(dtco)I_2$, and $Ni(dtch)_2I_2$. The diamagnetic $Ni(dtco)_2I_2$ is either planar or low-spin octahedral, whereas $Ni(dtco)I_2$ appears to be tetrahedral and $Ni(dtch)_2I_2$ octahedral. The solid complexes dissociate in nitromethane and acetone; we have attempted to identify the predominant species in solution by the use of spectral evidence. The perchlorate and tetrafluoroborate salts dissolve with loss of dithioether ligand, but in the presence of excess ligand, planar complexes are obtained. The chloride, bromide, and iodide salts dissolve to give tetrahedral complexes, $Ni(dithioether)X_2$, which probably contain chelated dithioether ligands. When excess ligand is added, octahedral complexes are obtained (except for $Ni(dtco)Br_2$ which remains tetrahedral); dtco complexes probably have four monodentate dithioether ligands and two halide ions, whereas dtch complexes may have two chelated dithioether ligands and two halide ions.

Introduction

Seven- and eight-membered ring systems containing two donor atoms are useful ligands for causing metal ions to exist in different geometries. Nickel(II) and copper(II) complexes of medium-ring *diamines* have been reported[2] and the structures of these complexes have been shown to be planar[2] or pyramidal[2,3] depending on the metal, the anion, and the solvent. We now report the preparation, properties, and structures of the complexes formed between nickel(II) and the medium-ring *dithioethers* 1,4-dithiacycloheptane (dtch) and 1,5-dithiacyclooctane (dtco) in the presence of various anions and solvents.[4]

Historically, acyclic dithioether complexes of nickel(II) were first prepared by Tschugaeff,[5] but only complexes having the stoichiometry $Ni(dithioether)_2(SCN)_2$ were obtained. Subsequently, bis complexes of 2,5-dithiahexane (dth) and 3,6-dithiaoctane (dto) with nickel(II) halides were prepared and a tris complex having the stoichiometry $Ni(dto)_3(ClO_4)_2$ was also isolated.[6] In all the above cases the complexes were octahedral. Macrocyclic rings containing four thioether donors also form complexes with nickel(II).[7] With these chelating agents, planar complexes are formed when perchlorate and tetrafluoroborate are the anions, whereas octahedral complexes are formed when halide or thiocyanate ions are present.

In this study it was observed that the stabilities of the medium-ring dithioether complexes of nickel(II) in solution were much lower than the stabilities of the corresponding diamine complexes.[2] Most of the structural evidence was obtained from analysis of the magnetic properties and infrared spectra of the solids and from the electronic absorption spectra of the complexes as solids and in solution with varying concentrations of ligands. Unfortunately we were unable to determine molecular weights of these complexes in solution either because of low solubilities or because of the necessity to add excess ligand to prevent dissociation. The crystal structure of $Ni(dtco)_2Cl_2$ was determined to obtain its stereochemistry and to confirm the assignment of its structure. X-Ray powder diffraction measurements were also obtained for some of the complexes.

Experimental Section

Materials.—Nickel(II) perchlorate was purchased from the G. Frederick Smith Chemical Co. and was used without further purification. Nickel(II) carbonate was purchased from the Allied Chemical and Dye Corp. and was used to prepare the hydrated nickel tetrafluoroborate salt by treatment with tetrafluoroboric acid. Hexaethanolnickel(II) perchlorate and tetrafluoroborate were prepared by the method of van Leeuwen.[8] Anhydrous nickel bromide and iodide were prepared by the addition of the appropriate acid to nickel(II) carbonate, and the resulting solid was dried under vacuum at 110°. Anhydrous nickel chloride was prepared from the hydrated salt by shaking with 2,2-dimethoxypropane.

Ligands.—The seven-membered cyclic dithioether 1,4-dithiacycloheptane was prepared using a modification of the method of Tucker and Reid.[9] The product was sublimed twice at 55–60° to achieve suitable purity; mp 47.5–48.3° (760 Torr). The eight-membered cyclic dithioether 1,5-dithiacyclooctane was prepared using the method described by Meadow and Reid[10] and by Leonard, Milligan, and Brown;[11] bp 67–68° (0.5 Torr), $n^{25}D$ 1.5770.

Bis(1,4-dithiacycloheptane)nickel(II) Tetrafluoroborate.—Hexaethanolnickel(II) tetrafluoroborate (2.5 g, 0.005 mol) was dissolved in a small amount of nitromethane (about 10 ml), and the solution was filtered in a drybox. To the filtrate was added 1.7 g (0.013 mol) of solid dtch, and the mixture was swirled for 1 min. The mixture was filtered in the drybox, and the orange powder was washed twice with small amounts of cold

---

[1] Alexander von Humboldt Fellow, 1970–1971.

[2] W. K. Musker and M. S. Hussain, *Inorg. Chem.*, **5**, 1416 (1966); **8**, 528 (1969).

[3] M. S. Hussain and H. Hope, *Acta Crystallogr., Sect. B*, **25**, 1866 (1969).

[4] N. L. Hill and W. K. Musker, *Inorg. Nucl. Chem. Lett.*, **6**, 79 (1970).

[5] L. Tschugaeff, *Ber. Deut. Chem. Ges.*, **41**, 2222 (1908), and later papers.

[6] (a) G. T. Morgan and W. Ledbury, *J. Chem. Soc.*, **121**, 2882 (1922); (b) G. T. Morgan, S. R. Carter, and F. W. Harrison, *ibid.*, **127**, 1917 (1925).

[7] W. Rosen and D. H. Busch, *J. Amer. Chem. Soc.*, **91**, 4694 (1969).

[8] P. W. N. M. van Leeuwen, *Recl. Trav. Chim. Pays-Bas*, **86**, 247 (1967).

[9] N. B. Tucker and E. E. Reid, *J. Amer. Chem. Soc.*, **55**, 775 (1933).

[10] J. R. Meadow and E. E. Reid, *ibid.*, **56**, 2177 (1934).

[11] N. J. Leonard, T. W. Milligan, and T. L. Brown, *ibid.*, **82**, 4083 (1960).

acetone. Additional product was obtained by concentrating the filtrate to one-third of its original volume using a rotary evaporator. The product was dried and the excess ligand was removed on the vacuum line. All attempts at recrystallization failed; mp 280°, dec pt 245–280°. *Anal.*[12] Calcd for $[Ni(C_5H_{10}S_2)_2](BF_4)_2$: C, 23.98; H, 4.03; S, 25.62. Found: C, 23.66; H, 4.24; S, 25.46.

