TABLE IV
ULTRAVIOLET AND VISIBLE SPECTRA OF NICKEL KETAZINES[a]

Compd	$\nu_1{}^b$	$10^{-3}\epsilon_M$	$\nu_2{}^b$	$10^{-3}\epsilon_M$	$\nu_3{}^b$	$10^{-3}\epsilon_M$	$\nu_4{}^b$	$10^{-3}\epsilon_M$
NiMMK	495	7.67	460 sh	8.80	390	17.9	344	15.7
NiMEK	498	7.85	460 sh	9.06	390	17.3	342	15.3
NiEEK	498	7.84	460 sh	8.88	390	17.3	342	15.2
NiMPrK	498	7.51	460 sh	8.64	390	16.7	342	14.8
NiMBuK	498	7.48	460 sh	8.75	390	16.8	342	14.8
NiMPhK	495	7.78	455 sh	9.14	390	16.7	336	14.8

[a] All spectra obtained in benzene. [b] In nm.

The early workers[2] in this area also reported the formation of a dark red solid for which varying analyses were obtained. We have characterized this compound as $Ni_2(L\text{-}H)_2(L\text{-}2H)$, where L-H and L-2H represent benzil monohydrazone minus one and two hydrogen atoms, respectively. As the condensation reactions proceed, this dark red-brown compound is slowly removed and orange-red crystals of the nickel ketazines are obtained. It is possible that the reaction proceeds *via* an equilibrium concentration of benzil monohydrazone, the nickel(II) ions coordinating the products or intermediates that are formed during the reaction.

Benzilacetone azine may be an intermediate in the formation of NiMMK since refluxing nickel acetate with this compound in the presence of benzil monohydrazone does result in the formation of a small amount of the condensation product. In the absence of the excess benzil monohydrazone, however, no reaction takes place.

Acknowledgment.—The authors gratefully acknowledge the assistance of Dr. James C. Tou of the Dow Chemical Co., Midland, Mich., for obtaining the high-resolution mass spectra and for helpful discussions.

Thiocarbamate Complexes. I. Preparation and Properties of Nickel(II) Derivatives[1]

BY B. JACK McCORMICK* AND BENJAMIN P. STORMER

The syntheses of six N,N-dialkylthiocarbamate complexes of nickel(II) are reported. These new chelates have the empirical formula $Ni(OSCNR_2)_2$, where R is CH_3, C_2H_5, $n\text{-}C_3H_7$, $n\text{-}C_4H_9$, $-(CH_2)_4-$, and $-(CH_2)_5-$. Molecular weight measurements suggest that the complexes are low polymers, and electronic spectral measurements coupled with the observed paramagnetic moments of *ca.* 3.25 BM indicate that the nickel(II) ions are in octahedral environments. It is proposed that the complexes exist in the solid state as *cyclic* oligomers in which the oxygen atoms are coordinated and the sulfur atoms bridge between adjacent metal ions. Infrared spectral studies suggest that canonical forms involving appreciable multiple bonding in the (OS)C–N bond are important. The spin-allowed "d–d" electronic transitions have been assigned, and the ligands have been found to lie between fluoride and water in the spectrochemical series. The polymeric structure of the complexes is ruptured by treatment with pyridine and bis adducts are formed. The adducts have been characterized by spectroscopic and magnetic measurements. Structural similarities among thiocarbamate and other complexes having $[Ni\text{-}O_4]$, $[Ni\text{-}O_2S_2]$, and $[Ni\text{-}S_4]$ donor atom sets are discussed.

Introduction

Complexes of ligands containing one or more sulfur donors have been of considerable recent interest. We have been particularly concerned with N,N-dialkyl-dithiocarbamate complexes,[2-5] which have long been known[6] but which continue to provide new and novel structures and reactions.[7,8]

Surprisingly, the ligational properties of analogous

N,N-dialkylthiocarbamates (abbreviated R_2tic) remain

$$\begin{array}{c} S^- \\ \diagdown \\ C\text{—}NR_2 = R_2\text{tic} \\ \diagup\!\!/ \\ O \end{array}$$
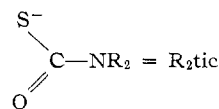
virtually unknown. To this time only derivatives of Cu(I) and Ag(I) are reasonably well characterized,[9,10] although complexes of several other similar sulfur–oxygen donors, such as monothiobenzoate, have been studied in some detail.[11-14] Comparative studies of

(1) Presented in part at the Second Central Regional Meeting of the American Chemical Society, Columbus, Ohio, June 1970.

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(3) B. J. McCormick, B. P. Stormer, and R. I. Kaplan, *ibid.*, **8**, 2522 (1969).

(4) B. J. McCormick and R. I. Kaplan, *Can. J. Chem.*, **48**, 1876 (1970).

(5) B. J. McCormick, R. I. Kaplan, and B. P. Stormer, *ibid.*, **49**, 699 (1971).

(6) G. D. Thorne and R. A. Ludwig, "The Dithiocarbamates and Related Compounds," Elsevier, New York, N. Y., 1962.

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(11) V. V. Savant, J. Gopalakrishnan, and C. C. Patel, *Inorg. Chem.*, **9**, 748 (1970).

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(13) G. A. Melson, N. P. Crawford, and B. J. Geddes, *ibid.*, **9**, 1123 (1970).

(14) C. Furlani, M. L. Luciani, and R. Candori, *J. Inorg. Nucl. Chem.*, **30**, 3121 (1968).

