

of a limited hemisphere of reciprocal space yielded a set of reflections that exhibited orthorhombic symmetry. The general reflection conditions of  $h + k$ ,  $h + l$ , and  $k + l = 2n$  for  $hkl$  indicated an  $F$ -centered lattice. The further general conditions for  $0kl$  of  $k + l = 4n$  with  $h$  and  $k$  both even, for  $hk0$  of  $h + k = 4n$  with  $h$  and  $k$  both even, and for  $h0l$  of  $h + l = 4n$  with  $k$  and  $l$  both even lead to the choice of the space group  $Fd2d$ , an alternate setting of space group No. 43,  $Fdd2$ . Unit cell dimensions were determined by using 62 unique reflections having  $2\theta$  between 15 and 35°. Subsequent solution and refinement of the structure confirmed the choice of  $Fd2d$ . No absorption correction was carried out.

The structure was solved by locating the Ba atom from a Patterson function and was confirmed by direct methods. The remaining non-hydrogen atoms were located by using several difference Fourier maps. The Ba atom is located on a crystallographic 2-fold axis. It is coordinated to two independent (by symmetry four) bidentate ligands:  $\text{HOCH}_2\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2$ . Two 2,6-di-*tert*-butylphenolate groups are located on the 2-fold axis and are hydrogen-bonded to the O atoms in the HOR-ligands. The two aromatic rings are approximately perpendicular to each other (interplanar angle 74°). The asymmetric unit also contains one molecule of solvent toluene (C(32)–C(38)). Almost all of the hydrogen atoms were located in a difference Fourier map following the initial refinement

of the structure. They were introduced in the final full-matrix least-squares refinement cycles in idealized fixed positions; only the two hydrogen atoms associated with the hydrogen bond were refined by using isotropic thermal parameters. No hydrogen atoms were introduced on the solvent molecule. All non-hydrogen atoms were refined by using anisotropic thermal parameters, except for those solvent atoms that were kept isotropic. The total number of variables was 286, giving a ratio of observations to variables of 12. The final difference map was essentially featureless. There were two peaks of about  $1.6 \text{ e}/\text{\AA}^3$  in the immediate vicinity of the Ba atom, and all other peaks were less than  $0.5 \text{ e}/\text{\AA}^3$ . The closest approach of the solvent molecule to the Ba complex is  $3.78 \text{ \AA}$  for C(33)–C(6).

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**Supplementary Material Available:** Tables of full crystallographic details, anisotropic thermal parameters, and complete bond distances and angles and drawings showing the complete atom-numbering scheme and vibrational ellipsoids (7 pages); a listing of  $F_o$  and  $F_c$  values (9 pages). Ordering information is given on any current masthead page.

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## Tetradentate Dithioamide Ligands and Their Nickel Complexes. Synthesis, Characterization, and Crystal Structure of a Mononuclear Neutral Complex, $\text{Ni}((\text{c-C}_5\text{H}_9)\text{NHC}(\text{S})\text{C}(\text{S})\text{N}(\text{CH}_2)_2\text{NC}(\text{S})\text{C}(\text{S})\text{NH}(\text{c-C}_5\text{H}_9))$

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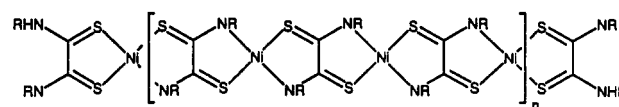
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N-Monosubstituted dithioamides react in a 2:1 stoichiometry with diamines to give tetradentate dithioamide ligands ( $\text{LH}_4$ ) of the general formula  $\text{RNHC}(\text{S})\text{C}(\text{S})\text{NH}(\text{CH}_2)_n\text{NHC}(\text{S})\text{C}(\text{S})\text{NHR}$  ( $\text{R} = \text{c-C}_5\text{H}_9$  and  $\text{c-C}_6\text{H}_{11}$ ,  $n = 2$ ;  $\text{R} = \text{n-C}_{12}\text{H}_{25}$  and  $\text{C}_6\text{H}_5\text{CH}_2$ ,  $n = 2-4$ ). Reaction of these ligands with Ni(II) gives cationic complexes of the general formula  $[\text{Ni}(\text{LH}_4)]^{2+}$  under acidic conditions, neutral complexes of formula  $\text{Ni}(\text{LH}_2)$  under neutral conditions, and a polymeric material of approximate formula  $(\text{Ni}_2\text{L})_n$  under basic conditions.  $\text{Ni}(\text{LH}_2)$  and  $[\text{Ni}(\text{LH}_4)]\text{Br}_2$  can be interconverted by protonation/deprotonation under extreme conditions. Associated with this interconversion is a color change from red ( $\text{Ni}(\text{LH}_2)$ ) to blue ( $[\text{Ni}(\text{LH}_4)]\text{Br}_2$ ). Crystals of the neutral complex  $\text{Ni}((\text{c-C}_5\text{H}_9)\text{NHC}(\text{S})\text{C}(\text{S})\text{N}(\text{CH}_2)_2\text{NC}(\text{S})\text{C}(\text{S})\text{NH}(\text{c-C}_5\text{H}_9))$  were grown from *n*-heptane/chloroform. This complex crystallizes in the orthorhombic space group  $Pbcn$  (No. 60) with cell dimensions  $a = 25.152$  (9)  $\text{\AA}$ ,  $b = 7.998$  (3)  $\text{\AA}$ ,  $c = 9.865$  (5)  $\text{\AA}$ , and  $V = 1984.5$  (1)  $\text{\AA}^3$ . For  $Z = 4$  and a formula weight of 459.34, the calculated density is  $1.537 \text{ g/cm}^3$ . Diffraction data (Mo  $K\alpha$ ) were collected with a Rigaku AFC5R diffractometer at 23 °C, and the structure was solved by the heavy-atom method. The final agreement factors were  $R = 0.065$  and  $R_w = 0.059$  for the 662 observed reflections.

### Introduction

Dithioamide (DTO) and its mono- and disubstituted derivatives have a varied and interesting coordination chemistry, and their intense chromophores<sup>1</sup> have led to a number of applications,<sup>2</sup> including an important imaging process.<sup>3</sup> The DTO ligands are exemplary of polyfunctional molecules that can, in principle, chelate in a variety of different ways; i.e., they are *flexidentate* ligands.<sup>4</sup> Attention has focused especially on their intensely colored neutral polymeric,  $[(\text{ML}')_n]$ ,<sup>5</sup> and cationic monomeric,  $[\text{M}(\text{L}'\text{H}_2)_2]\text{X}_2$ ,<sup>6</sup> complexes ( $\text{L}'\text{H}_2 =$  substituted bidentate DTO ligand;  $\text{X} =$  halide, oxyanion) of the periodic group 10 elements: Ni, Pd, and Pt. The particular complex formed depends on the reaction conditions and stoichiometry.

In the case of nickel(II), 1 equiv of metal ion reacts with 1 equiv of  $\text{L}'\text{H}_2$  in neutral or weakly acidic media to give a dark blue insoluble 1:1 polymer of undetermined molecular weight. In this material each ligand is believed to bridge between two nickel atoms, coordinating to each metal atom through one sulfur and one nitrogen, forming a five-membered chelate ring (see I).<sup>5b,6b,7</sup> It has been assumed that the chain terminates with the final DTO ligand coordinated in a bidentate  $\text{S}_2$ , rather than  $\text{N,S}$ , fashion.