Bis(1,4-dithiacycloheptane)nickel(II) Perchlorate.—This compound was prepared by the method given above using hexaethanolnickel(II) perchlorate (2.7 g) as the starting material; dec pt 100–200°. *Anal.* Calcd for $[Ni(C_5H_{10}S_2)_2](ClO_4)_2$: C, 22.83; H, 3.83; S, 24.38. Found: C, 22.90; H, 3.91; S, 23.88.

Bis(1,5-dithiacyclooctane)nickel(II) Tetrafluoroborate.—Hexaethanolnickel(II) tetrafluoroborate (2.5 g, 0.005 mol) was dissolved in a small amount of nitromethane (about 10 ml) and the solution was filtered in a drybox. To the filtrate was added, with stirring, 1.7 ml of dtco, to give a dark orange-red solution from which tiny brick red crystals formed. The crystals were collected on a filter, washed three times with acetone, and dried on the vacuum line; dec pt 140–290°. *Anal.* Calcd for $Ni(C_6H_{12}S_2)_2(BF_4)_2$: C, 27.25; H, 4.57; S, 24.25. Found: C, 27.13; H, 4.66; S, 23.81.

Bis(1,5-dithiacyclooctane)nickel(II) Perchlorate.—This compound was prepared by the method given above using hexaethanolnickel(II) perchlorate (2.7 g) and 1.7 ml of dtco. *Anal.* Calcd for $[Ni(C_6H_{12}S_2)_2](ClO_4)_2$: C, 26.01; H, 4.37; S, 23.14. Found: C, 26.03; H, 4.26; S, 23.17.

Bis(1,5-dithiacyclooctane)nickel(II) Chloride.—Anhydrous nickel(II) chloride (1.0 g) was dissolved in a small amount of absolute ethanol (10 ml), and the resulting yellow solution was filtered. dtco (2.5 ml) was added to the solution and the mixture was swirled until a large amount of yellow-brown precipitate formed. The mixture was allowed to stand (for 1 hr or more) until all of the solid had changed to olive or yellow-green. The solid was collected on a filter, washed twice with absolute ethanol, washed once with anhydrous ether, and dried on the vacuum line. The compound changed to the yellow-brown complex at 127°. *Anal.* Calcd for $Ni(C_6H_{12}S_2)_2Cl_2$: C, 33.82; H, 5.68. Found: C, 33.74; H, 5.56.

The yellow-brown complex which formed initially was isolated in the following way. Ethanolic solutions of nickel chloride and dtco were combined and the yellow-brown crystals which formed over a 1-hr period were filtered, washed twice with small amounts of cold absolute ethanol, and dried on the vacuum line. Any green crystals forming within 1 hr were removed, and the mixture was filtered immediately. The crystals turned green on standing over periods ranging from several days to months. The complex turned yellow-orange at 163–170°; dec pt 230°. *Anal.* Found: C, 28.57; H, 5.26; S, 25.08.

Tris(1,4-dithiacycloheptane)dinickel(II) Tetrabromide.—Anhydrous nickel(II) bromide (0.40 g) was shaken with 200 ml of acetone for 24 hr on a mechanical wrist-action shaker. The mixture was centrifuged and the turquoise supernatant liquid was decanted. dtch (0.6 g) was dissolved in a small amount of acetone and was added to this solution. The resulting olive-green solution was reduced to one-fifth of its original volume by blowing nitrogen over the surface of the solution. The dark olive crystals formed were filtered, washed rapidly with a small amount of cold acetone, and dried on the vacuum line; dec pt 250°. *Anal.* Calcd for $Ni_2(C_5H_{10}S_2)_3Br_4$: C, 21.46; H, 3.60. Found: C, 21.37; H, 3.60.

Tris(1,5-dithiacyclooctane)dinickel(II) Tetrabromide.—This compound was prepared by the method given above using dtco (0.5 ml) as the ligand. The solution was reduced to one-third of its original volume. The gold precipitate was filtered and washed with acetone, then with an acetone–ether mixture, and finally with anhydrous ether; dec pt 250°. *Anal.* Calcd for $Ni_2(C_6H_{12}S_2)_3Br_4$: C, 24.52; H, 4.11; S, 21.81. Found: C, 24.66; H, 4.10; S, 22.02.

Bis(1,4-dithiacycloheptane)nickel(II) Iodide.—Anhydrous nickel(II) iodide (0.40 g) was added to 180 ml of acetone and the mixture was swirled for several minutes. The mixture was centrifuged and the deep red-brown supernatant liquid was decanted. dtch (0.50 g) was dissolved in this solution. The solution was evaporated to one-third of its original volume using a stream of nitrogen. The dark brown crystals were collected in a filter, washed twice with small amounts of an acetone–ether solution, and washed with anhydrous ether; mp 186°. *Anal.* Calcd for $Ni(C_5H_{10}S_2)_2I_2$: C, 20.67; H, 3.47; S, 22.07. Found: C, 21.37; H, 3.43; S, 21.93.

Bis(1,5-dithiacyclooctane)nickel(II) Iodide.—This compound (black crystals) was prepared by the method given above using dtco (0.70 ml). Water must be rigorously excluded or a dark green complex containing one-half to one molecule of water per nickel atom is formed; mp 182°. *Anal.* Calcd for $Ni(C_6H_{12}S_2)_2I_2$: C, 23.67; H, 3.97; S, 21.06. Found: C, 23.72; H, 3.95; S, 21.38.

1,5-Dithiacyclooctanenickel(II) Iodide.—Bis(1,5-dithiacyclooctane)nickel(II) iodide or the dark green complex was heated at 110° under vacuum for 10 hr to form the brown solid. dtco collected on the cooler parts of the apparatus; dec pt 178–250°. *Anal.* Calcd for $Ni(C_6H_{12}S_2)I_2$: C, 15.64; H, 2.63. Found: C, 15.74; H, 2.66.

Electronic Absorption Spectra.—Near-infrared, visible, and ultraviolet spectra were measured on a Cary 14 recording spectrophotometer. Solution spectra were run in 1-cm and 1-mm matched quartz cells. For solid-state spectra, Nujol mulls of the ligands and complexes were soaked into Whatman No. 1 filter paper; Nujol-soaked filter paper was used as the reference. The Nujol-soaked filter paper was placed between sodium chloride plates to avoid decomposition of some of the nickel halide complexes in the near-infrared region.