TABLE I
ELECTRONIC SPECTRAL DATA

Compound[g]	Medium	$^3A_{2g} \rightarrow {}^3T_{2g}$ (ν_1)	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$ (ν_2)	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$ (ν_3)	
Ni(Me₂tic)₂	Solid		14,100		28,100[b]
Ni(Et₂tic)₂	Solid		14,300		27,800
Ni(Pr₂tic)₂	Solid	8460	13,900	23,400	27,800
	Benzene	8340 (18)[c]	14,000 (37)[c]	23,300[b] (~250)[d]	27,800 (430)[d]
Ni(Bu₂tic)₂	Solid	8340	13,900	22,900	25,800
	Benzene	8340 (18)[e]	14,100 (31)[f]	23,500[b] (~254)[f]	31,000[b] (~290)[f]
Ni((CH₂)₄tic)₂	Solid	8850	14,200	23,300[b]	25,600
Ni((CH₂)₅tic)₂	Solid	8770	14,500		28,600[b]
Ni(Me₂tic)₂(py)₂	Methylene chloride	9200 (26)	15,600 (43)	25,600[b]	
Ni(Et₂tic)₂(py)₂	Methylene chloride	9300 (45)	15,400 (48)	25,600[b]	
Ni(Pr₂tic)₂(py)₂	Solid		15,600	26,700	
	Methylene chloride	9300 (20)	15,600 (30)	25,300[b]	
Ni(Bu₂tic)₂(py)₂	Methylene chloride	9300 (20)	15,600 (30)	26,000[b]	
Ni((CH₂)₄tic)₂(py)₂	Solid		16,400, 14,300		
	Methylene chloride	9100 (20)	15,400 (34)	25,600[b]	
Ni((CH₂)₅tic)₂(py)₂	Methylene chloride	9300 (30)	15,600 (39)	25,600[b]	

^{a} ϵ is in M^{-1} cm^{-1}; the molecular weight used in determining molarity was that corresponding to the monomer. ^{b} Shoulder. ^{c} For 1.45×10^{-2} M solutions at 25°. ^{d} For 3.89×10^{-3} M solutions at 20°. ^{e} For 7.68×10^{-3} M solutions at 20°. ^{f} For 6.61×10^{-3} M solutions at 20°. ^{g} Me = CH₃; Et = C₂H₅; Pr = n-C₃H₇; Bu = n-C₄H₉; py = pyridine.

TABLE II
INFRARED DATA FOR LIGAND SALTS AND COMPLEXES

Compound[a]	δ(N—H)	ν(C≐N),[b] ν(C≐O)	ν(Ni—S)	ν(Ni—O)	Unassigned[c]
((CH₂)₄NH₂)((CH₂)₄tic)	1610	1500	...	...	1475, 1450, 1373, 1345, 1331, 1315, 1305, 1188, 1170, 1037, 932, 909
((CH₂)₅NH₂)((CH₂)₅tic)	1619	1500	...	...	1438, 1390, 1348, 1339, 1278, 1250, 1205, 1132, 1114, 1035, 997
Ni(Me₂tic)₂		1566	394	535	1418, 1401, 1385, 1338, 1264, 1132
Ni(Et₂tic)₂		1538	387	539	1436, 1408, 1379, 1363, 1350, 1310, 1270, 1220, 1138, 948
Ni(Pr₂tic)₂		1525, 1545 sh	385	540	1459, 1440, 1432, 1409, 1379, 1289, 1140, 960
Ni(Bu₂tic)₂		1529, 1541	387	532	1469, 1434, 1409, 1390, 1343, 1304, 1233, 1141, 1104, 901
Ni((CH₂)₄tic)₂		1539[d]	387	520	1474, 1457, 1389, 1341, 1326, 1226, 1195, 1189, 1049, 978, 945, 914
Ni((CH₂)₅tic)₂		1537, 1515 sh	384	529	1441, 1405, 1382, 1369, 1337, 1285, 1265, 1254, 1215, 1138, 1029, 1007
Ni(Pr₂tic)₂(py)₂		1540 sh, 1522, 1500	377	538, 547	1600, 1039, 777, 757, 705, 696
Ni((CH₂)₄tic)₂(py)₂		1532 sh, 1500	390	528	1600, 1040, 762, 700

^{a} Me = CH₃; Et = C₂H₅; Pr = n-C₃H₇; Bu = n-C₄H₉; py = pyridine. ^{b} See text. ^{c} These are bands in the parent complexes and ligands of medium to strong intensity in the 900–1500-cm⁻¹ region. The only bands reported for the adducts are those associated with coordinated pyridine. ^{d} Broad.

the structures and chemical properties of complexes of thio- and dithiocarbamate ligands are capable of providing information relating to the differences between sulfur and oxygen as donor atoms. An especially attractive feature of such studies is that the gross steric requirements of the ligands and the size of the chelate rings can be kept essentially constant; consequently, any observed differences between thio- and dithiocarbamate complexes should reflect, primarily, the differing donor properties of oxygen and sulfur atoms. With these ideas in mind we have initiated a broad study of complexes derived from thiocarbamate ligands, and reported here are some of the results that pertain to nickel(II).

Experimental Section

Reagents and General Techniques.—Carbonyl sulfide (97.5%) was used as received from the Matheson Co., Inc. Amines, obtained from commercial sources, were used without further purification. Optical spectra were recorded by using a Cary Model 14 spectrophotometer. Solutions for spectral studies were prepared from Fisher "Spectro-Grade" solvents. Diffuse reflectance spectra were obtained with a Cary Model 1411 attachment operating in the region 12,500–28,600 cm⁻¹ and MgCO₃ was the standard. Spectra of several of the compounds sus-pended in Nujol mulls were obtained in the region 8500–28,600 cm⁻¹. These spectra were essentially identical with those obtained by diffuse reflectance and solution techniques. Spectral data are given in Table I.