I

With 2 or more equivalents of  $\text{L}'\text{H}_2$  and from strongly acidic media, salts of monomeric cationic nickel(II) complexes, of the

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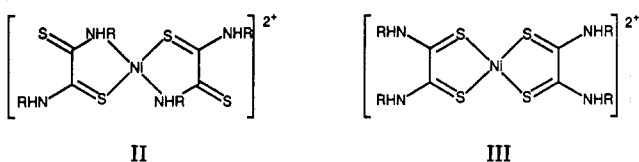
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**Table I.** Analytical Data,<sup>a</sup> Yields, and Melting Points for the LH<sub>4</sub> Ligands

LH <sub>4</sub> compd	formula	C		H		N		yield, %	mp, °C
		found	calc	found	calc	found	calc		
CP-C-II	C <sub>16</sub> H <sub>26</sub> N <sub>4</sub> S <sub>4</sub>	47.80	47.73	6.68	6.51	13.73	13.92	48	98–99
CH-C-II	C <sub>18</sub> H <sub>30</sub> N <sub>4</sub> S <sub>4</sub>	50.10	50.20	7.18	7.02	13.39	13.01	58	143–144
MD-C-II	C <sub>30</sub> H <sub>58</sub> N <sub>4</sub> S <sub>4</sub>	59.98	59.75	9.68	9.69	9.34	9.29	80	77–78
MC-C-III	C <sub>31</sub> H <sub>60</sub> N <sub>4</sub> S <sub>4</sub>	60.32	60.34	10.10	9.80	8.89	9.08	39	73–74
MD-C-IV	C <sub>32</sub> H <sub>62</sub> N <sub>4</sub> S <sub>4</sub>	61.00	60.90	9.88	9.90	9.09	8.88	87	83–84
MB-C-II	C <sub>20</sub> H <sub>22</sub> N <sub>4</sub> S <sub>4</sub>	53.40	53.78	4.86	4.96	12.18	12.54	73	123–124
MB-C-III	C <sub>21</sub> H <sub>24</sub> N <sub>4</sub> S <sub>4</sub>	54.68	54.75	5.30	5.25	12.00	12.16	11	127–128
MB-C-IV	C <sub>22</sub> H <sub>26</sub> N <sub>4</sub> S <sub>4</sub>	55.28	55.66	5.48	5.52	11.61	11.80	44	135–137

<sup>a</sup> In percent.

general formula [Ni(L'H<sub>2</sub>)<sub>2</sub>]<sub>2</sub>X<sub>2</sub>, have been obtained.<sup>6b,e</sup> In [Ni(L'H<sub>2</sub>)<sub>2</sub>]<sub>2</sub>X<sub>2</sub>, the ligands were first reported to coordinate in a bidentate N,S fashion (five-membered chelate ring), forming a square-planar complex of nearly C<sub>2h</sub> symmetry (II).<sup>6c,8</sup> However, recent work suggested that the ligands are probably bound in an S,S fashion (III),<sup>9</sup> and this has been confirmed by determination of the crystal structure of [Ni(N,N'-diethyl-DTO)<sub>2</sub>]Br<sub>2</sub>.<sup>10</sup>

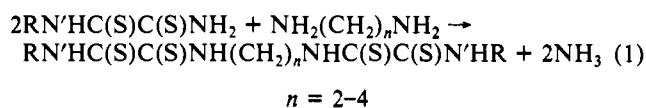


Monomeric neutral complexes of unsubstituted and N-substituted DTO ligands, of the general formula M(L'H)<sub>2</sub>, have been reported for Pd(II) and Pt(II).<sup>6c,11</sup> Crystallographic studies have confirmed S<sub>4</sub> coordination spheres about M(II) in these complexes.<sup>12</sup>

Unlike Pd and Pt, no monomeric neutral nickel complex of unsubstituted DTO has been reported. Neutral Ni complexes have been reported only for N,N'-disubstituted DTO ligands such as N,N'-dihexyl-DTO and N,N'-dibenzyl-DTO.<sup>13</sup> A crystallographic

study of the neutral quinoxaline-2,3-dithiol (or N,N'-1,2-phenylene-DTO) complex shows an S<sub>4</sub> environment about Ni.<sup>14</sup>

In this paper we report the synthesis of a series of new tetradentate DTO ligands (LH<sub>4</sub>) and their nickel complexes. The ligands were prepared by linking two N-substituted DTO ligands together via a short hydrocarbon chain. The reaction is illustrated in eq 1 and is a modification of the Wallach reaction.<sup>15</sup>



Because of the short hydrocarbon bridge, we believed that the formation of monomeric planar NiS<sub>4</sub> chelates would be unlikely. Instead, we expected the ligand structure to force the complexes to adopt the NiN<sub>2</sub>S<sub>2</sub> mode of coordination, an arrangement that has not previously been achieved among mononuclear DTO complexes of periodic group 10 metals, although it has been proposed for the (NiL)<sub>n</sub> polymers. We report here a crystallographic study of Ni((c-C<sub>5</sub>H<sub>9</sub>)NHC(S)C(S)N(CH<sub>2</sub>)<sub>2</sub>NC(S)C(S)NH(c-C<sub>5</sub>H<sub>9</sub>)) (abbreviated Ni(CP-C-II))<sup>16</sup> that has confirmed the N<sub>2</sub>S<sub>2</sub> coordination sphere for the neutral complexes. The syntheses, structures, and properties of the monomeric neutral and cationic and the polymeric nickel(II) complexes of these new (DTO)<sub>2</sub> ligands are reported and discussed.

## Experimental Section

**Physical Measurements.** Elemental analyses were performed by Galbraith Laboratories, Inc., or by staff in the Department of Chemistry at the University of Kansas. Infrared spectra were obtained by using a Perkin-Elmer 283B continuous-wave spectrophotometer or a Perkin-Elmer 1600 series Fourier transform spectrophotometer. <sup>1</sup>H NMR spectra and <sup>13</sup>C NMR spectra were recorded on either a Bruker AM-500 spectrometer, operating at 500.135 MHz for <sup>1</sup>H and 125.759 MHz for <sup>13</sup>C, or a Varian XL 300 spectrometer, operating at 300 MHz for <sup>1</sup>H and 75 MHz for <sup>13</sup>C, and were referenced to residual solvent resonances or TMS. Electron impact mass spectra were recorded by staff at the University of Kansas using a Ribermag R10-10 mass spectrometer operating at 70 eV. Electronic spectra were recorded by using a Varian Cary 2300 UV-vis spectrophotometer.

**Synthesis of the Ligands.** The various ligands were prepared by similar procedures, illustrated here for the specific example of MB-C-II.<sup>16</sup> In all cases the diamines were distilled from NaOH under N<sub>2</sub>. The progress of the reactions was followed by analytical TLC.

N-Monobenzyl-DTO (8.4 g, 0.04 mmol) was dissolved in methanol (60 mL), and aniline (3.6 mL) was added to the solution.<sup>17</sup> The mixture was stirred for 30 min under N<sub>2</sub>. The solution was warmed to 35 °C, and ethylenediamine (0.02 mmol) was added via syringe through a septum.<sup>18</sup> The mixture was then stirred for 4–8 h at 35 °C. The precipitate

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- (17) The preparations of the monododecyl derivatives did not require aniline.

Table II. Analytical Data<sup>a</sup> for the New Nickel Complexes

compd	formula	C		H		N		Ni		Br	
		found	calc	found	calc	found	calc	found	calc	found	calc
				NiLH <sub>2</sub>							
Ni(CP-C-II)	C <sub>16</sub> H <sub>24</sub> N <sub>4</sub> S <sub>4</sub> Ni	41.62	41.84	5.38	5.27	12.01	12.20				
Ni(CH-C-II)	C <sub>18</sub> H <sub>28</sub> N <sub>4</sub> S <sub>4</sub> Ni	44.79	44.36	6.03	5.79	11.49	11.50				
Ni(MD-C-II)	C <sub>30</sub> H <sub>56</sub> N <sub>4</sub> S <sub>4</sub> Ni	54.38	54.61	8.78	8.55	8.15	8.49				
Ni(MD-C-III)	C <sub>31</sub> H <sub>58</sub> N <sub>4</sub> S <sub>4</sub> Ni	55.68	55.26	8.79	8.68	8.19	8.32				
Ni(MD-C-IV)	C <sub>32</sub> H <sub>60</sub> N <sub>4</sub> S <sub>4</sub> Ni	54.73	55.88	8.99	8.79	7.90	8.15				
Ni(MB-C-II)	C <sub>20</sub> H <sub>20</sub> N <sub>4</sub> S <sub>4</sub> Ni	48.20	47.72	4.38	4.00	10.58	11.13				
Ni(MB-C-III)	C <sub>21</sub> H <sub>22</sub> N <sub>4</sub> S <sub>4</sub> Ni	48.89	48.75	4.52	4.29	11.01	10.83				
				[Ni(LH <sub>4</sub> )]Br <sub>2</sub>							
[Ni(CP-C-II)]Br <sub>2</sub>	C <sub>16</sub> H <sub>26</sub> N <sub>4</sub> S <sub>4</sub> NiBr <sub>2</sub>	30.39	30.94	4.82	4.22	9.01	9.02	8.13	9.45	23.79	25.72
[Ni(CH-C-II)]Br <sub>2</sub>	C <sub>18</sub> H <sub>30</sub> N <sub>4</sub> S <sub>4</sub> NiBr <sub>2</sub>	33.35	33.30	4.92	4.66	8.53	8.63	8.33	9.04	22.41	24.61
[Ni(MD-C-II)]Br <sub>2</sub>	C <sub>30</sub> H <sub>58</sub> N <sub>4</sub> S <sub>4</sub> NiBr <sub>2</sub>	44.85	43.86	8.14	7.12	6.99	6.82				
				(Ni <sub>2</sub> L) <sub>n</sub>							
Ni <sub>2</sub> (MD-C-II)	C <sub>30</sub> H <sub>54</sub> N <sub>4</sub> S <sub>4</sub> Ni <sub>2</sub>	49.80	50.29	7.68	7.60	8.29	7.82				
Ni <sub>2</sub> (MD-C-III)	C <sub>31</sub> H <sub>56</sub> N <sub>4</sub> S <sub>4</sub> Ni <sub>2</sub>	48.20	50.97	7.99	7.73	7.51	7.67				
Ni <sub>2</sub> (MD-C-IV)	C <sub>32</sub> H <sub>58</sub> N <sub>4</sub> S <sub>4</sub> Ni <sub>2</sub>	51.15	51.63	8.30	7.85	7.10	7.53				