Infrared Absorption Spectra.—Infrared spectra were measured on a Beckman IR-12 infrared spectrophotometer. Hexachlorobutadiene mulls on potassium bromide or sodium chloride plates were used in the 1250–4000-cm^{-1} region, Nujol mulls on potassium bromide plates were used in the 400–1700-cm^{-1} region, and Nujol mulls in polyethylene envelopes were used in the 200–650-cm^{-1} region. The positions and intensities of all the bands are listed in the Ph.D. thesis of N. L. H.

Magnetic Susceptibility Measurements.—Magnetic susceptibilities were measured using the Gouy method at room temperature as described before[2] and are listed in Table I.

TABLE I

MAGNETIC PROPERTIES OF SOLID MEDIUM-RING DITHIOETHER COMPLEXES OF NICKEL(II) AT ROOM TEMPERATURE

Compound	Temp, °C	Dia cor × 10^{-6}	$10^{-6}\chi_m^{cor}$	μ_{eff}, BM
$[Ni(dtch)_2](BF_4)_2$	24.2	269	88	0.46[a]
$[Ni(dtch)_2](ClO_4)_2$	24.3	259	107	0.50[a]
$[Ni(dtco)_2](BF_4)_2$	24.6	292	14	0.18[a]
$[Ni(dtco)_2](ClO_4)_2$	24.9	282	100	0.49[a]
$Ni(dtco)_2Cl_2$	25.1	262	3819	3.04
Yellow-brown complex	23.8	200	3750	3.0
$Ni_2(dtch)_3Br_4$[b]	24.7	216	4301	3.21
$Ni_2(dtco)_3Br_4$[b]	24.0	234	4687	3.35
$Ni(dtch)_2I_2$	25.0	293	4323	3.23
$Ni(dtco)_2I_2$	25.0	312	163	0.62[a]
$Ni(dtco)_2(H_2O)_nI_2$	25.2	323	253	0.78[a]
$Ni(dtco)I_2$	24.0	215	3115	2.73

[a] The effective magnetic moments of these complexes are much lower than the usual value near 3.2 BM for fully paramagnetic nickel(II) complexes, and they are therefore considered diamagnetic complexes. [b] The magnetic susceptibilities are calculated for one nickel atom.

X-Ray Powder Diffraction Measurements.—X-Ray powder diffraction spectra were measured on a General Electric XRD-6 X-ray diffractometer with a recorder. The region scanned was $2\theta = 60°$ or 70° to 5°. A copper target was used with a nickel filter and a xenon detector. The finely ground sample was spread on a glass slide and was held in place by glue deposited from a xylene–glue solution. The slide was placed in a holder at the center of the goniometer. The position and intensities of the peaks are tabulated in the thesis of N. L. H.

Results and Discussion

The nickel(II) complexes prepared in this study are quite stable in the solid state in the absence of moisture. Only the yellow-brown complex prepared from $NiCl_2$

---

[12] Analyses were performed by Galbraith Microanalytical Laboratories, Knoxville, Tenn., and by Berkeley Microanalytical Laboratory, University of California, Berkeley, Calif.

TABLE II

ELECTRONIC ABSORPTION SPECTRA OF SQUARE-PLANAR NICKEL(II) COMPLEXES OF MEDIUM-RING DITHIOETHERS

Complex	Color	λ^{-1}(nitromethane), cm^{-1}	ϵ, M^{-1} cm^{-1}	λ^{-1}(solid), cm^{-1}	Transition
$Ni(dtch)_2(BF_4)_2$	Orange	8,800			
		20,700		21,500 m	$^1A_g \rightarrow {}^1B_{1g}$
				29,000 s	$^1A_g \rightarrow {}^1B_{2u}$, $^1B_{3u}$
				34,300 m	
				37,000 sh	
$Ni(dtch)_2(ClO_4)_2$	Orange	9,500	14		
		20,650	420	21,350 m	$^1A_g \rightarrow {}^1B_{1g}$
				29,300 s	$^1A_g \rightarrow {}^1B_{2u}$, $^1B_{3u}$
				33,800 m	
				36,500 sh	
$Ni(dtco)_2(BF_4)_2$	Brick red	20,300	840	20,500 m	$^1A_g \rightarrow {}^1B_{1g}$
		26,000	11,600	25,500 s	$^1A_g \rightarrow {}^1B_{2u}$, $^1B_{3u}$
				31,350 sh	
				33,800 s	
				36,700 sh	
$Ni(dtco)_2(ClO_4)_2$	Brick red	20,200	915	20,500 m	$^1A_g \rightarrow {}^1B_{1g}$
		25,800	13,600	25,200 s	$^1A_g \rightarrow {}^1B_{2u}$, $^1B_{3u}$
				31,000 sh	
				33,900 s	
				36,600 sh	

and dtco is unstable and changes to green $Ni(dtco)_2Cl_2$ on standing. In general, the complexes decompose in hydroxylic solvents and are insoluble in nonpolar solvents, although $Ni(dtco)_2Cl_2$ is stable in alcohol. Most of the complexes dissociate reversibly in nitromethane, acetone, and dichloromethane, and these solvents have been used in spectral analysis. However, conductance measurements of halide complexes in acetone show that most of these species are unionized even in the presence of excess ligand, indicating that dissociation proceeds by loss of dithioether ligand rather than by loss of halide. Only the system NiI_2 with excess dtco gives appreciable conductance which varies with ligand concentration.

Perchlorate and Tetrafluoroborate Complexes.—Medium-ring dithioether complexes of nickel(II) are planar when perchlorate or tetrafluoroborate is the anion. Infrared analyses of the BF_4^- and ClO_4^- vibrational frequencies indicate no splitting of the antisymmetric bend frequencies (523 cm^{-1} for BF_4^- and 625 cm^{-1} for ClO_4^-), a weak splitting of the antisymmetric stretch absorption (near 1100 cm^{-1}) in the BF_4^- complexes, and weak symmetric stretch absorptions for $Ni(dtch)_2(BF_4)_2$ near 768 cm^{-1} and for $Ni(dtco)_2(ClO_4)_2$ near 930 cm^{-1}. By comparison with known ClO_4^- vibrational frequencies[13] it appears that the anions are either very weakly coordinated or slightly distorted from pure T_d symmetry by lattice forces. The diamagnetism of the complexes also supports a planar structure.

