

=  $(0.53-10.9) \times 10^{-3} M$  values were computed from eight data sets, each set containing from five to seven observations. The results were  $(3.28 \pm 1.70) \times 10^4$  and  $(3.43 \pm 0.87) \times 10^4$ , respectively, from observations at 7240 and 9605 Å.

The reaction of  $O_2$  (saturated solution in 1.0  $M$   $HClO_4$  at 25°) with  $Np(III)$  (*ca.*  $2 \times 10^{-4} M$ ) is complete within the 10-sec time of mixing and initial observation. The reaction of  $Np(IV)$  with  $O_2$  is measurable but orders of magnitude slower. For example, after *ca.* 16 hr (concentration of  $O_2$  kept constant at saturation in 0.01  $M$   $HClO_4$ , 25°) a solution originally  $9.81 \times 10^{-4} M$  in  $Np(IV)$  decreased to  $5.92 \times 10^{-4} M$   $Np(IV)$ .<sup>8</sup>

Table I contains a summary of pertinent experimental

TABLE I  
PER CENT  $Np(V)$  PRODUCED FROM THE  
REACTION  $Np(III) + O_2^a$

[ $HClO_4$ ], $M$	$I^c$	$10^4[Np(III)]$ , $M$	% $Np(V)^d$	Exptl redn power $\times 10^4$ , ml/mequiv	Calcd redn power $\times 10^4$ , ml/mequiv
0.029	0.029	19.3	43.7 ± 0.05	3.84 ± 0.15	5.33
0.015	0.015	11.6	40.0 ± 0.6	2.26 ± 0.15	2.70
0.0076	0.0076	5.32	36.0 ± 0.1	1.32 ± 0.05	1.39
0.0070	1.0	5.55	29.2 ± 2.5	1.30 ± 0.09	1.39
0.121	1.0	5.29	19.0 ± 0.3	1.33 ± 0.03	1.39
0.714	1.0	5.61	16.0 ± 0.1	1.56 ± 0.01	1.50
1.1	1.1	4.36	17.5 ± 0.2	1.24 ± 0.01	1.27
1.1	1.1	5.15	18.0 ± 0.1	1.39 ± 0.01	1.39
1.1	1.1	14.7	21.6 ± 0.1	4.70 ± 0.07	5.33
4.4	4.4	20.5	2.14 ± 1.4	4.80 ± 0.04	5.33

<sup>a</sup> Average of two or three determinations; uncertainty is average deviation from mean. <sup>b</sup> Initial concentration in reaction vessel. <sup>c</sup> Maintained with  $LiClO_4$ . <sup>d</sup> %  $Np(V) = [Np(V)] / ([Np(IV)] + [Np(V)]) \times 100$ . <sup>e</sup> Based on calculated initial [ $Np(III)$ ], in sample titrated.

results. It is of interest to note that (a) the major product is  $Np(IV)$ , (b) the most important path that results in the production of  $Np(V)$  is not strongly dependent on hydrogen ion concentration, and (c) for initial concentrations of  $Np(III)$  less than  $9 \times 10^{-4} M$  the reducing power of the spent reaction mixture is the same as that of the original solution.

The last point noted, as well as the spectrophotometric observations, is consistent with the interpretation that hydrogen peroxide is produced in the course of the reaction between oxygen and  $Np(III)$ . A further implication is that hydrogen peroxide does not compete favorably as an oxidant with oxygen under these experimental conditions.

A summary of the results obtained from some observations on the reaction between  $H_2O_2$  and  $Np(III)$  is presented in Table II. It should be noted that it was not possible to describe either the rate of disappearance of  $Np(III)$  nor the rate of appearance of  $Np(V)$  by simple first- or second-order rate laws. The concentration of  $Np(V)$  as a function of time (monitored at

(7) The data were not consistent with a model based on the formation of a 1:1 complex. Indirect support for the formulation advanced is provided by analogy with the  $Pu(IV)-H_2O_2$  system as discussed by R. E. Conrick and W. H. McVey, *J. Amer. Chem. Soc.*, **71**, 1534 (1949).