<sup>a</sup> In percent.

that formed was collected by filtration. The filtrate showed only a trace of product by TLC and was discarded. The crude product was recrystallized from cyclohexane/chloroform (9:1). The yields and melting points for the various ligands are given in Table I.

**Synthesis of the Neutral Complexes Ni(LH<sub>2</sub>).** Method 1.<sup>19</sup> The cationic complex [Ni(MD-C-II)]Br<sub>2</sub> (0.25 mmol) was suspended in toluene (250 mL), and Et<sub>3</sub>N (0.55 mmol) was added with stirring. A dark red color appeared immediately. Stirring was continued for 2 h. The Et<sub>3</sub>NHBr that had formed was removed, together with unreacted starting material, by filtration. The filtrate was evaporated to dryness, and the red-violet product, Ni(MD-C-II), was dried in vacuo.

**Method 2.** The free ligand, LH<sub>4</sub> (1.1 mmol), was dissolved in acetone (60 mL) and Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O (1.0 mmol) in 1:1 acetone/water (80 mL) was added. A red-violet precipitate formed immediately, and the resulting mixture was stirred for 2 h at room temperature. The precipitate was then collected by filtration and washed thoroughly with 1:1 acetone/water. The crude products thus obtained were purified by extraction with warm acetone followed by chromatography on SiO<sub>2</sub>. The violet acetone-insoluble residue, which remained after the acetone extraction, was discarded. Chromatography on SiO<sub>2</sub> using toluene or benzene as eluent generated as many as four bands: yellow (free ligand), violet, blue (faint), and red (Ni(LH<sub>2</sub>)). The violet and blue bands did not represent much material and were not studied further. The red band (neutral complex) was collected, and if necessary, as evidenced by extraneous spots from analytical TLC, the complex was recrystallized from methanol/dichloromethane or other appropriate solvents. Some representative yields are 63% for Ni(CH-C-II) and 90% for Ni(MD-C-II). Analytical data appear in Table II.

**Synthesis of the Cationic Complexes [Ni(LH<sub>4</sub>)]Br<sub>2</sub>.** Method 1. The free ligand (1.0 mmol) was dissolved, with warming, in glacial acetic acid (100 mL). A solution containing HBr (10 mL of 47%) and Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O (1.0 mmol) in glacial acetic acid (30 mL) was then added with stirring to the ligand solution. A dark blue-black precipitate formed immediately. The product [Ni(LH<sub>4</sub>)]Br<sub>2</sub> was separated, washed thoroughly with warm acetic acid, and dried in vacuo. Yields were as follows: [Ni(CP-C-II)]Br<sub>2</sub>, 80%; [Ni(CH-C-II)]Br<sub>2</sub>, 72%; [Ni(MD-C-II)]Br<sub>2</sub>, 70%. Analytical data appear in Table II.

**Method 2.** Ni(LH<sub>2</sub>) (ca. 20 mg) was dissolved in dichloromethane (ca. 2 mL). HBr gas was passed through the red solution for several minutes whereupon the red color was discharged and a blue color obtained. For LH<sub>2</sub> = MD-C-II and CP-C-II, a dark blue precipitate formed (cationic complex). This precipitate was collected, washed with a small quantity of dichloromethane, and dried in vacuo. For LH<sub>2</sub> = CH-C-II, no precipitate formed, and so the blue reaction solution was taken to dryness; the resulting dark blue residue (cationic complex) was subsequently dried in vacuo. IR spectra for the MD-C-II and CP-C-II cationic complexes prepared by method 2 were essentially identical with spectra for the cations prepared by method 1. For [Ni(CH-C-II)]Br<sub>2</sub>, however, there were slight differences in the IR spectra of samples prepared by the two methods. But when a method 1 sample of [Ni(CH-

Table III. X-ray Crystal Data for Ni(CP-C-II)

NiS <sub>4</sub> N <sub>4</sub> C <sub>16</sub> H <sub>24</sub>	fw = 459.34
a = 25.152 (9) Å	space group = <i>Pbcn</i> (No. 60)
b = 7.998 (3) Å	T = 23 °C
c = 9.865 (5) Å	λ = 0.71069 Å
V = 1984.5 (1) Å <sup>3</sup>	ρ <sub>calc</sub> = 1.537 g cm <sup>-3</sup>
Z = 4	μ(Mo Kα) = 13.93 cm <sup>-1</sup>
transm factors = 0.89–1.00	R = 0.065; R <sub>w</sub> = 0.059

C-II)]Br<sub>2</sub> was dissolved in dichloromethane and the solution evaporated, the residue showed an IR spectrum similar to that for the method 2 sample.

The protonation of the neutral complexes was also attempted by using aqueous HBr but without success. (1) A mixture of Ni(LH<sub>2</sub>), excess 47% HBr, and glacial acetic acid was stirred at 25 °C for 2 days. The red color of the nearly insoluble Ni(LH<sub>2</sub>) remained unchanged. (2) A solution of Ni(LH<sub>2</sub>) in DMF (1 × 10<sup>-4</sup> M) was divided into four 10-mL aliquots. HBr (0.1 M in DMF prepared by using 47% aqueous HBr) was added to the aliquots in mole ratios (Ni(LH<sub>2</sub>):H<sup>+</sup>) of 1:1, 1:2, 1:3, and 1:4. The UV-vis spectra of the acidified solutions were unchanged from that of Ni(LH<sub>2</sub>).

**Preparation of the Polymer (Ni<sub>2</sub>L)<sub>n</sub>.** A solution containing the free ligand (1.0 mmol) in acetone was added to a stirred solution of Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O (2.2 mmol) in 1:1 acetone/ammonium hydroxide (200 mL). A dark red-violet precipitate formed immediately. Stirring was continued for 2 h. The product was then collected on a fine frit, washed thoroughly with a mixture of ammonia and acetone, and dried in vacuo. Analytical data appear in Table II.

**Thermal Techniques.** DSC and TGA analyses were run at heating rates of 10°/min (except where noted), controlled by a Du Pont Instruments 9900 computer/thermal analyzer under nitrogen purge (50 mL/min). DSC samples were run on a Du Pont Model 912 dual sample DSC (3–5 mg, closed pan) and calibrated with indium standards. TGA samples (10–15 mg) were run on a Du Pont Model 951 TGA. Du Pont DSC, TGA, and DSC purity software programs were used for all thermal data calculations.

**X-ray Data Collection and Reduction, Structure Solution, and Refinement for Ni(CP-C-II).** A red-brown plate crystal of Ni(CP-C-II) having approximate dimensions of 0.300 × 0.100 × 0.030 mm was mounted on a glass fiber. All measurements were made on a Rigaku AFC5R diffractometer with graphite-monochromated Mo Kα radiation and a 12-kW rotating anode generator (Table III).

Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range 15° < 2θ < 25°, corresponded to an orthorhombic cell with dimensions a = 25.152 (9) Å, b = 7.998 (3) Å, c = 9.865 (5) Å, and V = 1984.5 (1) Å<sup>3</sup>. For Z = 4 and a formula weight of 459.34, the calculated density is 1.537 g/cm<sup>3</sup>. On the basis of the systematic absences of 0kl, k ≠ 2n; h0l, l ≠ 2n; and hko, h + k ≠ 2n, and the successful solution and refinement of the structure, the space group was determined to be *Pbcn* (No. 60).

The data were collected at a temperature of 23 ± 1 °C by using the ω-scan technique to a maximum 2θ value of 44.9°. ω scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.34° with a take-off angle of 6.0°. Scans of (1.50 +

(18) Reaction temperature was 50–55 °C for the monododecyl derivatives.

(19) Only Ni(MD-C-II) was prepared by this method, since method 2 was found to be more straightforward. Ni(MD-C-II) can also be prepared by method 2.

0.30 (tan  $\theta$ ) $^\circ$  were made at a speed of 1.0 $^\circ$ /min (in  $\omega$ ). Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. The diameter of the incident beam collimator was 0.5 mm, and the crystal to detector distance was 40 cm.

A total of 1540 reflections were collected. The intensities of three representative reflections, which were measured after every 150 reflections, remained constant throughout data collection, indicating crystal and electronic stability (no decay correction was applied).

The linear absorption coefficient for Mo K $\alpha$  is 13.9 cm $^{-1}$ . An empirical absorption correction, based on azimuthal scans of several reflections, was applied that resulted in transmission factors ranging from 0.89 to 1.00. The data were corrected for Lorentz and polarization effects.

The structure was solved by the heavy-atom method. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculation in idealized positions ( $d_{C-H}$  = 0.95 Å) and were assigned isotropic thermal parameters that were 20% greater than the equivalent value of the atom to which they were bonded. The final cycle of full-matrix least-squares refinement was based on 662 observed reflections ( $I > 2.00\sigma(I)$ ) and 114 variable parameters and converged (largest parameter shift was 0.03 times its esd) with unweighted and weighted agreement factors of

$$R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.065$$

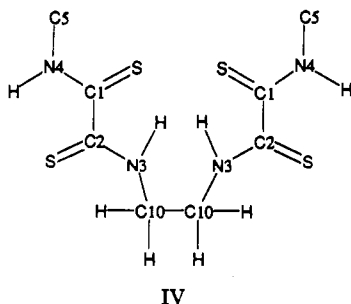
$$R_w = [\sum_w (|F_o| - |F_c|)^2 / \sum_w w F_o^2]^{1/2} = 0.059$$

The standard deviation of an observation of unit weight was 1.26. The weighting scheme was based on counting statistics and included a factor ( $p = 0.05$ ) to downweight the intense reflections. Plots of  $\sum_w (|F_o| - |F_c|)^2$  versus  $|F_o|$ , reflection order in data collection,  $(\sin \theta)/\lambda$ , and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.53 and -0.53 e/Å $^3$ , respectively.

Neutral-atom scattering factors were taken from Cromer and Waber.<sup>20</sup> Anomalous dispersion effects were included in  $F_c$ ,<sup>21</sup> the values for  $\Delta f'$  and  $\Delta f''$  were those of Cromer.<sup>22</sup> All calculations were performed by using the TEXSAN<sup>23</sup> crystallographic software package of the Molecular Structure Corp. Other crystal data details appear in Table III.

## Results

**Tetradentate DTO Ligands.** Tetradentate DTO ligands have been prepared by the reaction of  $N'$ -substituted DTO ligands with di-, tri-, and tetramethylenediamine (see eq 1), in methanol, at slightly elevated temperatures (35–55  $^\circ$ C), under  $N_2$ . For the MB-C-II, MB-C-III, MB-C-IV, CP-C-II, and CH-C-II derivatives,<sup>16</sup> aniline was added to the reaction mixture. Yields varied from a low of 11% for MB-C-II to a high of 87% for MD-C-IV (Table I). Elemental analyses (Table I) were within acceptable limits (0.4%) for all of the ligands, and a parent ion was observed for each ligand by electron impact mass spectrometry. On the basis of their  $^{13}C$  and  $^1H$  NMR spectra, the ligands have symmetric structures (structure IV). Tables of  $^{13}C$  and  $^1H$  NMR data and of selected infrared bands for several of the ligands are available as supplementary material.



IV

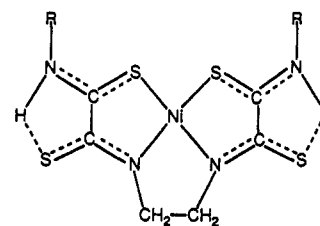
**Table IV.** Electronic Spectral Data for the Nickel Complexes

compd	medium	$\lambda_{max}$ , nm ( $10^{-3}\epsilon$ )		
		Ni(LH $_2$ )		
Ni(CP-C-II)	KBr	539	500	354
Ni(CH-C-II)	KBr	542	500	366
Ni(MD-C-II)	KBr	552	508 sh	340 sh
Ni(CP-C-II)	CHCl $_3$	525 (12.6)	484 (11.0)	352 (10.3)
Ni(CH-C-II)	CHCl $_3$	526 (12.3)	486 (10.8)	353 (10.0)
Ni(MD-C-II)	CHCl $_3$	526	485	353
[Ni(LH $_4$ )]Br $_2$				
Ni(CP-C-II) $^{2+}$	KBr	639	590	545
Ni(CH-C-II) $^{2+}$	KBr	630	578	540
Ni(MD-C-II) $^{2+}$	KBr	618	570	528
Ni(MD-C-II) $^{2+}$	CHCl $_3$	627	575	536
Ni(CH-C-II) $^{2+}$	CHCl $_3$	617	576	537
Ni(CP-C-II) $^{2+}$	DMF		529	490
Ni(CH-C-II) $^{2+}$	DMF		528	489
Ni(MD-C-II) $^{2+}$	DMF		525	483
(Ni $_2$ L) $_n$				
(Ni $_2$ (MD-C-II)) $_n$	KBr		588	
(Ni $_2$ (MD-C-III)) $_n$	KBr		588	
(Ni $_2$ (MD-C-IV)) $_n$	KBr		560	

**Table V.** Positional Parameters for Ni(CP-C-II)

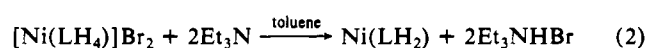
atom	x	y	z	B(eq), Å $^2$
Ni	1/2	0.5556 (3)	3/4	2.5 (1)
S1	0.4515 (1)	0.3745 (4)	0.6422 (4)	3.2 (2)
S2	0.3981 (1)	0.8374 (5)	0.4637 (4)	4.2 (2)
C1	0.4162 (4)	0.513 (1)	0.546 (1)	2.6 (6)
C2	0.4289 (4)	0.697 (1)	0.562 (1)	2.4 (6)
N3	0.4647 (4)	0.724 (1)	0.656 (1)	2.7 (5)
N4	0.3791 (4)	0.475 (1)	0.462 (1)	3.0 (6)
C5	0.3593 (4)	0.303 (2)	0.442 (2)	3.1 (7)
C6	0.3247 (6)	0.294 (2)	0.317 (2)	5.0 (9)
C7	0.2862 (7)	0.159 (2)	0.345 (2)	7 (1)
C8	0.2785 (6)	0.149 (2)	0.495 (2)	6 (1)
C9	0.3244 (6)	0.244 (2)	0.558 (1)	5.0 (8)
C10	0.4845 (5)	0.896 (1)	0.686 (1)	4.3 (8)

**Neutral Ni(LH $_2$ ) Complexes. Synthesis.** Two synthetic routes were used to prepare neutral nickel(II) complexes of a number of the new tetradentate DTO ligands. The species were expected to have structure V. The first method involved deprotonation



V

of a cationic complex (eq 2). This method was used only for Ni(MD-C-11). The second method was more direct and did not



involve the isolation of the cationic intermediates. It was used for all of the neutral Ni(LH $_2$ ) complexes listed in Table II. The reaction follows eq 3.