The electronic absorption spectra of the complexes in the visible region (Figure 1 and Table II) are also typical of planar nickel(II). The $^1Ag \rightarrow {}^1B_{1g}$ transitions (D_{2h} symmetry) at 20,000–21,500 cm^{-1} correspond to the $^1A_{1g} \rightarrow {}^1A_{2g}$ transitions (D_{4h} symmetry) seen in the spectra of other nickel(II) complexes.[3,14,15] The values for the extinction coefficients of this transition in nitromethane are extremely high (ϵ 420–915) compared with the values given for the planar macrocyclic tetrathioether complexes of nickel(II) reported by Rosen and Busch (ϵ 260–270).[7] The high intensity seems to result from the proximity of the band to an intense band around 25,000–30,000 cm^{-1} (ϵ 12,000 for the dtco complexes). The intense band is strongly ligand dependent and can be attributed to a parity-allowed charge-transfer transition. The maximum in the dtco complexes is near 26,000 cm^{-1}; in the dtch complexes it is near 29,000 cm^{-1}, whereas in solid $Ni(TTP)(ClO_4)_2$, the band appears at 31,250 cm^{-1}.[7] This band does not appear in the analogous amine complexes, $Ni(daco)_2(ClO_4)_2$, $Ni(dach)_2(ClO_4)_2$, and $Ni(cyclam)(ClO_4)_2$,[16] which contain no lone pair on the donor atom, suggesting that the band in the dtco and dtch com-

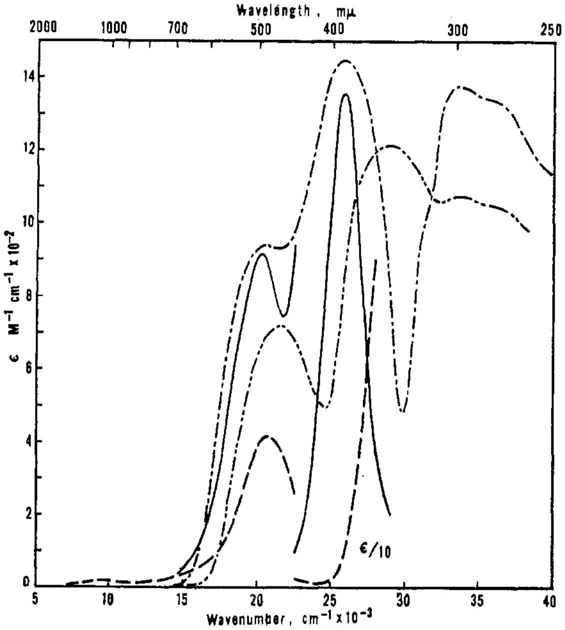


Figure 1.—Electronic absorption spectra of square-planar nickel(II) complexes of medium-ring dithioethers: —·—·—, $Ni(dtco)_2(ClO_4)_2$, solid (arbitrary absorption scale); ——, $Ni(dtco)_2(ClO_4)_2$, nitromethane solution; —·····—, $Ni(dtch)_2(ClO_4)_2$, solid (arbitrary absorption scale); - - - - -, $Ni(dtch)_2(ClO_4)_2$, nitromethane solution.

---

[13] B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 3091 (1961).

[14] L. Sacconi, *Transition Metal Chem.*, **4**, 199 (1968).

[15] The state symbols for the local symmetry of these complexes are based on D_{2h} symmetry rather than D_{4h} symmetry to include the lone pairs on sulfur which lie in the equatorial plane (Figure 2).

[16] B. Bosnich, M. L. Tobe, and G. A. Webb, *Inorg. Chem.*, **4**, 1109 (1965).

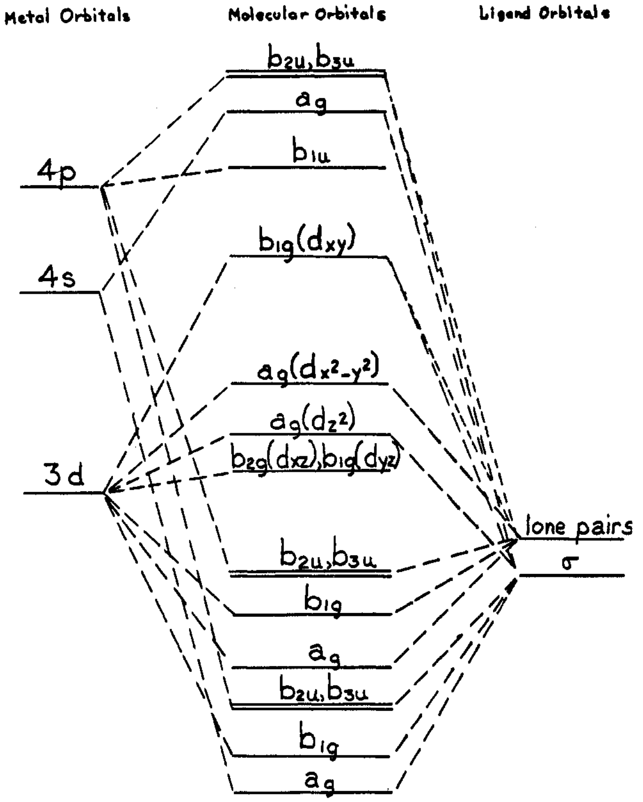
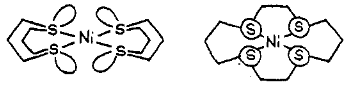


Figure 2.—Molecular orbital energy scheme for square-planar nickel(II) complexes with in-plane electron lone pairs.

plexes may be due to the $^1A_g \rightarrow {}^1B_{2u}$, $^1B_{3u}$ transition (Figure 2).

Although we cannot definitely account for the differences between the positions and intensity of the charge-transfer band in dtco, dtch, and TTP, it is worthwhile pointing out that the sp^3-hybridized lone pairs on sulfur in the dtco complexes are constrained to lie in the plane of the nickel atom and the four sulfur atoms by the conformations of the chelate rings, whereas in the TTP complexes the lone pairs are nearly perpendicular to this plane. Thus, dtco and TPP complexes can be viewed as *electronic isomers* if only the local symmetry



around nickel is considered, and differences in the spectra may be attributed to the different spatial distribution of electrons. Transitions at energies higher than 31,000 cm^{-1} probably can be attributed to other charge-transfer bands, but the specific orbitals involved have not been determined.