(8) It should be noted that although *ca.* 40% of the  $Np(IV)$  was oxidized, the reducing powers of aliquots of the initial and final reaction mixtures (measured by  $Ce(IV)$  consumption) were identical.

TABLE II

THE  $Np(III)-H_2O_2$  SYSTEM<sup>a</sup>

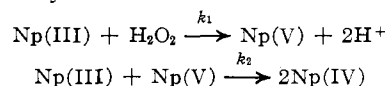
$10^4$ [ $Np(III)$ ], $M$	$\frac{[Np(IV)]}{([Np(III)] + [Np(IV)])}$	$\frac{[H_2O_2]}{[Np(IV)]}$	% $Np(V)^c$	$K,^d$ $M^{-1} sec^{-1}$
4.28 <sup>b</sup>	0.363	0.520	60.5 ± 1.1	36, 31 <sup>e</sup>
3.12-4.90	0.260-0.530	0.530	14.1 ± 1.5	38
1.26-6.63	0.023-0.530	1.06	23.4 ± 1.8	35, 34 <sup>e</sup>
4.23 <sup>b</sup>	0.530	1.06	78.3 ± 3.1	

<sup>a</sup> 25°, 1.0  $M$   $HClO_4$ ; uncertainties are average deviations from mean. Initial concentrations of  $Np(III)$ ,  $Np(IV)$ , and  $H_2O_2$  were used in calculation of ratios. <sup>b</sup> In 0.10  $M$   $HClO_4$ . <sup>c</sup> %  $Np(V) = ([Np(V)] \text{ formed}) / ([Np(III)] + [Np(IV)]) \times 100$ . <sup>d</sup> Calculated from limiting slopes at 9805 Å. Rate parameters are defined as  $(d[Np(V)]/dt)_{t=0} = k[H_2O_2] = -(d[Np(III)]/dt)_{t=0}$ . Uncertainties of 10% associated with these rate constants: see A. Zielen, J. C. Sullivan, D. Cohen, and J. C. Hindman, *J. Amer. Chem. Soc.*, **80**, 5632 (1958), for vicissitudes encountered in the calculation of rate parameters from limiting slopes. <sup>e</sup> Calculated from limiting slopes at 2670 Å.

9805 Å) increased to a maximum value before reaching the final value.

The salient points to be noted from these data are (a) the percentage of  $Np(V)$  formed is not directly proportional to increased ratio of peroxide to initial concentrations of  $Np(III)$  and  $Np(IV)$ , (b) the percentage of  $Np(V)$  formed is not dependent upon the mole fraction of  $Np(IV)$  originally present, and (c) the initial rate parameters for the disappearance of  $Np(III)$  or appearance of  $Np(V)$  are the same within the limitation noted.

The data that have been presented are consistent with the following comments. (1) The oxidation of  $Np(III)$  by oxygen can be described in terms of either an initial 1- or 2-equiv change. There is no compelling evidence presented that would serve as a basis for discrimination between these mechanisms. (2) The oxidation of  $Np(III)$  by hydrogen peroxide may involve a minor path of sequential 1-equiv changes. The major path may well be



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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,  
UNIVERSITY OF CALIFORNIA, RIVERSIDE, CALIFORNIA 92502

### Base-Induced Configurational Changes in Titanium(III) D-(−)-1,2-Propylenediaminetetraacetate<sup>1</sup>

BY KENNETH P. CALLAHAN, GORDON A. OSTROM,<sup>†</sup>  
AND RICHARD M. WING\*

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Complexes of  $d^1$  metals, although labile, can be

\* To whom correspondence should be addressed.

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studied and isolated in their optical enantiomers by the use of multidentate chelating agents which render the complexes relatively inert. We have previously reported<sup>2</sup> the stereospecific synthesis of a dimeric molybdenum(V) complex of D(-)-1,2-propylenediaminetetraacetic acid<sup>3</sup> (PDTA), **1**. We now wish to discuss our observations on the complex formed between **1** and trivalent (d<sup>1</sup>) titanium, particularly the sign inversion of the 5500-Å circular dichroism band occasioned by alterations in pH.