Infrared spectra were measured with Beckman IR-8 and IR-12 spectrometers, and the samples were mulled with either Nujol or a fluorocarbon oil. Data are given in Table II. Magnetic measurements were made at three field strengths with a Guoy balance of standard design. The calibrant was [Ni(en)₃]S₂O₃.[15] The observed susceptibilities were field independent and the reported magnetic moments are corrected for ligand diamagnetic contributions.[16] Conductivities were measured at 25° for 10⁻³ M solutions (benzene) by using a Beckman RC-18 conductivity bridge. Molecular weights were determined in benzene at 42.6° with a Coleman-Hitachi Model 115 vapor pressure osmometer. Carbon, hydrogen, nitrogen, and sulfur elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn., and Chemalytics, Inc., Tempe, Ariz.

Ligands.—In general ligands were not isolated in the preparations leading to metal complexes, although it was possible to prepare and isolate easily white solid salts of 1-piperidylthiocarbamate and 1-pyrrolidylthiocarbamate. In each case the cationic counterion was a quaternary ammonium group derived from the parent amine. In a typical preparation carbonyl sulfide was bubbled through a solution of 2 ml of piperidine in

(15) N. F. Curtis, *J. Chem. Soc.*, 3147 (1961).

(16) B. Figgis and J. Lewis, "Modern Coordination Chemistry," Interscience, New York, N. Y., 1960.

TABLE III
ANALYTICAL AND MAGNETIC DATA AND MELTING POINTS

Compound[a]	Mp,[b] °C	% calcd				% found				$10^6\chi_g$, cgsu	μ_{eff}^{cor},[d] BM
		C	H	N	S	C	H	N	S[c]		
Ni(Me₂tic)₂	275	26.99	4.53	10.49	24.02	26.89	4.52	10.44	23.89	16.23	3.25
Ni(Et₂tic)₂	236	37.17	6.23	8.98	19.85	36.92	6.01	8.69	17.83	13.69	3.29
Ni(Pr₂tic)₂	197	44.34	7.44	7.42	16.91	44.61	7.50	7.54	15.68	10.69	3.18
Ni(Bu₂tic)₂	164	49.66	8.34	6.44	14.73	49.10	8.18	6.23	12.80	9.51	3.23
Ni((CH₂)₄tic)₂	252	37.64	5.05	8.78	20.10	37.39	5.17	8.93	18.53	14.25	3.33
Ni((CH₂)₅tic)₂	244	41.52	5.81	8.07	18.47	40.60	5.70	8.00	16.74	12.57	3.27
Ni(Pr₂tic)₂(py)₂	...	53.64	7.13	10.43	...	53.30	6.84	10.39	...	7.26	3.15
Ni((CH₂)₄tic)₂(py)₂	...	50.33	5.49	11.74	...	50.22	5.39	11.93	...	8.15	3.13

[a] Me = CH₃; Et = C₂H₅; Pr = n-C₃H₇; Bu = n-C₄H₉; py = pyridine. [b] With decomposition in each case. [c] All sulfur analyses were low and variable; however, in view of the generally excellent C, H, and N analyses and our previous difficulties in obtaining reliable S analyses for metal complexes, we are inclined to regard the reported values as indicative of analytical errors, rather than impurities or misformulation. [d] Per nickel(II) ion at room temperature (293–294°K).

50 ml of dry diethyl ether for 15 min. The resulting white precipitate was isolated by filtration, washed with diethyl ether, and dried *in vacuo* over P₄O₁₀. *Anal.* Calcd for C₁₁H₂₂N₂OS: C, 57.44; H, 9.67. Found: C, 57.39; H, 9.63.

Synthesis of Complexes of the Type Ni(R₂tic)₂.—Six complexes were prepared. In each case the preparative procedures used were basically the same. Carbonyl sulfide was bubbled for 10 min through 0.04 mol of the appropriate amine dissolved in 30 ml of absolute ethanol to provide a solution of the ligand R₂tic. To this solution was added 0.01 mol of NiCl₂·6H₂O dissolved in 30 ml of absolute ethanol. Cooling of the resultant solution in ice for 30 min resulted in the formation of a yellow-green solid which was isolated by filtration. This solid was washed with three 50-ml portions of absolute ethanol and dried *in vacuo* over P₄O₁₀. The *n*-propyl and *n*-butyl derivatives could be recrystallized from *n*-hexane, but the remaining four complexes were insoluble in noncoordinating solvents. Analytical results and melting points are documented in Table III along with magnetic susceptibility and moment data.

Bispyridinebis(*N*-pyrrolidylthiocarbamato)nickel(II).—Two grams of bis(*N*-pyrrolidylthiocarbamato)nickel(II) was stirred in a solution of 30 ml of absolute ethanol and 2 ml of pyridine for 20 min during which time a light green precipitate formed. This precipitate was isolated by filtration and recrystallized from a mixed ethanol–pyridine solution (15:1) to obtain the pure product. The product was dried in a stream of nitrogen for 2 hr and then was placed in a desiccator over P₄O₁₀ for 12 hr. Upon heating the product (95° (10⁻¹ mm)) for 6 hr, 2 mol of pyridine was lost. Analytical data are given in Table III.