**Characterization.** Elemental analyses (Table II) for the neutral complexes were within acceptable limits (<0.4%) for most of the compounds. Electron impact mass spectra showed the expected molecular ions for Ni(CP-C-II), Ni(CH-C-II), and Ni(MD-C-II), together with easily rationalized fragment ions resulting from loss of organic groups from the complexes. Mass spectra of the remaining Ni(LH $_2$ ) compounds did not show their respective mo-

- (20) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2A.
- (21) Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781.
- (22) Cromer, D. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.3.1.
- (23) TEXSAN-TEXRAY Structure Analysis Package, Molecular Structure Corp., 1985.

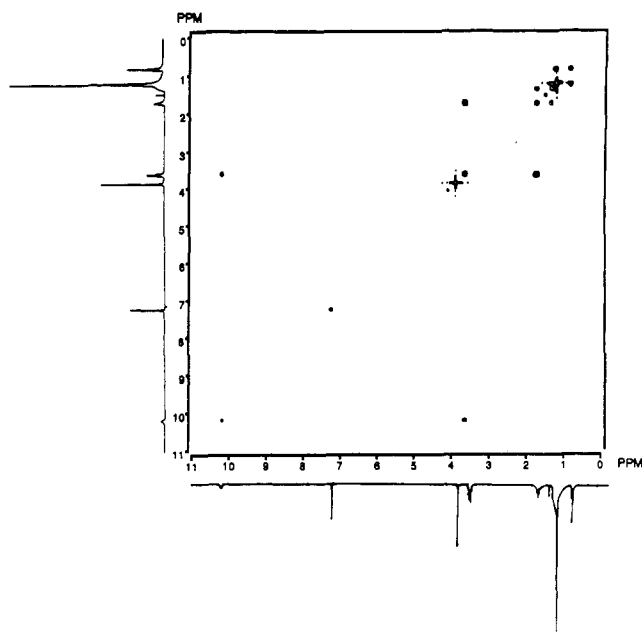


Figure 1. Two-dimensional  $^1\text{H}$  NMR spectrum of Ni(MD-C-II) in chloroform- $d$ .

lecular ions, the highest mass peaks observed being those of the free ligands.

Tables of  $^{13}\text{C}$  and  $^1\text{H}$  NMR data, selected infrared bands, and mass spectral data for several of the neutral Ni(II) complexes are available as supplementary material. Electronic spectral data are reported in Table IV. Ni(MD-C-II) was studied by 2D NMR spectroscopy (see Figure 1). Ni(CP-C-II) was studied by X-ray diffraction (Table III and supplementary material), and its molecular geometry is shown in Figure 3. Positional parameters for Ni(CP-C-II) are listed in Table V.

In the  $^1\text{H}$  NMR spectra of the neutral complexes one of the resonances assignable to NH protons in the free ligands disappears completely. This indicates that the two protons lost from the ligand when the metal binds must come from equivalent sites. The coupling pattern of Ni(MD-C-II), as elucidated by 2D  $^1\text{H}$  NMR spectroscopy (Figure 1), shows that the proton on N4 ( $\delta = 10.20$ ) is coupled to the protons on C5, providing unambiguous assignment of that resonance. Consequently, the two protons removed from the ligands ( $\text{LH}_4$ ) in forming the complexes ( $\text{Ni}(\text{LH}_2)$ ) are, as expected, those of the inner N atoms (N3).

Generally, DTO ligands exhibit bands of medium to strong intensity near  $1500\text{ cm}^{-1}$ , which are assigned to vibrations of predominantly C-N character.<sup>6b,7,12a,24</sup> For the ligands, one  $\nu_{\text{CN}}$  band is observed at  $1502\text{--}1520\text{ cm}^{-1}$ . In contrast, the  $\text{Ni}(\text{LH}_2)$  complexes exhibit two  $\nu_{\text{CN}}$  bands, one at higher energy ( $1549\text{--}1569\text{ cm}^{-1}$ ) and the other at lower energy ( $1472\text{--}1482\text{ cm}^{-1}$ ). The band at higher energy is consistent with coordination of an NCS fragment to the metal through sulfur. Similar shifts have been reported for bidentate DTO complexes of Pd(II), Ni(II), and Cu(II).<sup>7,12a,24</sup> Unlike their bidentate analogues, the tetradentate ligands are also coordinated through the nitrogens of NCS fragments, and thus, a  $\nu_{\text{CN}}$  band is observed at lower energy. However, it should be noted that the shift to lower energy is perhaps smaller than it might otherwise be, because the coordinated nitrogen has been deprotonated in forming the complex. Deprotonation without coordination should shift the  $\nu_{\text{CN}}$  band to higher energy. The observed shift to lower energy is an indication of the strength of the corresponding Ni-N bond.

Thermal properties were examined for two of the ligands and their neutral complexes. The differential scanning calorimetry (DSC) of the free ligand MD-C-II shows essentially a single melting point centered at  $75.6\text{ }^\circ\text{C}$ , although a small impurity

feature appeared at  $65\text{ }^\circ\text{C}$ . The thermogravimetric analysis (TGA) of the ligand is typical of dithiooxamides and involves volatilization coupled with decomposition, leaving behind an amorphous decomposition product. Weight loss does not begin, however, until  $260\text{ }^\circ\text{C}$ .

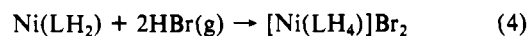
The DSC of the neutral nickel(II) complex of MD-C-II (Figure 2A) shows that a small amount of free ligand contaminant was present in the sample, giving a barely detectable endotherm at the ligand melting point. This was followed by two weak, but reproducible, endotherms centered at  $107$  and  $167\text{ }^\circ\text{C}$ . If these are due to reversible phase transitions, then a second cooling/heating cycle would again show them. On the second scan (Figure 2B), the  $107\text{ }^\circ\text{C}$  feature is completely lost while the lower temperature transition in the  $70\text{ }^\circ\text{C}$  region is enhanced in both intensity and complexity and the  $167\text{ }^\circ\text{C}$  transition appears to be unaffected. Assigning the increase in the  $70\text{ }^\circ\text{C}$  region to an increase in the amount of free ligand present leads to the inference the thermal decomposition process gives polymer and free ligand, as has been reported for complexes of simpler dithiooxamide ligands.<sup>25</sup> A third cycle (Figure 2C) also showed some decrease in the intensity and change in shape of the high-temperature peak ( $165\text{ }^\circ\text{C}$ ). Visual observation revealed that the sample melts to a deep red oil at  $167\text{ }^\circ\text{C}$  and that the oil cools to a red solid. Melting points have not been observed for other neutral nickel(II) complexes of dithiooxamide ligands. TGA revealed (Figure 2D) no weight loss below about  $230\text{ }^\circ\text{C}$ , after which a complicated decomposition process occurs. The two main weight loss transitions calculate to be  $26.1\%$  and  $24.1\%$ , respectively, values that compare reasonably well with those expected for loss of a dodecyl group ( $25.6\%$ ). However, more rational possibilities follow from the results with the ligand CH-C-II and its neutral nickel(II) complex.

The DSC of the free ligand CH-C-II is clean with a single sharp melting point centered at  $141.6\text{ }^\circ\text{C}$ . The TGA of the compound is typical, involving a complicated decomposition/volatilization beginning at about  $250\text{ }^\circ\text{C}$  and ending in an amorphous product. The DSC of the neutral nickel(II) complex of this ligand, while reproducible, provides only limited information. Exothermic decomposition starting at about  $225\text{ }^\circ\text{C}$  and an endotherm that starts at  $250\text{ }^\circ\text{C}$  are accompanied by weight losses calculated to be  $15.43\%$  ( $118.86\text{ Da}$ ) ( $\text{Da} = \text{Dalton}$ ) and  $23.49\%$  ( $109.80\text{ Da}$ ), respectively. These may be compared to the loss of the elements of cyclohexyl mercaptan ( $128.2\text{ Da}$ ) and cyclohexyl isocyanide ( $109.17\text{ Da}$ ). The TGA is also a little unusual in that the complex does not decompose gradually. The exothermic decomposition appears in the DSC as a sharp change from exotherm to endotherm and in the TGA as a sharp onset of weight loss. Similar behavior has been reported earlier.<sup>25</sup> Finally, substantial residue remains even at  $800\text{ }^\circ\text{C}$ .