Solution spectra of the planar dtch complexes were only obtained in nitromethane, whereas the spectra of the dtco complex complexes can be observed in both nitromethane and acetone. The low stability constants of the complexes are indicated by the changes in intensities of the absorptions upon dilution: the intensities fall off more rapidly than predicted by Beer's law. Nitromethane solutions undergo marked color changes with temperature: the dtch complexes change from red-orange at 100° to pale blue at −28°; the dtco complexes change from deep red-orange at 100° to light yellow at −28°. In the dtch complexes the $^1A_{1g} \rightarrow {}^1B_{1g}$ transition at 20,500 cm^{-1} decreases in intensity as the temperature is lowered (slightly more than double the absorbance at room temperature than at 8°), whereas the peak near 9000 cm^{-1} increases. It is possible that this thermochromic behavior results from an equilibrium between the planar complex and a new species which is formed in solution which absorbs near 9000 cm^{-1}. Although the dtco complexes show a decrease in the band near 20,000 cm^{-1}, no band develops in the near-infrared region. At present we are unable to account for the differences in behavior between the dtco and dtch complexes.

Chloride Complexes.—Nickel(II) chloride forms stable complexes with dtco but not with dtch. The structure of $Ni(dtco)_2Cl_2$ was most interesting to us since the complex was found to be paramagnetic. Earlier work[2] showed that when two eight-membered rings function as chelating agents, the axial positions of the central metal ion are highly shielded and octahedral coordination is unlikely. Hence, the paramagnetism was most unexpected. In addition, the electronic absorption spectra of solid $Ni(dtco)_2Cl_2$ and of its acetone solutions containing excess dtco were inconsistent with a planar structure but displayed a pattern typical of octahedral nickel(II) (Figure 3; Table III). To resolve these inconsistencies, the crystal structure of the complex was determined. The structure consists of a two-dimensional network of nickel atoms and dtco ligands with the dtco ligands bridging the nickel ions and the chloride ions coordinated to nickel and perpendicular to the NiS_4 plane (I).[17] The reason that bridging ligands rather than

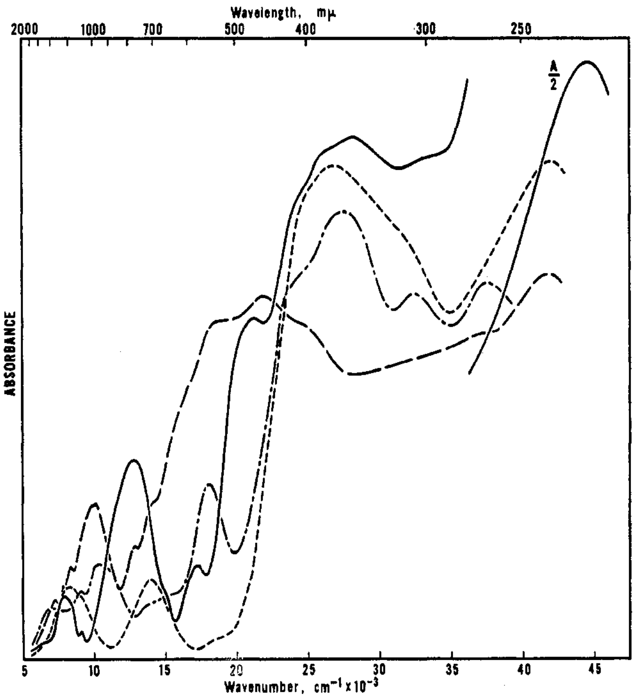


Figure 3.—Electronic absorption spectra of solid nickel(II) halide complexes of medium-ring dithioethers: -----, $Ni(dtco)_2Cl_2$; – – – – –, $Ni(dtco)I_2$; —— $Ni_2(dtch)_3Br_4$; –·–·– $Ni_2(dtco)_3Br_4$.

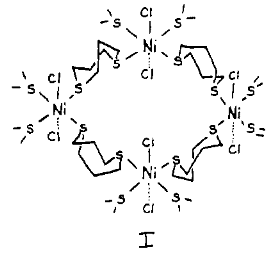
---

[17] N. L. Hill and H. Hope, to be submitted for publication.

TABLE III
ELECTRONIC ABSORPTION SPECTRA OF NICKEL(II) HALIDE COMPLEXES OF MEDIUM-RING DITHIOETHERS

Complex	Color	λ^{-1}(soln), cm^{-1}	ϵ, M^{-1} cm^{-1}	λ^{-1}(solid), cm^{-1}	Transition
Ni(dtco)$_2$Cl$_2$	Yellow-green	7,850^{a,b}	28	8,260 m	${}^3B_{1g} \rightarrow {}^3E_g{}^a$
				9,050 sh	${}^3B_{1g} \rightarrow {}^3B_{2g}$
		13,200	34	14,050 m	${}^3B_{1g} \rightarrow {}^3E_g{}^b$
		18,900 sh		18,750 sh	${}^3B_{1g} \rightarrow {}^3A_{2g}{}^b$
		21,400 sh		21,800 sh	${}^3B_{1g} \rightarrow {}^3E_g{}^c$
		25,700 sh		26,800 s	
		30,000	3800	32,000 sh	
				41,800 s	
Yellow-brown complex	Yellow-brown			6,780 sh	${}^3B_{1g} \rightarrow {}^3B_{2g}$
				7,900 m	${}^3B_{1g} \rightarrow {}^3E_g{}^a$
				12,900 m	${}^3B_{1g} \rightarrow {}^3E_g{}^b$
				16,870 sh	
				18,050 sh	${}^3B_{1g} \rightarrow {}^3E_g{}^c$
				25,300 s	
				28,800 s	
Ni$_2$(dtch)$_3$Br$_4$	Dark olive green			7,930 w	${}^3E' \rightarrow {}^3E''(F)$
				12,800 m	${}^3E' \rightarrow {}^3A_1''$, ${}^3A_2'$, ${}^3A_2''(F)$
				17,000 w	${}^3E' \rightarrow {}^1E''(D)$
				21,000 m	${}^3E' \rightarrow {}^3E''(P)$
				27,600 s	
				44,700 vs	
Ni$_2$(dtco)$_3$Br$_4$	Gold	7,460^{a,c}	33	7,400 w	
		9,150	54	9,000 w	
		10,200	81	10,300 mw	
		10,770 sh			
		18,300	140	18,100 m	
		26,700	3450	27,400 s	
				32,400 m	
				37,400 ms	
Ni(dtch)$_2$I$_2$	Dark brown	7,350^{b,d}	31	7,640 w	${}^3B_{1g} \rightarrow {}^3E_g{}^a$
				8,450 w	${}^3B_{1g} \rightarrow {}^3B_{2g}$
		13,530	151	13,340 m	${}^3B_{1g} \rightarrow {}^3E_g{}^b$
		21,100	2560	20,750 s	
		25,950 sh		22,850 s	
		28,900 sh			
		31,400	4650	29,100 vs	
		34,400 sh		34,600 sh	
Ni(dtco)I$_2$	Brown	7,350^d	42	7,250 w	
		8,450 sh		8,330 w	
		9,950	197	10,150 m	${}^3T_1(F) \rightarrow {}^3A_2(F)$
		13,100	103	12,900 w	${}^3T_1(F) \rightarrow {}^1T_2(D)$
				14,000 sh	${}^3T_1(F) \rightarrow {}^1E(D)$
		16,100 sh		15,900 sh	${}^3T_1(F) \rightarrow {}^3T_1(P)$
		19,750	2760	18,200 sh	
		23,000	3520	21,800 s	
		26,840	3310	24,800 sh	
		37,300	1250	36,800 sh	
Ni(dtco)$_2$I$_2$	Black			~13,500 sh	
				17,800 s	
				22,000 vs	
				25,300 sh	
				30,600 sh	
				33,200 s	
				37,600 s	
Ni(dtco)$_2$(H$_2$O)$_n$I$_2$	Dark green			13,500 s	
				~21,700 sh	
				25,000 s	${}^1A_g \rightarrow {}^1B_{2u}$, ${}^1B_{3u}$
				29,900 sh	
				32,800 sh	
				35,500 s	