Podlahova and Podlaha<sup>4</sup> have investigated the titanium(III)-ethylenediaminetetraacetic acid (EDTA) system and reported a reversible pH dependence in the electronic spectrum which was interpreted in terms of three different complexes—HTiEDTA(H<sub>2</sub>O), TiEDTA<sup>-</sup>, and Ti(OH)EDTA<sup>2-</sup>—containing, respectively, pentacoordinate, hexacoordinate, and pentacoordinate ligands. The electronic spectrum of the Ti(III)-D(-)PDTA system shows, as expected, similar pH dependence.

The circular dichroism (CD) spectrum of the Ti(III)-D(-)PDTA system exhibits reversible pH dependence, with the 5500-Å CD band actually inverting in sign as pH is progressively increased. The shape of this band at several different pH values is shown in Figure 1.

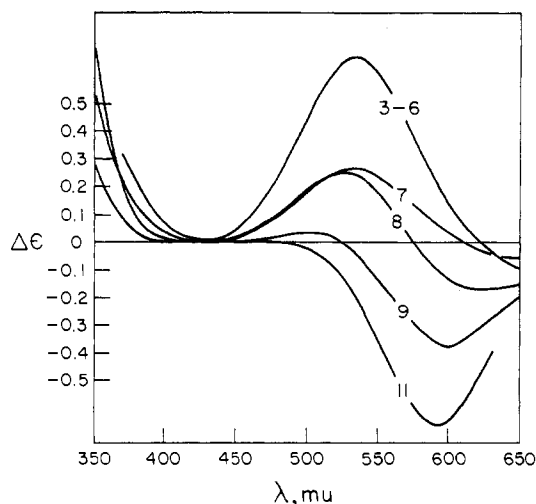


Figure 1.—pH variation of the circular dichroism of TiPDTA. pH values or ranges are quoted on each curve.

Podlahova's work<sup>4</sup> has indicated that in the pH range in which the CD sign inversion occurs, one acetate arm of the hexadentate ligand is removed from the coordination sphere, and a hydroxide ion replaces it. Such a process, however, is not predicted<sup>5,6</sup> to invert the chirality of the complex; four of the five chelate rings would not have been affected by the formation of the hydroxo complex. Furthermore, a change of conformation of the ligand places the methyl group, formerly equatorial, in an axial position and is highly un-

favorable energetically.<sup>7</sup> Thus there is no stock explanation for the observed sign inversion.

Firth, *et al.*,<sup>8</sup> have noted inversion in CD spectra of some derivatives of vitamin B<sub>12</sub> upon cooling their samples to liquid nitrogen temperature and attributed this to the existence of an equilibrium between two "molecular forms" of their compounds, the differences between them perhaps only due to conformational changes. A similar case is not expected in Ti(D(-)-PDTA)<sup>-</sup> because of the great stereospecificity of the ligand as well as the close correspondence between the pH dependence of the spectral changes and Podlahova's titration curve,<sup>4</sup> indicating chemical change in the complex rather than intrastructural effects. Furthermore, a conformational change of the ligand alone could not be responsible for the alterations observed in the visible spectrum.

Hare and coworkers<sup>9</sup> have also noted sign inversions in CD spectra for several complexes of Cu(II) with amino acids. The sign inversion was accompanied by a change in ligand conformation and coordination number forced by chelation; one of the ligand backbones originally in its preferred conformation is forced into an energetically unfavorable conformation by closing another chelate ring. In the case at hand, however, a chelate ring is being broken rather than formed, and the coordination number is unchanged, with hydroxyl replacing carboxylate.<sup>4</sup> Less strain is now expected in the propylenediamine backbone and consequently greater freedom for the backbone to keep its preferred conformation.