**Cationic  $[\text{Ni}(\text{LH}_4)]\text{Br}_2$  Complexes.** Reaction of  $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  with  $\text{LH}_4 = \text{CP-C-II}$ ,  $\text{CH-C-II}$ , or  $\text{MD-C-II}$  in glacial acetic acid in the presence of the strong acid HBr gave salts of cationic complexes of the general formula  $[\text{Ni}(\text{LH}_4)]\text{Br}_2$ . These compounds precipitated directly from the reaction mixture as dark blue-black solids, a behavior completely analogous to that of bidentate dithiooxamide derivatives.

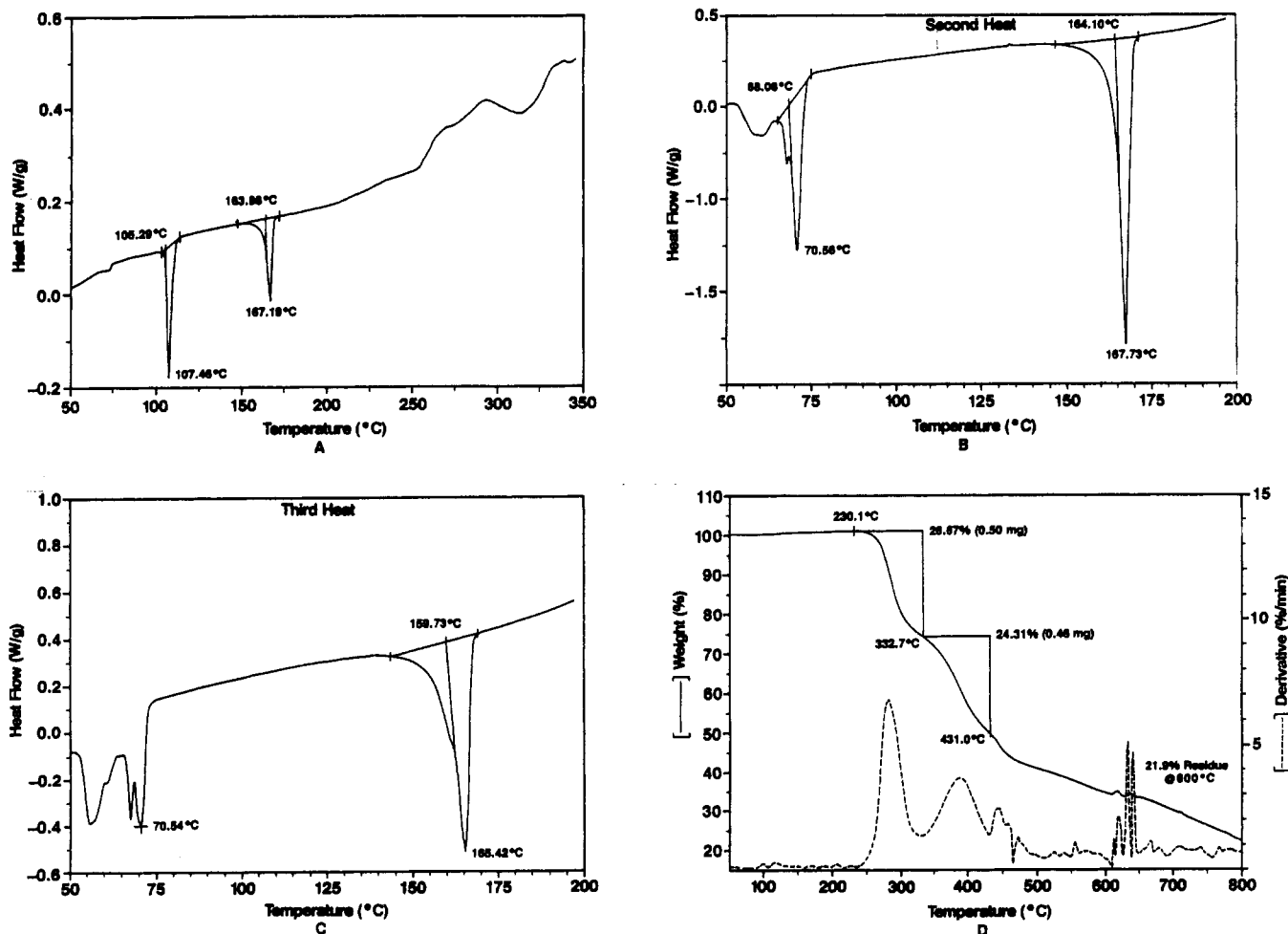
Elemental analyses (see Table II) show significant deviations from the calculated values. However, due to their very limited solubilities in common organic solvents and water, attempts to purify these products failed. A parent ion was observed by fast atom bombardment mass spectroscopy for  $[\text{Ni}(\text{CH-C-II})]\text{Br}_2$ . No ions of significant intensity were observed by this technique for the other two cationic complexes that were prepared. Infrared data for the cationic complexes are available as supplementary material.

The cationic complexes can also be prepared by reaction of their neutral counterparts with HBr gas in dichloromethane solvent (eq 4). No reaction of the  $\text{Ni}(\text{LH}_2)$  complexes occurs with aqueous

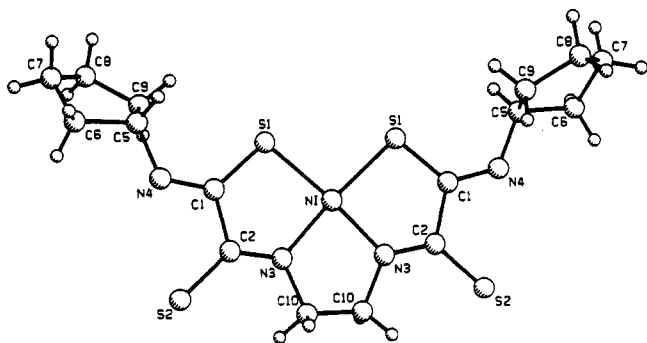


(24) Sloodmaekers, B.; Perlepes, S. P.; Desseyne, H. O. *Spectrochim. Acta* 1989, 45A, 1211.

(25) Whitcomb, D. R.; Jubran, N.; Busch, D. H. *Thermochim. Acta* 1990, 167, 111.



**Figure 2.** Differential scanning calorimetry (DSC) of the neutral complex Ni(MD-C-II): (A) first scan, no preheating; (B) second scan, obtained after preheating sample to 125 °C and cooling to room temperature; (C) third scan, obtained after a second preheating treatment to 125 °C. Thermal gravimetric analysis (TGA) of Ni(MD-C-II) is shown in (D).



**Figure 3.** PLUTO diagram of Ni(CP-C-II).

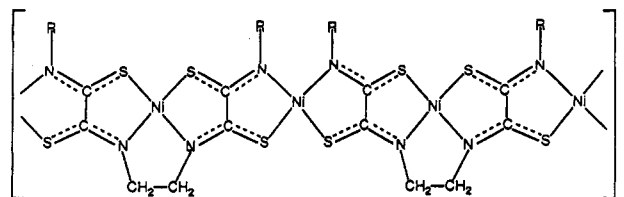
HBr in either DMF solution or as a suspension in glacial acetic acid, attesting to the strongly acidic conditions required for their protonation. The cationic complexes are readily converted back to the neutral complexes by reaction with weak bases such as  $\text{Et}_3\text{N}$ .

The facile interconversion of the neutral and cationic complexes by protonation/deprotonation suggests that their coordination spheres are the same ( $\text{NiN}_2\text{S}_2$ ). The strongly acidic conditions required for formation of the cationic complexes is consistent with the site of protonation being the weakly basic exo-sulfur atoms. Whereas in the free ligands all the nitrogens are protonated, in the complexes the inner coordinated nitrogens, which have a large degree of  $\text{sp}^2$  character, can only be protonated with either a significant distortion from planarity of the NiSCCN chelate rings or removal of N from the coordination sphere about nickel.

**Polymeric  $(\text{Ni}_2\text{L})_n$  Compounds.** Reaction of the tetradentate monododecyl-DTO ligands, MD-C-II, MD-C-III, and MD-C-IV,

with nickel(II) under basic conditions gave dark violet insoluble compounds that are believed to be polymeric. Elemental analyses for these compounds are given in Table II. The calculated values, which are for polymers of infinite chain length and, hence, the ideal Ni:ligand ratio of 2:1, show rough agreement.