[a] Acetone solution. [b] The solution contains excess ligand. [c] The empirical formula in acetone solution is Ni(dtco)Br$_2$. [d] Dichloromethane solution.



I

chelated ligands are found is probably due to the rather strong donor ability of chloride ion compared to the dithioether, since in the presence of weaker coordinating ions (ClO_4^- and BF_4^-) the ligand does behave as a chelating agent. Packing forces may also be responsible for the polymeric nature of the complex.

On dissolution in acetone, the polymeric solid dissociates, but on addition of excess dtco, a spectrum is observed which is almost identical with that of the

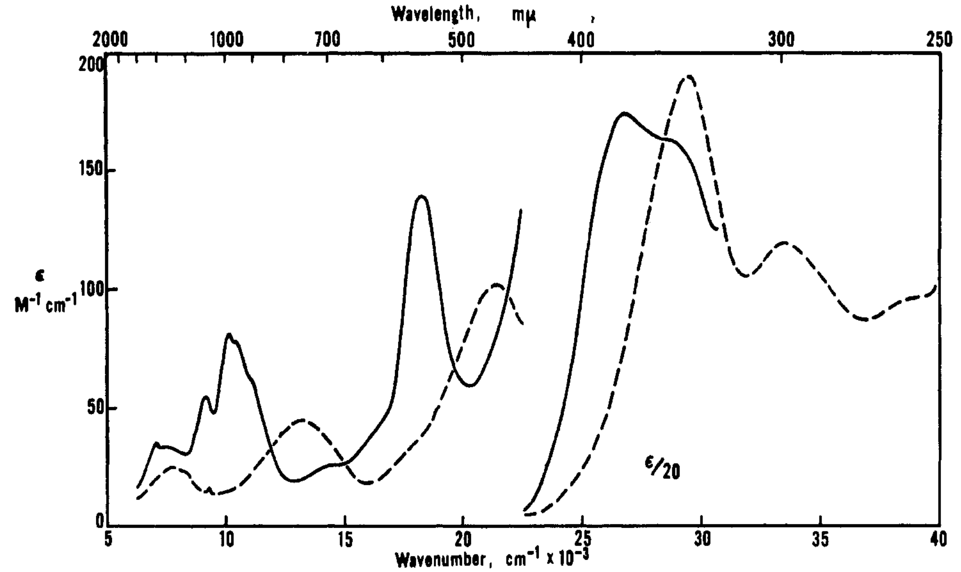
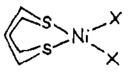
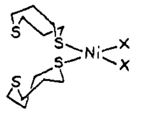


Figure 4.—Electronic absorption spectra of nickel(II) bromide complexes of medium-ring dithioethers in solution: ——, $NiBr_2$ + dtco, distorted tetrahedral complex, in acetone; ----, $NiBr_2$ + dtch, octahedral complex, in dichloromethane.

original solid (Table III). The spectrum of the solution before excess dtco is added resembles that of tetrahedral nickel(II) and suggests that the species of solution has either structure II or III (X = Cl). Structure III is considered less likely based on comparative studies of complexes containing bromide and iodide where a similar spectrum was observed when the ligand to metal ratio was only 1:1.

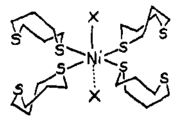


II



III

In the presence of excess dtco, it is suggested that the ligand functions simply as a monodentate ligand to give a species represented by IV (X = Cl). The spectrum of the yellow-brown complex of variable composition, which is formed initially in the preparation of $Ni(dtco)_2Cl_2$ in ethanol, corresponds to an octahedral species, but a satisfactory structure has not yet been formulated for it.

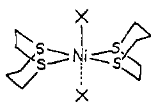


IV

The spectra and assignments for the electronic absorptions of $Ni(dtco)_2Cl_2$ and of its acetone solution are given in Table III. The extinction coefficients for this complex are also much higher than many complexes of nickel(II) and may be attributed to the tailing of a strong band near 30,000 cm^{-1} into the visible region. This band may be related to the band observed in the same region in the perchlorate salts, but it should be noted that the intensity of this band is only about one-third of that observed in the planar complexes.

Bromide Complexes.—Although dtch complexes containing chloride were not isolated, both dtch and dtco form stable complexes in the presence of bromide; however, the stoichiometry of the complexes $Ni_2L_3Br_4$ is unusual. The magnetic moments of the complexes are consistent with either distorted octahedral, tetrahedral, or pyramidal species. Thus, the electronic absorption spectra were used extensively to elucidate the structures of the solids and their solutions (see Table III for spectral bands and their assignments).

The pattern of absorption of solid $Ni_2(dtco)_3Br_4$ and of acetone solutions containing $NiBr_2$ and dtco strongly resembles the spectra of some distorted tetrahedral nickel(II) complexes (Figures 3 and 4). A similar spectrum was also observed in solutions of $NiBr_2$ containing low concentrations of dtch, but the tetrahedral spectrum is partially obscured by peaks which correspond to nickel bromide and to an octahedral species. However, in the presence of a 5:1 dtch:Ni^{2+} ratio only the spectrum of an octahedral species was observed (Figure 4). It is interesting to note that the amount of ligand required to achieve an octahedral spectrum with dtch and $NiBr_2$ *was much less* than that required with dtco + $NiCl_2$. On this basis we have concluded that the octahedral species present with $NiBr_2$ + dtch may be represented as V (X = Br) rather than IV (X = Br).