Bispyridinebis(*N,N*-di-*n*-propylthiocarbamato)nickel(II).—To a saturated solution of bis(*N,N*-di-*n*-propylthiocarbamato)-nickel(II) in 20 ml of anhydrous diethyl ether was added 2 ml of pyridine. To the resulting emerald green solution was added *n*-hexane until the solution became cloudy. This solution then was cooled in ice, and a green crystalline solid formed. The solid product was washed with two 50-ml portions of *n*-pentane and was dried over P₄O₁₀ for 12 hr. By heating the compound at 95° (10⁻¹ mm) for 60 hr it was possible to drive off 2 mol of pyridine. Decomposition took place with liberation of pyridine at 100°. Analytical results are given in Table III.

Results and Discussion

Syntheses and General Properties.—Treatment of *N,N*-dialkylthiocarbamate salts with Ni²⁺ ions in absolute ethanol produces yellowish green compounds having the empirical formula Ni(R₂tic)₂. In the present study R was CH₃, C₂H₅, *n*-C₃H₇, *n*-C₄H₉, –(CH₂)₄–, and –(CH₂)₅–. The *n*-propyl and *n*-butyl derivatives are soluble in a variety of noncoordinating organic solvents, in which they are nonelectrolytes, but the remaining four complexes are insoluble. All of the complexes are insoluble in water. The compounds are relatively stable when dry, although noticeable decomposition begins to take place after exposure to the atmosphere for several weeks. For this reason, freshly prepared samples were used for all measurements and characterizational procedures. The *n*-propyl derivative offered the best combination of stability and solubility

of all six complexes; hence, this compound was chosen, in many cases, for detailed study.

Structure.—That the structures of nickel(II) thiocarbamate complexes are fundamentally different from those of the dithiocarbamates, which are planar[7,8] and diamagnetic, is immediately suggested by the observed paramagnetic moments of 3.18–3.33 BM. Moments in this range are characteristic of nickel(II) in octahedral geometries,[17] although it is not possible to rule out tetrahedral or five-coordinate geometries[18] on the basis of the magnetic data alone. However, the electronic spectra of the complexes are quite indicative of octahedral symmetry (*vide infra*). Taken together the magnetic and electronic spectral data make it possible to conclude with confidence that the nickel(II) ions are in octahedral or distorted octahedral environments. Octahedral structures consistent with the empirical formula can be achieved if the oxygen atoms are coordinated and the sulfur atoms bridge between adjacent metal ions. This type of ligand bonding is found in the hexameric copper(I) derivative of *N,N*-di-*n*-propylthiocarbamate in which the copper ions, which form an almost regular octahedron, are three-coordinate, each bonding to two bridging sulfur atoms and an oxygen atom.[10]

Further evidence that the thiocarbamates of nickel-(II) are polymerized through bridging sulfur atoms is provided by the results of molecular weight determinations for the *n*-propyl and *n*-butyl derivatives in benzene. The experimentally determined molecular weights vary as a function of concentration, as shown in Figure 1. These results are quite significant in terms of the solution behavior of the complexes, and it can be seen that the degree of polymerization decreases with decreasing concentration. The behavior of the soluble complexes in solutions of noncoordinating solvents has been studied in detail and the results will be presented elsewhere.[19] Suffice it to point out here that in very concentrated solutions at 42.6° the observed molecular weights of the *n*-propyl and *n*-butyl derivatives asymptotically approach that calculated for a hexamer (2273) and pentamer (2177), respectively. While these results are of limited accuracy at the higher concentrations because of deviations from ideal solution behavior, they do strongly suggest the existence of discrete hexamers and pentamers in the solid state.

(17) B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, **6**, 37 (1964).
(18) L. Sacconi, P. Nannelli, N. Nardi, and U. Campigli, *Inorg. Chem.*, **4**, 943 (1965).
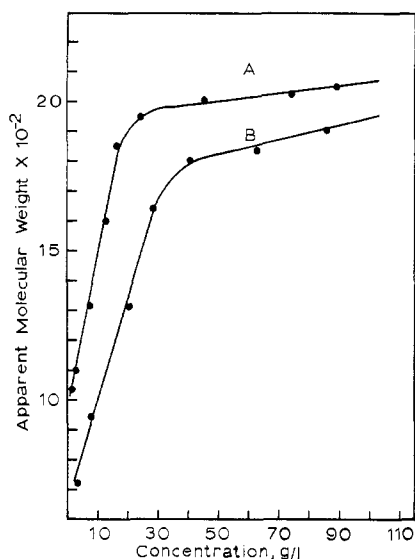(19) B. J. McCormick and B. P. Stormer, to be submitted for publication.

Figure 1.—Apparent molecular weight of $Ni(Pr_2tic)_2$ (A) and $Ni(Bu_2tic)_2$ (B).

Numerous structural possibilities have been considered. Structures analogous to that of bis(acetylacetonato)nickel(II)[20] would require both bridging oxygen and sulfur atoms. Since there is no precedence for this type of bonding mode, we have sought other possibilities. In order for linear chains of the type proposed for the structure of nickel(II) thiocarboxylates[11] to be finite, "end groups" or nonoctahedral metal atoms are required. These requirements are not consistent with the observed stoichiometry or electronic spectra. On the other hand *cyclic* chain structures can be envisioned which are consistent with all of the properties observed for the complexes under study. A representation of the bonding in this type of structure is given in Figure 2. Although a hexamer is shown, it is possible to de-
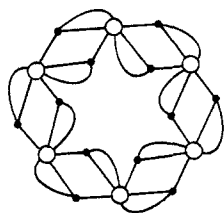
Figure 2.—Diagrammatic representation of the proposed bonding.
in $[Ni(Pr_2tic)_2]_6$. The curved lines represent $S\overset{\overset{C}{\diagup}\diagdown}{}O$ ligand fragments, with the closed circles identifying the sulfur donors. The open circles represent nickel atoms.

sign similar structures with both higher and lower degrees of polymerization,[21,22] and we propose that all of the complexes prepared in this work are cyclic oligomers similar to that shown in Figure 2. The number of nickel atoms in the chain may vary from one complex to another; it is possible that variations in chain size account, in part, for the observed differences in solubility behavior.