No  $\nu_{\text{NH}}$  bands are seen in IR spectra of the  $(\text{Ni}_2\text{L})_n$  polymers, and their absence is consistent with the expected complete deprotonation of the ligands. In contrast, the neutral complexes show an  $\nu_{\text{NH}}$  band at ca.  $3050\text{ cm}^{-1}$ , and the cationic complexes show an  $\nu_{\text{NH}}$  band near  $3200\text{ cm}^{-1}$ . The cationic complexes also show a broad band between  $2650$  and  $2850\text{ cm}^{-1}$ . This broad band, which is absent in the neutral complexes, is assigned as  $\nu_{\text{NH}}$  for an N-H-Br hydrogen bond. A possible structure for the polymeric materials is shown in VI.



VI

## Discussion

**Structure of Ni(CP-C-II).** The molecular geometry of the neutral complex Ni(CP-C-II) (V) is shown in Figure 3. The ligand is tetradentate and coordinates to nickel in a symmetric, nearly planar SNNS fashion, forming three fused five-membered chelate rings. About nickel, the geometry is distorted from square

**Table VI.** Selected Interatomic Angles (deg) and Distances (Å) for Ni(CP-C-II) and Related Ni Complexes

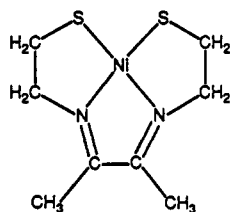
	Angles		
	Ni(CP-C-II) (V)	VII <sup>a</sup>	VIII <sup>b</sup>
S1-Ni-S1'	96.3 (2)	97.3 (4)	96.7
N3-Ni-N3'	87.0 (7)	82.9 (11)	82.1
N3-Ni-S1	88.4 (3)	90.0 (9)	91.5
N3-Ni-S1		89.8 (9)	89.9
N4-C1-S1	126 (1)		
N4-C1-C2	117 (1)		
S1-C1-C2	118 (1)		
N3-C2-S2	128 (1)		
N3-C2-C1	112 (1)		
S2-C2-C1	120 (1)		
C2-N3-C10	122 (1)		
C2-N3-Ni	123.9 (8)		
C10-N3-Ni	114.3 (8)		
C1-N4-C5	123 (1)		
C1-S1-Ni	97.6 (5)		
C10-C10-N3	110.0 (7)		

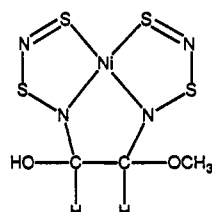
	Distances			
	Ni(CP-C-II) (V)	VII <sup>a</sup>	VIII <sup>b</sup>	IX <sup>c</sup>
Ni-S1	2.171 (4)	2.168 (11)	2.139	2.169
Ni-S1		2.146 (11)	2.132	2.165
Ni-N3	1.86 (1)	1.86 (2)	1.861	
Ni-N3		1.85 (3)	1.860	
C1-S1	1.70 (1)			
C2-S2	1.67 (1)			
C1-N4	1.29 (1)			
C2-N3	1.31 (1)			
C5-N4	1.47 (1)			
C10-N3	1.49 (1)			
C1-C2	1.52 (2)			
C10-C10'	1.49 (3)			

<sup>a</sup> (*N,N'*-Bis(mercaptoethyl)biacetyl diiminato)nickel(II); see structure VII.<sup>26</sup> <sup>b</sup> [Ni(C<sub>3</sub>H<sub>6</sub>O<sub>2</sub>N<sub>4</sub>S<sub>4</sub>)]; see structure VIII.<sup>27</sup> <sup>c</sup> Bis(quinoxaline-2,3-dithiolato)nickel(II); see structure IX.<sup>14b</sup>

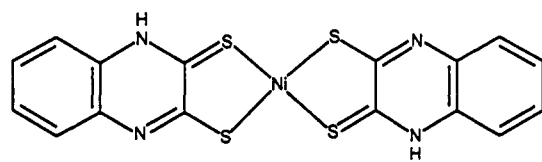
planar to a nearly trapezoidal arrangement. This is evidenced by an obtuse S-Ni-S angle (96.3°), an acute N-Ni-N angle (87.0°), and identical N-Ni-S angles (88.4°). A similar trapezoidal geometry has been observed in other tetradentate SNNS complexes of Ni. Listed in Table VI are the corresponding angles about Ni for (*N,N'*-bis(mercaptoethyl)biacetyl diiminato)nickel(II) (structure VII) and Ni(C<sub>3</sub>H<sub>6</sub>O<sub>2</sub>N<sub>4</sub>S<sub>4</sub>) (structure VIII).<sup>26,27</sup> Note



VII



VIII



IX

especially the obtuse S-Ni-S angles (97.3 and 96.7°, respectively) and the acute N-Ni-N angles (82.9 and 82.1°, respectively). There is a slight tetrahedral distortion (<0.07 Å) from planarity of the NiN<sub>2</sub>S<sub>2</sub> subunit in V. A similar distortion was noted for VII.

Both the Ni-N (1.86 Å) and Ni-S (2.171 Å) distances are in the range expected for planar Ni(II) complexes, and they also compare favorably with those reported for VII (Ni-N<sub>av</sub> = 1.85 Å and Ni-S<sub>av</sub> = 2.157 Å; see Table VI).<sup>29</sup> For VIII, the Ni-N<sub>av</sub> distance is comparable (1.861 Å), but the Ni-S<sub>av</sub> distance is somewhat shorter (2.135 Å) than that in V.

Important interatomic distances in the ligand suggest a delocalized electronic structure (Table VI). The C1-S1 and C2-S2 distances, at 1.70 and 1.67 Å each, are significantly shorter than would be expected for C-S single bonds. For example, in VII, where S is bonded to an sp<sup>3</sup> carbon, the C-S distances are each 1.82 Å. The structures of other substituted DTO ligands and their complexes show similarly short C-S bonds (see above). Indeed, the C-S bond lengths in V are comparable to those in the dithiocarbonyl complexes [Ni(S<sub>2</sub>CPh)<sub>2</sub>]<sub>3</sub> and [Ni(S<sub>2</sub>CCH<sub>2</sub>Ph)<sub>2</sub>]<sub>2</sub> (Ni-S<sub>av</sub> = 1.68 and 1.69 Å, respectively), where the formal C-S bond order is 1.5.<sup>29</sup> Also, the C1-N4 and C2-N3 distances are much shorter than the C-N single bonds, C5-N4 and C10-N3, in the same molecule, indicating considerable multiple-bond character. Despite the evident delocalization over each of the two distinct NCS subunits and the flatness of the NiS1C1C2N3 chelate rings, it does not appear that the delocalization extends between the two NCS subunits and across the C1-C2 bond. At 1.52 Å, this bond is of normal length for a C-C single bond.

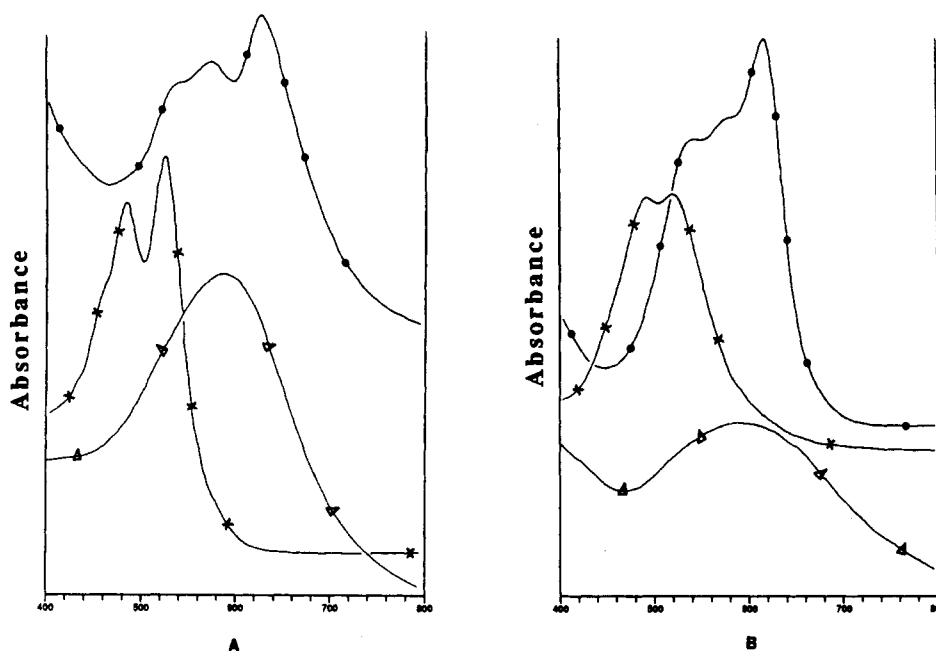
The C-S and C-N distances in the S1C1N4 and S2C2N3 subunits are complementary. That is, the longer C1-S1 distance (1.70 Å), a result of S-coordination to Ni, is complemented by a shorter C1-N4 distance (1.29 Å). The reverse is true for the S2C2N3 subunit. Here, the longer C2-N3 length (1.31 Å), a result of N-coordination to Ni, is complemented by a shorter C2-S2 length (1.67 Å). In each subunit the sums of the C-S and C-N distances are nearly the same (2.99 and 2.98 Å). A similar complementary effect was observed in bis(quinoxaline-2,3-dithiolato)nickel(II) (structure IX).<sup>14b</sup> In this case both sulfurs are coordinated to Ni, but one of the nitrogens is protonated and the other is not. In IX the two complementary C-S/C-N distance pairs are 1.703/1.333 Å (protonated nitrogen) and 1.732/1.313 Å.