The CD spectrum in the charge-transfer region is invariant with pH. McCaffery, Mason, and Norman<sup>10</sup> have observed that the complexes (-)Co((+)pn)<sub>3</sub><sup>3+</sup> and (+)Co((+)pn)<sub>3</sub><sup>3+</sup> (pn = 1,2-propylenediamine) show CD bands of opposite sign in the d-d region of the spectrum but that the charge-transfer transitions have the same sign. In these complexes the ligands are arranged about the metal in opposite chiralities but maintain the same k conformation<sup>7</sup> in which the methyl group is equatorial. The authors concluded<sup>10</sup> that the signs of d-d transitions must reflect the absolute configuration (*i.e.*, ligand chirality about the metal) but the charge-transfer transitions reflect chelate ring conformations. Such an explanation is impossible in the case of Ti(D(-)PDTA)<sup>-</sup>, however; to explain the observed pH behavior of the CD spectrum the absolute configuration about the metal atom would have to change, but at the same time the ligand conformation would remain the same. Changing the absolute configuration around the metal would entail either forming the mirror image of Ti(D(-)PDTA)<sup>-</sup>, which is the chelate with L(+)PDTA, or altering the chirality of the ligand wrapping, which would force the methyl group into an axial conformation and alter the ligand

(7) E. J. Corey and J. C. Bailar, *J. Amer. Chem. Soc.*, **81**, 2620 (1959).

(8) R. A. Firth, H. A. O. Hill, J. M. Pratt, R. J. P. Williams, and W. R. Jackson, *Biochemistry*, **6**, 2178 (1967).

(9) K. M. Wellman, T. G. Mecca, W. Mungall, and C. R. Hare, *J. Amer. Chem. Soc.*, **90**, 805 (1968).

(10) A. J. McCaffery, S. F. Mason, and B. J. Norman, *Chem. Commun.*, 49 (1965).

(2) R. M. Wing and K. P. Callahan, *Inorg. Chem.*, **8**, 2303 (1969).

(3) F. P. Dwyer and F. L. Garvan, *J. Amer. Chem. Soc.*, **81**, 2955 (1959).

(4) J. Podlahova and J. Podlaha, *J. Inorg. Nucl. Chem.*, **28**, 2267 (1966).

(5) J. I. Legg and B. E. Douglas, *J. Amer. Chem. Soc.*, **88**, 2697 (1966).

(6) C. J. Hawkins and Erik Larsen, *Acta Chem. Scand.*, **19**, 185 (1965).

conformation. Thus the ligand conformation cannot remain the same if the absolute configuration around the metal must change.

Douglas<sup>11,12</sup> has investigated the CD spectra of hexadentate and pentadentate EDTA complexes of Co(III) and reported only minor differences between them, consisting of shifts in maxima caused by alterations in the ligand field upon introduction of heterogroups in the coordination sphere and changes in the relative heights of CD peaks. There were no observed inversions; the progression of positive and negative peaks appears the same in all cases, if the wavelength shifts are taken into account. Thus an explanation of the anomalous behavior found for  $\text{Ti}(\text{D}(-)\text{PDTA})^-$  must be consistent with the nonobservance of such an effect in the case of  $\text{CoEDTA}^-$ .

Hoard has performed an X-ray diffraction study on  $\text{CoEDTA}^-$ <sup>13</sup> and found evidence for strain in some of the chelate rings. He found considerably more strain extant in  $\text{HNi}(\text{H}_2\text{O})\text{HEDTA}$ ,<sup>14</sup> which contains pentadentate EDTA, and attributed the change between Co(III) and Ni(II) to the increase in the octahedral radii of the metals, 1.22 to 1.39 Å. It can be deduced that  $\text{TiEDTA}^-$  should exhibit severe strain in its chelate rings, for its octahedral radius is even larger than that of Ni(II); extrapolation from Pauling's radius<sup>15</sup> for Ti(IV) gives a value of 1.46 Å as the octahedral radius of Ti(III), which is compatible with the Ti-Cl distances found<sup>16</sup> in the various forms of  $\text{TiCl}_3$ . Given these data, one might expect that Ti(III) would not form a hexadentate EDTA complex, for the smaller Ni(III) complex is known<sup>14</sup> to be pentadentate; however, Podlahova's infrared data<sup>4</sup> indicate hexadentate coordination in the alkali metal salts of  $\text{TiEDTA}^-$ , and no similar study has been performed on the Ni(II) system. Thus there is no evidence against the existence of a sexadentate  $\text{Ni}^{\text{II}}\text{EDTA}$ , and it is quite conceivable that the nickel system could undergo the structural changes postulated<sup>4</sup> in the Ti(III) system, going from pentadentate to hexadentate and back to pentadentate as the pH is increased. Indeed, we have observed CD sign inversions upon a pH titration of the  $\text{Ni}^{\text{II}}(\text{D}(-)\text{PDTA})^-$  system.