Infrared Spectra.—Infrared spectral studies of thio-

(20) G. J. Bullen, R. Mason, and P. Pauling, *Inorg. Chem.*, **4**, 456 (1965).
(21) The preliminary results from an X-ray diffraction study of the *n*-propyl derivative indicate that, in fact, a cyclic hexameric structure of the type shown in Figure 2 is correct.[22]
(22) P. F. Method and R. V. Chastain, Jr., private communication.

carbamates have not been carried out in detail, but by analogy to other similar, but better characterized ligands, it is possible to make some empirical band assignments which seem fairly secure.

Spectra were obtained for the two isolable salts, and broad bands characteristic[23] of quaternary ammonium groups were observed in both salts in the 2400–2600-cm^{-1} region. Additional pertinent data are given in Table II and a spectrum of piperidinium N-piperidyl-thiocarbamate is shown in Figure 3A.
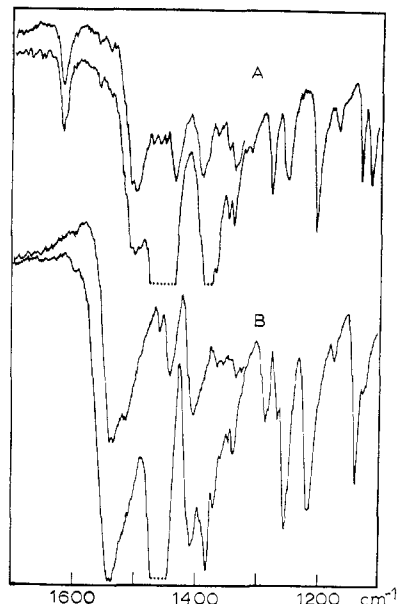

Figure 3.—Infrared spectra of piperidinium N-piperidylthio-carbamate (A) and bis(N-piperidylthiocarbamato)nickel(II) (B). The spectral traces originating at 1320 cm^{-1} were obtained for fluorocarbon mulls. The truncated bands are Nujol absorptions.

The carbonyl stretching frequency in the ligand salts and complexes might be expected in the 1500–1550-cm^{-1} region, as this frequency has been assigned previously at 1500, 1508, and 1520 cm^{-1} in $Na(C_6H_5-COS)$,[11] $Ni(C_6H_5COS)_2$,[11] and $Ni(C_6H_5COS)_2 \cdot 0.5C_2H_5-OH$,[13] respectively. In the thiocarbamate case the assignment of the carbonyl stretch is rendered difficult because a $C\cdots N$ stretching frequency is expected in the same region. It is well known that a strong, broad band at *ca.* 1500 cm^{-1} is very characteristic of the infrared spectra of dithiocarbamate ligands and complexes,[2-7] and it has been shown rather conclusively that this band is a $C\cdots N$ stretching frequency which arises from contributions of dipolar resonance forms of type 1 to the overall electronic structure.[24-26] The

$$\overset{S^-}{\underset{S^-}{\diagup}}C\overset{+}{=}NR_2$$

1
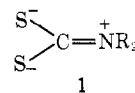
substitution of more electronegative oxygen for sulfur atoms in going from dithio- to thiocarbamates would

(23) N. B. Colthup, L. H. Daly, and S. E. Wiberly, "Introduction to Infrared and Raman Spectroscopy," Academic Press, New York, N. Y., 1964.
(24) J. Chatt, L. A. Duncanson, and L. M. Venanzi, *Suom. Kemistilehti B*, **29**, 75 (1956).
(25) K. Nakamoto, J. Fujita, R. A. Condrate, and Y. Morimoto, *J. Chem. Phys.*, **39**, 423 (1963).
(26) D. Coucouvanis and J. P. Fackler, Jr., *Inorg. Chem.*, **6**, 2047 (1967).

not tend to decrease the importance of canonical forms in which there is appreciable mesomeric electron drift away from the nitrogen atom, and it is reasonable to expect that similar resonance forms of type **2** will play an

$$
\begin{array}{c}
\text{O}^- \\
\diagdown \\
\diagup \quad \text{C}=\overset{+}{\text{N}}\text{R}_2 \\
\text{S}^-
\end{array}
$$

2
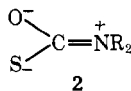
important role in the description of thiocarbamate ligands and complexes.

A further complication in assigning the C⋯O and C⋯N stretching frequencies arises from the similar masses of the nitrogen and oxygen atoms. Almost certainly these two modes will be highly coupled.

In the two ligand salts strong, broad band envelopes were observed at 1500 cm^{-1}, and in the complexes similar envelopes, which were split in some cases, were found from 1525 to 1566 cm^{-1}, as illustrated in Figure 3B. We suggest that these band envelopes contain *both* the C⋯O and C⋯N stretching frequencies. In the butyl derivative two bands are clearly resolved in the envelope, but detailed assignment of the two bands seems hazardous at this time.