None of the hydrogen atoms for V was located. Those shown in Figure 3 are for idealized positions. Two hydrogen atoms not shown are those of the N4 and N4' amide moieties. Above, we proposed their attachment to N4 and N4' on the basis of <sup>1</sup>H NMR evidence. Note that the C1-N4-C5 angle (123°) is near the trigonal-planar value, suggesting that the amide hydrogens of N4 and N4' are in the plane and directed toward the coplanar atoms S2 and S2'. The possibility exists for an intramolecular hydrogen bond, though it should be rather weak because of the somewhat long N4-S2 distance.

**Electronic Spectra.** UV-visible spectral data for three of the neutral complexes are listed in Table IV. Each neutral complex exhibits two well-resolved bands near 500 nm and a third band near 350 nm. The intensities of the bands near 500 nm ( $\epsilon = 10000$ - $12600$ ) are consistent with their being of the charge-transfer type. The solution (chloroform) and solid-state (KBr) spectra are similar and quite broad, though the bands are shifted somewhat to shorter wavelengths in solution. As Figure 4 shows, the general character of these spectra is very similar to that of the corresponding complexes of the long-known symmetrically disubstituted bidentate DTO ligands. Because of the differences in donor atoms used in chelation for the two families of complexes, this was not necessarily expected. The similarity is probably a consequence of the fact that, in the charge-transfer transitions, the donor electrons remain at closely similar energies and the

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**Figure 4.** Electronic spectra (visible region, wavelengths in nm) for the cationic ( $\cdot$ ), neutral ( $\times$ ), and polymeric ( $\Delta$ ) Ni(II) complexes of the tetradentate (DTO)<sub>2</sub> ligand MD-C-II (A) and the cationic ( $\cdot$ ), neutral ( $\times$ ), and polymeric ( $\Delta$ ) Ni(II) complexes of the bidentate DTO ligand *N,N'*-dicyclohexyl-DTO (B). Spectra for the cationic and neutral complexes were recorded in chloroform. Spectra for the polymeric materials were recorded in KBr. Absorbances are not to scale.

ligand acceptor orbitals are not greatly altered by the different modes of chelation.

Electronic spectra for each of the cationic complexes,  $[\text{Ni}(\text{L}-\text{H}_4)]\text{Br}_2$ , are similar (Table IV), and when compared to those of their neutral counterparts,  $\text{Ni}(\text{LH}_2)$ , the absorption bands in the visible region are shifted to lower energies. In addition, while only two well-resolved bands are seen near 500 nm in spectra of the neutral complexes, three bands are clearly evident above 500 nm for the cationic compounds. A very similar spectral pattern is also seen in the cationic Ni(II) complexes of symmetrically substituted bidentate DTO ligands (Figure 4). As was noted above for the neutral complexes, this similarity between spectra for tetradentate and bidentate complexes is unexpected in view of their different ligand donor sets ( $\text{N}_2\text{S}_2$  versus  $\text{S}_4$ ). The multiple bands in the visible region for the cationic Ni(II) complexes of symmetrically substituted bidentate DTO ligands,  $[\text{Ni}(\text{L}'\text{H}_2)_2]\text{Br}_2$ , have been assigned as  $\text{M}(\text{d})-\text{L}(\pi^*)$  transitions.<sup>9b</sup> Given their similarity, this assignment is probable for the visible bands of the tetradentate cationic complexes. The band that occurs near 350 nm in the neutral complexes is either absent or obscured in spectra of the cationic complexes.

The electronic spectra of the cations measured in a poor donor solvent, such as chloroform, were found to be in good agreement with their spectra when the samples were dispersed in KBr. When recorded in the more polar solvent DMF, however, a considerable shift in the bands in the visible region was observed, together with a reduction in the number of resolved bands in this region from three to two. Interestingly, the two new bands in DMF solution are very close in energy to those observed for their neutral analogues. A similar dependence of the band maxima on the donor properties of the solvent has been previously demonstrated for the bidentate ligand derivatives,<sup>30</sup>  $[\text{Ni}(\text{L}'\text{H}_2)_2]\text{Br}_2$ . This dependence is believed to be due to a hydrogen-bonding interaction of the solvent with the amide hydrogens of the complex or even complete deprotonation to give a monocation or a neutral complex. As was discussed above, deprotonation of the cationic complexes to give the neutral complexes requires only a weak base such as  $\text{Et}_3\text{N}$ . However, an important difference between the spectra of the

cationic complexes in DMF solution and the neutral complexes is the absence of a well-resolved band near 350 nm in the former.

The solid-state electronic spectra for the polymeric compounds in KBr (Table IV, Figure 4) show a broad unresolved band in the visible region centered near 580 nm. They are clearly different from both the neutral and cationic complexes but are very similar to those of their polymeric bidentate DTO analogues.

All of the tetradentate complexes, be they neutral, cationic, or polymeric, have an intense band in the UV region near 310 nm. A band at this wavelength is also present in the free ligands. For the  $[\text{Ni}(\text{L}'\text{H}_2)_2]\text{Br}_2$  complexes, an intense band in the UV region at 315 nm was assigned as  $\text{L}(\pi)-\text{L}(\pi^*)$ ,<sup>9b</sup> and this assignment is reasonable for the 310-nm band of the tetradentate compounds.

### Summary

Tetradentate ligands have been synthesized by linking two substituted DTO's via a short hydrocarbon chain. Cationic, neutral, and polymeric Ni(II) complexes of these new ligands have been prepared and studied. The crystal structure of one of the neutral complexes ( $\text{Ni}(\text{CP-C-II})$ ) has been solved, demonstrating the  $\text{N}_2\text{S}_2$  chelating nature of the ligand. Interconversion of the neutral and cationic complexes was found possible by protonation/deprotonation. The protonation reaction requires very acidic conditions. This interconversion suggests that the coordination environment in the cationic complexes is the same as that for the neutral complexes ( $\text{N}_2\text{S}_2$ ). It is interesting to note that the electronic properties of the three different forms of complexes studied for the tetradentate ligands are remarkably similar to their counterparts derived from bidentate DTO ligands, despite the difference in the coordination environments for both the neutral and cationic compounds ( $\text{N}_2\text{S}_2$  versus  $\text{S}_4$ ).

**Acknowledgment.** The support of this research by the 3M Co. is gratefully acknowledged.

**Supplementary Material Available:** Complete listings of bond lengths, bond angles, X-ray crystal data, conformation angles, intermolecular distances, general temperature factor expressions ( $U$ 's), hydrogen atom coordinates, and least-squares planes for V and tables of  $^{13}\text{C}$  and  $^1\text{H}$  NMR data, selected IR bands, and mass spectral data for various ligands ( $\text{LH}_4$ ) and their complexes ( $\text{Ni}(\text{LH}_2)$ ,  $[\text{Ni}(\text{LH}_4)]\text{Br}_2$ ,  $(\text{Ni}_2\text{L})_n$ ) (12 pages); a listing of calculated and observed structure factors for V (9 pages). Ordering information is given on any current masthead page.

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