The major difference between  $\text{Co}^{\text{III}}\text{EDTA}^-$  and  $\text{Ti}^{\text{III}}\text{EDTA}^-$  lies in their widely different octahedral radii and the consequent differences in strain in their chelate rings. Since the cobalt complex shows no sign inversion in the CD, but the titanium complex does, it is felt that these structural differences must be responsible for their differing optical behavior.

The most obvious means of strain relief in these compounds is a distortion from a perfect octahedral geometry to a lower energy conformation in which orbital

overlap, ring strain, and steric repulsions are played against one another to establish a minimum in the molecular potential energy. Consequently, one might expect that the coordinated atoms in  $\text{Ti}(\text{D}(-)\text{PDTA})^-$  would describe a highly distorted octahedron, in other words, the  $\text{Ti}(\text{III})$  ion will be in an inherently helical crystal field.

Upon relief of some of the ring strain as a consequence of the formation of  $\text{Ti}(\text{OH})(\text{D}(-)\text{PDTA})^{2-}$ , a new energy minimum will be obtained in which the coordinating atoms have been displaced relative to one another. This change may be similar in kind to that illustrated in Figure 2. Such a change in the coordination topology

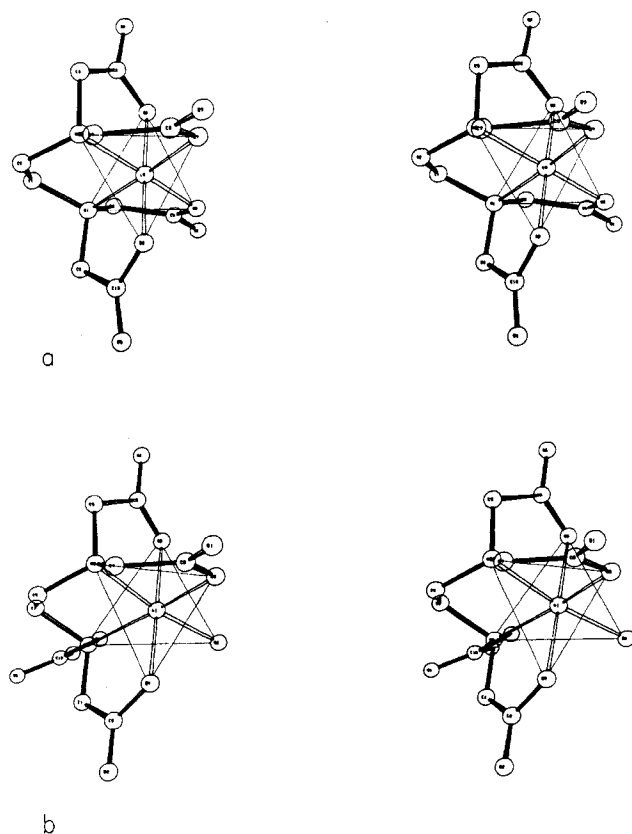


Figure 2.—A hexadentate (a) ( $\text{CoEDTA}^-$ )<sup>13</sup> and a pentadentate (b) ( $\text{Ni}(\text{H}_2\text{O})\text{HEDTA}$ )<sup>14</sup> metal-EDTA complex. These are stereopairs and are best seen with the aid of a hand viewer.

thus leads to a modified helical crystal field and changes in the  $d-d$  or metal centered portion of the CD spectrum.<sup>17,18</sup>