In spite of the difficulties in making accurate assignments of ν(C⋯O), it is clear that the infrared spectra are consistent with the bonding shown in Figure 2. Should the oxygen atom not be coordinated, a carbonyl stretching frequency would be expected well above 1600 cm^{-1}.[28]

Assignment of the Ni–S stretching frequencies can be made with some confidence as the sharp band of moderate intensity observed in the complexes at 389 ± 5 cm^{-1}. The assignment of this band is made on the basis of previous work which has placed the nickel–sulfur stretching frequency near 400 cm^{-1} in metal dithiocarbamates and xanthates.[24,27,28]

Nickel–oxygen stretching frequencies are tentatively assigned as the band of medium intensity found at 530 ± 10 cm^{-1}. This assignment compares with those that have placed ν(Ni–O) at *ca.* 500 and 570 cm^{-1} in monothio-β-diketone[29] and thiobenzoate[10] complexes of nickel(II), respectively.

Electronic Spectra.—Solution spectra were measured for the soluble complexes Ni(Pr$_2$tic)$_2$ and Ni(Bu$_2$tic)$_2$ over the range 7150–31,000 cm^{-1}. While it is clear from the molecular weight measurements that the complexes depolymerize to some extent upon dissolution, it should be pointed out that the very close similarity of solid and solution spectra, as illustrated in Figure 4, indicates that the predominant species observed were the same in both cases. It was found that the solution spectra do not obey Beer's law. This observation again suggests that depolymerization takes place in solution. Because of the spectral nonideality of the solutions the data given in Table I and Figure 4 refer to specific concentrations, as indicated. A more detailed description and interpretation of the spectral dependence on concentration will be given elsewhere.[19]

The electronic spectra are quite typical of those exhibited by nickel(II) in octahedral environments, as three moderately intense, characteristic ligand field
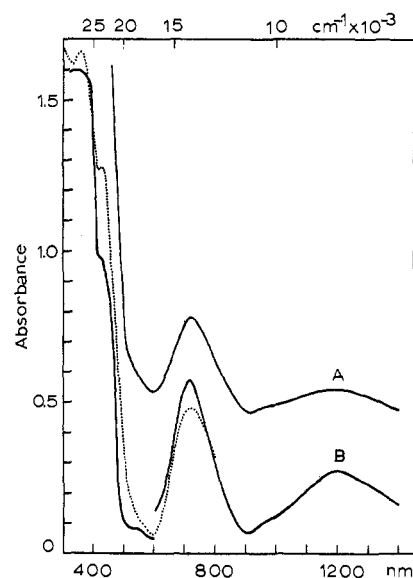

Figure 4.—Electronic spectra of Ni(Pr$_2$tic)$_2$: ⋯⋯, diffuse reflectance; A, Nujol mull; B, benzene solutions. The concentrations used in obtaining the solution spectra were 1.45×10^{-2} M above 600 nm and 3.89×10^{-3} M below 600 nm. See text for additional details.

bands were observed.[30] One band was found in the infrared region near 8500 cm^{-1} and two bands were located in the visible region around 14,000 and 23,000 cm^{-1}. The low-energy band, which is assigned to the $^3A_{2g} \rightarrow {}^3T_{2g}$ transition, is broad and symmetrical with an intensity ($\epsilon \sim 20$) consistent with the assignment as a spin-allowed, Laporte-forbidden transition. On the high-energy side of the band envelope there is a weak shoulder at *ca.* 10,000 cm^{-1} which may result from distortions from octahedral symmetry. The band at *ca.* 14,000 cm^{-1} is assigned to the $^3A_{2g} \rightarrow {}^3T_{1g}$(F) transition. Again the intensity ($\epsilon \sim 35$) and energy are characteristic of nickel(II) in octahedral environments. The third ligand field transition, $^3A_{2g} \rightarrow {}^3T_{1g}$(P), is assigned as the shoulder or barely distinct band at *ca.* 23,000 cm^{-1}. This band can be observed in spectra of the solid compounds, except in the methyl, ethyl, and piperidyl derivatives where it appears to be buried under an intense band whose maximum is around 28,000 cm^{-1}. The intensity of the third transition (ν_3) is higher than is normally observed for ligand field bands, but it is clear that this band gains intensity by virtue of being a shoulder on the intense absorption of higher energy. The strong band at 28,000 cm^{-1} is probably charge transfer in nature; however, the ultraviolet spectra of the complexes and ligands have not been studied in detail and an assignment will not be attempted here.

From the spectral assignments made above it is possible to determine Dq for the complexes. Equating the $^3A_{2g} \rightarrow {}^3T_{2g}$ (ν_1) splittings with $10Dq$ gives values in the range 860 ± 25 cm^{-1}. Owing to the broadness of the bands assigned as ν_1 and the consequent inaccuracies in determining the band centers, we are reluctant to attach great significance to the small differences in Dq that are observed with changes in the R groups. By using the relationship $15B = \nu_2 + \nu_3 - 3\nu_1$ and solid-state spectral data, values of the Racah parameter B were calculated as 795, 785, and 730 cm^{-1} for the propyl,

(27) G. W. Watt and B. J. McCormick, *Spectrochim. Acta*, **21**, 753 (1965).

(28) G. Durgaprasad, D. N. Sathyanarayana, and C. C. Patel, *Can. J. Chem.*, **47**, 631 (1969).

(29) S. H. H. Chaston, S. E. Livingstone, T. N. Lockyer, V. A. Pickles, and J. S. Shannon, *Aust. J. Chem.*, **18**, 673 (1965).

(30) L. Sacconi, *Transition Metal Chem.*, **4**, 199 (1968).

butyl, and pyrrolidyl complexes, respectively. The differences in B probably reflect the inaccuracy in determining the frequency of the shoulder assigned as ν_3.