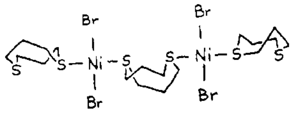


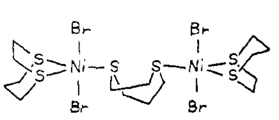
V

Two chelated dtch ligands in the trans configuration about the metal ion do not block the axial positions as effectively as dtco and octahedral complexes can be obtained.[2]

A continuous variation study of acetone solutions of dtco and $NiBr_2$ showed that the species present in solution contains only 1 mole of dtco per mole of $NiBr_2$. On this basis we have concluded that the species present in solution is tetrahedral with a chelated ligand similar to II (X = Br). Even when a large excess of dtco is added, the spectrum of the solution shows that the predominant species is tetrahedral.

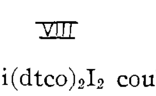
The possible structures of the solid $Ni_2L_3Br_4$ species deserve some comment. Since the solid golden colored dtco complex exhibits a tetrahedral spectrum similar to that found in acetone solution, a possible representation is VI with dtco functioning both as a monodentate ligand and as a bridging group. Solid $Ni_2(dtch)_3Br_4$ is different from the dtco complex and the pattern of its absorption spectrum (Table III) is consistent with a trigonal-bipyramidal structure which can most simply be represented as VII. However, a polymeric structure with dtch functioning as a bridging ligand cannot be ruled out.

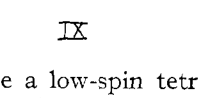

VI


VII

Iodide Complexes.—Three different solid complexes containing iodide have been isolated: $Ni(dtch)_2I_2$, $Ni(dtco)_2I_2$, and $Ni(dtco)I_2$ (Table III). The bis-dtco complex is diamagnetic whereas the bis-dtch complex is paramagnetic. The mono-dtco complex is prepared either by heating the solid bis complex under vacuum or by dissolution in dichloromethane; $Ni(dtch)_2I_2$ remains intact when heated under vacuum. The spectral properties of $Ni(dtco)I_2$ suggest a tetrahedral structure with very little distortion (Figure 3). However, the magnetic moment of $Ni(dtco)I_2$ is quite low (2.7 BM) when compared with other tetrahedral complexes suggesting that under the vigorous synthetic conditions some residual diamagnetic species are still present in the solid.

Magnetic susceptibility data indicate that $Ni(dtco)_2I_2$ is planar as expected for a chelated dtco complex; however, the strong iodide charge-transfer band which gives the complex its black color indicates that the iodide is not a free ion and must be in close proximity to the metal ion. That the complex decomposes thermally with loss of ligand also suggests a close association between iodide and the metal complex. Thus, possible structures for $Ni(dtco)_2I_2$ are VIII or IX. Alternatively, $Ni(dtco)_2I_2$ could have a low-spin tetragonally distorted octahedral structure similar to $Ni(dtco)_2Cl_2$ (I) or a square-pyramidal structure similar to $Ni(TTP)I_2$.[7] However, a square-pyramidal structure is deemed unlikely on the basis of the expected screening effect of the two chelated dtco ligands.[2] From spectral evidence alone it is difficult to predict the structure of this complex. On addition of excess ligand in solution, an octahedral species is formed which may have structure IV. Because of steric interactions this species may lose iodide ion easily thereby accounting for the increase in electrical conductivity as the ligand concentration is increased.


VIII


IX

The $Ni(dtch)_2I_2$ has a tetragonally distorted octahedral structure since it is isomorphous with $Cu(dtch)_2(ClO_4)_2$ where weak ClO_4^- coordination has been observed.[18] An octahedral structure similar to V (X = I) is most attractive since it would account for the thermal stability of the dtch complex relative to that of the dtco complex.

The electronic spectra of the iodide complexes in acetone and dichloromethane indicate a mixture of species depending on ligand concentration. The predominant species seen when solid $Ni(dtco)_2I_2$ or $Ni(dtco)I_2$ is dissolved is a tetrahedral species (probably II; X = I), and if a slight excess of dtco is added, the absorptions due to the tetrahedral species do not increase, suggesting that the tetrahedral complex is rather stable in solution. However, as additional ligand is added, the spectrum becomes more complicated; with sufficient ligand the spectrum corresponds to that of an octahedral complex. When more ligand is added at this point, the spectrum shows that additional species are present.

When $Ni(dtch)_2I_2$ is dissolved, a tetrahedral spectrum is initially observed (similar to II; X = I), but as excess dtch is added, the pattern of absorption simply changes to that of an octahedral species (similar to V; X = I) without the development of any additional peaks (Figure 5).

Spectral Analysis.—The electronic spectra of tetragonally distorted high-spin octahedral nickel(II) complexes have been well studied and discussed. The electronic spectra in the d–d transition region consist of two fairly weak absorptions (which may be very close together) in the near-infrared region ($^3B_{1g} \rightarrow {}^3E_g{}^b$ and $^3B_{1g} \rightarrow {}^3B_{2g}$), a triangular or double peak of about the same intensity at 13,500–20,000 cm^{-1} ($^3B_{1g} \rightarrow {}^3E_g{}^b$ and $^3B_{1g} \rightarrow {}^3A_{1g}{}^a$), and a slightly stronger peak at 21,000–30,000 cm^{-1} ($^3B_{1g} \rightarrow {}^3E_g{}^c$). The peaks occur in the lower part of the energy ranges for octahedral complexes containing thioether and halogen donor atoms, since thioethers and halides are weak-field ligands.

The ligand field strength parameters Dq_{xy} (equatorial) and Dq_z (axial) have been calculated from the electronic spectra of tetragonally distorted high-spin octahedral nickel(II) complexes.[19] Using the wave numbers given in Table III for the $^3B_{1g} \rightarrow {}^3B_{2g}$ (νB_{2g}) and $^3B_{2g} \rightarrow {}^3E_g{}^a$ (νE_g) transitions and assuming that halide ions are axial, except in the yellow-brown complex, which is assumed to contain bridging equatorial chlorines, the values in Table IV are calculated for Dq_{xy} and Dq_z.

Rosen and Busch have calculated a Dq_{xy} value of 1070 cm^{-1} for the macrocyclic tetrathioether TTP in the complexes $Ni(TTP)(SCN)_2$, $Ni(TTP)Cl_2$, and $Ni(TTP)Br_2$.[7] Thus the following spectrochemical series for octahedral nickel(II) complexes can be tabulated: TTP, dth > dtco > dtch > chloride (nonbridging) > bromide > iodide, chloride (bridging). The order dth > dtco > dtch can be understood in terms of the ability of the

---

(18) N. L. Hill and W. K. Musker, to be submitted for publication.