Little more can be said about the anomalous behavior of  $\text{TiPDTA}^-$ , but several implications can be derived from the observations. First, it is obvious that as a general rule, absolute configurations of metal complexes cannot be deduced from the signs of their CD transitions in the  $d-d$  region of the spectrum for we have observed sign inversion without a change in absolute configuration. Such a relationship between ligand conformation and the sign of charge-transfer transitions may still be valid, however, since these bands, which have a large amount of ligand character in the ground-state wave

(11) B. E. Douglas, R. A. Haines, and J. G. Brushmiller, *Inorg. Chem.*, **2**, 1194 (1963).

(12) R. A. Haines and B. E. Douglas, *ibid.*, **4**, (1965).

(13) H. A. Weakleim and J. L. Hoard, *J. Amer. Chem. Soc.*, **81**, 549 (1959).

(14) G. S. Smith and H. L. Hoard, *ibid.*, **81**, 556 (1959).

(15) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.

(16) G. Natta, P. Corradini, and G. Allegra, *J. Polym. Sci.*, **51**, 399 (1961).

(17) A. G. Karipides and T. S. Piper, *J. Chem. Phys.*, **40**, 674 (1964).

(18) R. M. Wing and R. Eiss, *J. Amer. Chem. Soc.*, **92**, 1929 (1970).

function, have not been observed to show sign inversion upon pH alteration. Second, the widespread tendency to correlate ligand chirality with optical behavior must be seriously questioned. The spatial arrangements of chelate rings may, in fact, be only a small factor in determining the signs of CD transitions, and, instead, the positions of the ligating atoms and their distortions from octahedral positions may be the determining factors.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,  
ILLINOIS INSTITUTE OF TECHNOLOGY, CHICAGO, ILLINOIS 60616

### Some Nickel(II) Complexes with Sulfur-Containing Schiff Base Ligands<sup>1a</sup>

BY GEORGE R. BRUBAKER,\* JEAN C. LATTA,<sup>1b</sup>  
AND DOLORES C. AQUINO<sup>1c</sup>

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The diverse stereochemistry and varied stereochemical equilibria of nickel(II) complexes with multidentate  $\beta$ -keto amine and salicylaldehyde ligands has been discussed in detail.<sup>2</sup> Busch and his coworkers<sup>3-7</sup> have carefully studied some complexes of nickel(II) with various 2-aminoethanethiol derivatives, including some  $\alpha$ -diimine ligands derived from  $\alpha$ -diketones and 2-aminoethanethiol. In contrast with the chemistry of  $\beta$ -keto imine complexes, for example, the chemistry of the latter compounds is relatively simple. Nickel(II) complexes with mercapto amines and mercapto imines invariably exist in the low-spin planar configuration. The only substantial deviation from this simple stereochemistry is found in the marked tendency for the formation of polynuclear species involving bridging sulfur atoms, though such complexes have not been reported for  $\alpha$ -diketobis(2-mercaptoethylimine) ligands. We report the synthesis of some nickel(II) complexes with sulfur-containing  $\beta$ -keto amine ligands and the details of the structure elucidation.

#### Experimental Section

**Physical Measurements.**—The visible and ultraviolet spectra were obtained in 1,2-dichloroethane using either a Cary Model 14 or a Beckman Model DB-G recording spectrophotometer; matched 10-mm cells were used for all measurements. Infrared spectra were obtained using either a Beckman Model IR-12 or a Perkin-Elmer Model 257 spectrophotometer. Both potassium bromide disk and Nujol mull techniques were employed. The

\* To whom correspondence should be addressed.

(1) (a) Presented in part before the division of Inorganic Chemistry, 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969; see Abstracts, No. INOR 113. (b) Taken, in part, from the M. S. Thesis of J. C. L., Illinois Institute of Technology, June 1970. (c) NSF Undergraduate Research Participant, Summer 1968.

(2) S. Y. Shaw and E. P. Dudek, *Inorg. Chem.*, **8**, 1360 (1969), and references cited therein.