The values obtained for Dq place thiocarbamate ligands close to water in the spectrochemical series. More specifically the following series for octahedral nickel(II) involving comparable ligands can be established: fluoride[31] < ethylenethiourea[31] < R$_2$tic < water[31] < thiobenzoate[32] < thioglycolate.[33] It is also well known that monothio-β-diketone, alkyl xanthate, and dialkyldithiocarbamate ligands lie between water and fluoride in the spectrochemical series.[34,35] We conclude that R$_2$tic ligands are similar in field strength to these ligands. However, it is not appropriate to attempt to establish a detailed ordering of the four types of ligands because the bulk of the work on monothio-β-diketone, alkyl xanthate, and dialkyldithiocarbamate complexes of nickel(II) has been with planar rather than octahedral compounds. Additionally, the Dq values obtained in this work apply only to thiocarbamate ligands in bridging situations; Dq for monomeric thiocarbamate complexes might be expected to be somewhat higher than those reported here.

Pyridine Adducts.—All six of the thiocarbamates prepared in this work dissolve in pyridine and in noncoordinating solvents containing pyridine to give green solutions which have essentially identical electronic spectra (Table I). In two cases green crystalline products were isolated which had the composition Ni-(R$_2$tic)$_2$(py)$_2$, as shown in Table III. Solid products can be isolated, no doubt, for the remaining four derivatives by similar procedures. That the complexes react with pyridine to form bis adducts was further substantiated by the results of experiments in which the isolated green solids were heated *in vacuo*. Quantitative measurements of the weight loss showed that 2 mol of pyridine was liberated per mole of adduct in each case. The products remaining after heating had the same color, elemental composition, and infrared spectra as the parent thiocarbamates from which the adducts were synthesized.

The adducts are soluble in many organic solvents; however, the resulting solutions are unstable, as evidenced by a color change to purple over a period of ~24 hr. The purple products were not characterized. The solid adducts appear to be stable indefinitely at room temperature.

The infrared spectra of Ni(Pr$_2$tic)$_2$(py)$_2$ and Ni-((CH$_2$)$_4$tic)$_2$(py)$_2$ are consistent with adduct formation, as bands quite characteristic[36,37] of coordinated pyridine are observed (Table II). The band envelopes assigned to ν(C$\doteq$O) and ν(C$\doteq$N) in the parent complexes are found in the infrared spectra of the adducts as characteristic features. In the adducts, this envelope has the same intensity as but slightly more structure than in the parent complexes. Nevertheless, it remains impossible to assign the individual constituent frequencies. It is

of significance that no new bands appear above 1550 cm^{-1} in the adducts other than those associated with pyridine. This indicates that the oxygen atoms remain coordinated. The frequencies assigned as ν(Ni-O) and ν(Ni-S) appear to be little affected by adduct formation, as bands very similar to those observed in the parent thiocarbamates are found in the adducts. Frequencies are given in Table II.

The magnetic moments of the two crystalline adducts (Table III) are consistent with octahedral structures, as are the electronic spectra. Electronic spectral data are given in Table I and typical spectra are illustrated in Figure 5. Band assignments analogous to those pro-
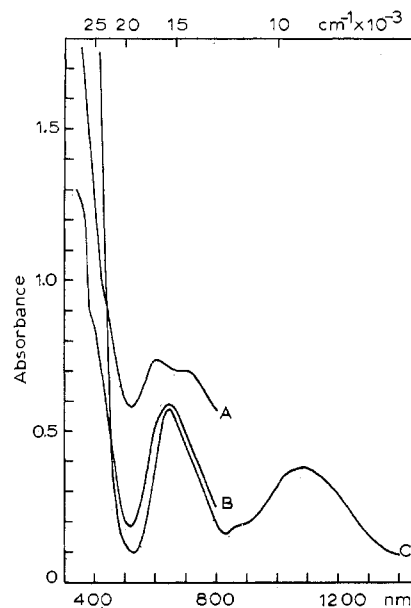

Figure 5.—Electronic spectra of the pyridine adducts. Spectra A and B are for Ni((CH$_2$)$_4$tic)$_2$(py)$_2$ and Ni(Pr$_2$tic)$_2$(py)$_2$, respectively, by diffuse reflectance techniques. Spectrum C is for Ni(Pr$_2$tic)$_2$(py)$_2$ in methylene chloride, 1.89 × 10^{-2} M.

posed for the parent complexes can be made for the adducts with confidence as indicated in Table I. The most significant feature of the electronic spectra is the hypsochromic shift of the ligand field bands that occurs upon adduct formation. This shift undoubtedly arises from the substitution in the coordination sphere of strong-field pyridine for weak-field, bridging sulfur donors when the parent cyclic oligomers are ruptured to form the adducts. In the diffuse reflectance spectrum of Ni((CH$_2$)$_4$tic)$_2$(py)$_2$ the ^{3}A$_{2g}$ → ^{3}T$_{1g}$(F) transition is resolved into two components (Figure 5). This band splitting probably reflects the low symmetry of the complex, as similar splittings have been observed in other complexes, such as *trans*-dichlorobis(pyridine)nickel-(II),[38] which have a symmetry lower than O_h.

Conclusions

It is of interest to compare the structure of nickel(II) thiocarbamate complexes with those of other complexes involving four-membered chelate rings having the donor atom sets [Ni-O$_4$], [Ni-O$_2$S$_2$], and [Ni-S$_4$]. In the first category are complexes of carboxylic acids; unfortunately the structures of only two of these compounds have been established, those of Ni(O$_2$CH)$_2$·

(31) Dq values taken from A. B. P. Lever, "Inorganic Electronic Spectroscopy," Elsevier, New York, N. Y., pp 333–340.