(19) A. B. P. Lever, *Coord. Chem. Rev.*, **3**, 119 (1968).

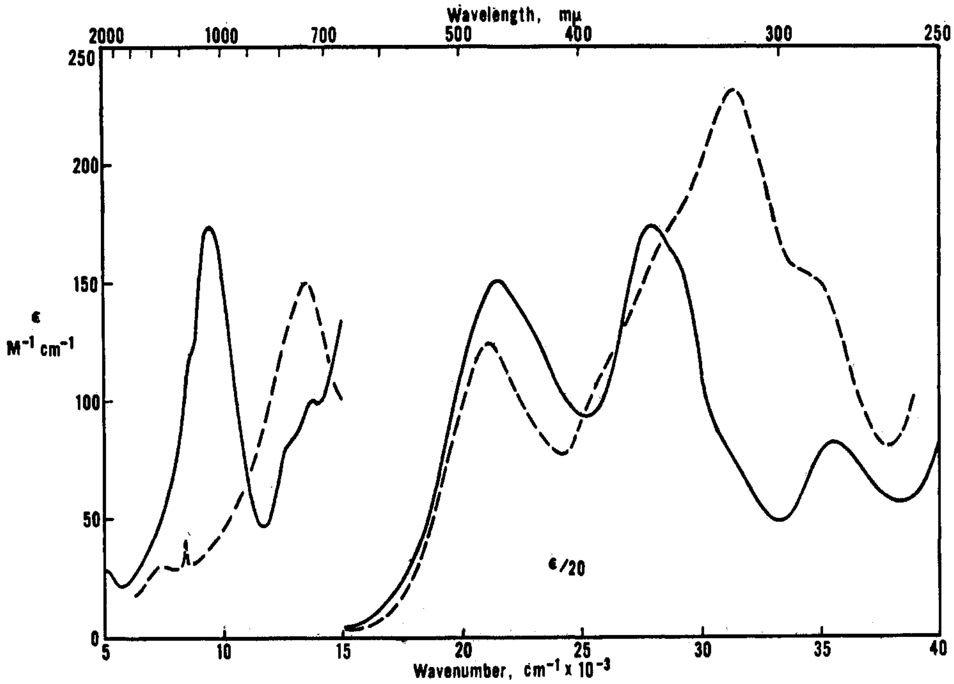


Figure 5.—Electronic absorption spectra of nickel (II) iodide complexes of 1,4-dithiacycloheptane in dichloromethane: ———, tetrahedral complex; ----, octahedral complex.

TABLE IV

Complex	Dq_{xy}, cm^{-1}	Donor atom	Dq_z, cm^{-1}	Donor atom
$Ni(dtch)_2Cl_2$[a] (Nujol mull)	1063	S	737	Cl
$Ni(dtco)_2Cl_2$ (Nujol mull)	905	S	747	Cl
Yellow-brown complex (Nujol mull)	678	Cl	902	S
$Ni(dtch)_2Br_2$[b]				
Acetone soln	838	S	722	Br
Dichloromethane soln	837	S	713	Br
$Ni(dtch)_2I_2$ (Nujol mull)	845	S	683	I

[a] Wave numbers obtained from a Nujol mull spectrum of solid $Ni(dth)_2Cl_2$: ${}^3B_{1g} \rightarrow {}^3E_g{}^a$, 900 cm^{-1}; ${}^3B_{1g} \rightarrow {}^3B_{2g}$, 1063 cm^{-1}.
[b] The electronic absorption spectra of octahedral nickel(II) bromide complexes with dtch in solution are reported in the Ph.D. thesis of N. L. H.

ligand to place the sulfur lone pairs into an optimum position for bonding to the metal atom: the more flexible ligand should achieve better bonding and therefore have a higher ligand field strength. Molecular models show that almost no strain is required to achieve the optimum equatorial bonding of TTP. Medium-ring dithioethers are below all amines but are above all halides except fluoride in ligand field strength.

The electronic spectra of the nickel iodide complexes in solution and solid $Ni(dtco)I_2$ are typical of tetrahedral nickel(II) complexes with ligands of fairly low ligand field strengths. The following approximate energies above the ground state for d–d transitions were estimated using a value of Dq = 500 cm^{-1}:[14] ${}^3T_2(F)$, 5000 cm^{-1}; ${}^3A_2(F)$, 10,000 cm^{-1}; ${}^1T_2(D)$, 12,000 cm^{-1}; ${}^1E(D)$, 12,500 cm^{-1}; ${}^3T_1(P)$, 16,500 cm^{-1}. The absorptions observed at energies lower than 1700 cm^{-1} were assigned using these values (Table III). The ${}^3T_1(F) \rightarrow {}^3T_2(F)$ transition occurs at energies lower than the energy range scanned and was not observed.

The other tetrahedral species exhibit spectra of distorted tetrahedral complexes. The absorptions near 10,500 and 18,000 cm^{-1} (see Figures 3 and 4) would be the ${}^3T_1(F) \rightarrow {}^3A_2(F)$ and ${}^3T_1(F) \rightarrow {}^3T_1(P)$ transitions. In distorted tetrahedral nickel(II) complexes, the triplet–singlet transitions decrease in energy and increase in intensity, and one of the components of the now nondegenerate ${}^3T_1(F) \rightarrow {}^3T_2(F)$ transition moves to higher energy.[20,21] The weak broad peak near 7500 cm^{-1} would be one of the ${}^3T_1(F) \rightarrow {}^3T_2(F)$ transitions. The sharp peak and shoulder near 10,500 cm^{-1} could be due to two triplet → singlet transitions superimposed on the ${}^3T_1(F) \rightarrow {}^3A_2(F)$ transition. The peak near 9000 cm^{-1} is too strong and broad to be a ligand vibrational overtone and too narrow for a triplet → triplet transition. The band is probably another triplet → singlet transition resulting from a lowering of symmetry from T_d and causing the two triplet → singlet bands to be split into three or more absorptions.

Acknowledgment.—We thank the National Science Foundation (GP-8518) for support of this research.

(20) L. Sacconi, I. Bertini, and F. Mani, *Inorg. Chem.*, **6**, 262 (1967).
(21) L. Sacconi and I. Bertini, *ibid.*, **7**, 1178 (1968).