(32) Dq of 901 cm^{-1} calculated from data given in ref 11.

(33) J. T. Morrison and W. A. Baker, Jr., *Inorg. Chim. Acta*, **3**, 463 (1969).

(34) C. K. Jørgensen, *J. Inorg. Nucl. Chem.*, **24**, 1571 (1962).

(35) S. H. H. Chaston, S. E. Livingstone, and T. N. Lockyer, *Aust. J. Chem.*, **19**, 1401 (1966).

(36) N. S. Gill, R. H. Nuttall, D. E. Scaife, and D. W. Sharp, *J. Inorg. Nucl. Chem.*, **18**, 79 (1961).

(37) B. J. McCormick, *Can. J. Chem.*, **47**, 4283 (1969).

(38) S. M. Nelson and T. M. Sheperd, *J. Chem. Soc.*, 3276 (1965).

$2H_2O^{39}$ and $Ni(O_2CCH_3)_2 \cdot 4H_2O$,[40] and in both cases the water molecules are coordinated. Consequently, these compounds are not strictly comparable to $Ni(R_2tic)_2$ complexes and all that can be said by way of structural comparison is that the carboxylate ligands bridge rather than chelate. Previous reports of complexes having the $[Ni-O_2S_2]$ donor atom set in four-membered rings are limited to two studies of thiocarboxylate compounds.[11-13] Based on chemical and spectroscopic studies Savant and coworkers[11] formulated $Ni(OSCC_6-H_5)_2$ as a *linear* polymer involving bonding similar to that reported here for the thiocarbamates. The other thiocarboxylate complex, for which the structure has been established by X-ray studies,[12,13] has the formula $Ni(OSCC_6H_5)_2 \cdot 0.5C_2H_5OH$ and involves coordinated ethanol and bridging, but not chelating, thiobenzoate ligands. The two nickel ions per unit are square planar $(Ni-S_4)$ and square pyramidal $(Ni-O_5)$, respectively. The structure of $Ni(OSCC_6H_5)_2 \cdot 0.5C_2H_5OH$ is thus distinctly different from that of the thiocarbamates. Differences between thiocarboxylates and thiocarbamates as ligands may reflect to a large extent the importance of canonical forms of type 2 in the latter, but additional study will be required before this factor can be properly assessed. Structures involving the $[Ni-S_4]$ donor atom set are well documented.[7,8] In all cases planar geometries have been observed and sulfur–nickel interactions between adjacent molecular units have been found to be weak or nonexistent. Thus, the effect of substituting an oxygen for a sulfur atom in four-membered chelate rings where canonical forms of type 2 are important appears to be one of increasing the bridging tendency of the remaining sulfur donor. This, in turn, probably indicates that the sulfur atom assumes mercaptide character or, in other words, carries a high negative charge. In this regard it is of interest to note that a structure having a Ni–S bridging system very similar to that reported here has been found for the mercaptide complex $[Ni(SC_2H_5)_2]_6$.[41] The high negative charge on the sulfur donors in thiocarbamates results from contributions from canonical form 2.

(39) K. Krogmann and R. Mattes, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, **118**, 291 (1963).

(40) J. N. van Niekerk and F. R. L. Schoening, *Acta Crystallogr.*, **6**, 609 (1963).

(41) P. Woodward, L. F. Dahl, E. W. Abel, and B. C. Crosse, *J. Amer. Chem. Soc.*, **87**, 5251 (1965).

At this point it is appropriate to compare the coordination and basic structure of thiocarbamate complexes of nickel(II)[42,43] with that which has been reported for Ag(I)[9] and Cu(I),[10] although detailed structural comparisons must await the results of an X-ray crystallographic study.[21] An immediately obvious facet of such a comparison is that all of the structures involve oligomers in which the oxygen atoms are coordinated and the sulfur atoms bridge. Thus the mercaptide character of the sulfur donor is again apparent. That the Ag(I), Cu(I), and Ni(II) derivatives of N,N-di-n-propylthiocarbamate all exist as hexamers appears to be coincidental in light of the facts that the Ag(I) and Cu(I) ions form an octahedron whereas the Ni(II) ions are found in a cyclic chain. A significant difference between the nickel(II) and the coinage metal derivatives is that in the latter the thiocarbamate ligands are not chelated. This difference may reflect the relative sizes of the metal atoms, the ligand "bite" being insufficiently large to form chelates with ions having a radius larger than that of nickel(II).

Some comment on the adducts can be made. It is well known that many planar $[Ni-S_4]$ complexes form bis adducts with nitrogenous bases.[7,26] Likewise it has been reported that thiocarboxylates of nickel(II) form adducts.[11,13] The nickel thiocarbamates thus appear to parallel the behavior of other similar complexes in adduct-forming ability. Removal of the coordinated pyridine molecules from $Ni(Pr_2tic)_2(py)_2$ and $Ni((CH_2)_4tic)_2(py)_2$ produces compounds having the same spectral properties and composition as the parent thiocarbamates from which the adducts were derived; however, it is highly unlikely that the molecular structures are identical.

(42) While the present paper was in preparation, a brief note was published[43] in which a compound formulated as $Ni((CH_2)_4(tic))_2$ was reported. This compound seems to have electronic spectral properties analogous to those given here, but the infrared and magnetic moment data appear to differ somewhat from that obtained for the $Ni((CH_2)_4(tic))_2$ prepared in this work.

(43) E. M. Krankovits, R. J. Magee, and M. J. O'Connor, *Inorg. Nucl. Chem. Lett.*, **7**, 541 (1971).