(3) D. H. Busch and D. C. Jicha, *ibid.*, **1**, 872 (1962).

(4) D. H. Busch and D. C. Jicha, *ibid.*, **1**, 87 (1962).

(5) C. A. Root and D. H. Busch, *ibid.*, **7**, 789 (1968).

(6) D. H. Busch and M. C. Thompson, *J. Amer. Chem. Soc.*, **86**, 213 (1964).

(7) D. H. Busch, D. C. Jicha, M. C. Thompson, J. W. Wrathall, and E. Blinn, *ibid.*, **86**, 3642 (1964).

nuclear magnetic resonance spectra were obtained on a Varian A-60 spectrometer in saturated carbon disulfide solution. Tetramethylsilane was used as the standard. Molecular weights were determined with the Perkin-Elmer Hitachi Model 115 vapor pressure osmometer in *N,N*-dimethylacetamide. Analyses were performed by either Alfred Bernhardt Mikroanalytisches Laboratorium, Elbach, West Germany, or Micro-Tech Laboratories, Inc., Skokie, Ill.

**Materials.**—The metal salts employed were of reagent grade or the equivalent.  $\beta$ -Aminoethanethiol hydrochloride (96%) was obtained from Evans Chemetics, New York, N. Y. Acetylacetone, *o*-aminobenzenethiol, and salicylaldehyde (practical) were obtained from Eastman. All materials were used as obtained, without further purification.

**Preparations.** **Bis(2-(2-mercaptoethyl)imino-4-pentanato)dinickel(II), Ni<sub>2</sub>(AME)<sub>2</sub>.**—Two and a half grams (0.022 mol) of 2-mercaptoethylamine hydrochloride and 5.89 g (0.06 mol) of potassium acetate were dissolved in 50 ml of methanol and the potassium chloride removed by filtration. To the filtrate was added 2.47 ml (0.024 mol) of acetylacetone and the solution was heated on a steam bath for 10–15 min. This was added to a solution of 4.98 g (0.02 mol) of nickel acetate tetrahydrate in 50–100 ml of hot methanol. The product was filtered and purified by continuous extraction into benzene and recovered by evaporating to dryness. The burgundy red complex is soluble in common organic solvents. Molecular weight in *N,N*-dimethylacetamide: calcd for dimer, 432; found, 505. *Anal.* Calcd for Ni<sub>2</sub>C<sub>11</sub>H<sub>11</sub>NSO: C, 38.93; H, 5.13; N, 6.49; S, 14.85. Found: C, 39.12; H, 5.11; N, 6.59; S, 14.70.

**Bis(2-(2-mercaptoethyl)salicylaldiminato)dinickel(II), Ni<sub>2</sub>(SME)<sub>2</sub>.**—This compound was prepared in the same manner using 2.50 g of 2-mercaptoethylamine hydrochloride, 5.89 g of potassium acetate, 2.51 ml (0.024 mol) of salicylaldehyde, and 4.98 g of nickel acetate tetrahydrate. The red-brown complex is soluble in polar organic solvents. Molecular weight in *N,N*-dimethylacetamide: calcd for dimer, 476; found, 632. *Anal.* Calcd for Ni<sub>2</sub>C<sub>9</sub>H<sub>9</sub>NSO: C, 45.43; H, 3.81; N, 5.89; S, 13.48. Found: C, 46.14; H, 3.93; N, 5.95; S, 12.70.

**Bis(2-(2-mercaptoethyl)imino-4-pentanato)dinickel(II), Ni<sub>2</sub>(AMA)<sub>2</sub>.**—The nickel(II) complex of 2-(2-mercaptoethyl)imino-4-pentanone was prepared similarly using 2.36 ml (0.022 mol) of 2-mercaptoaniline, 2.47 ml of acetylacetone, 5.89 g of potassium acetate, and 4.98 g of nickel acetate tetrahydrate. The red-brown complex is soluble in polar organic solvents. Molecular weight in *N,N*-dimethylacetamide: calcd for dimer, 572; found, 676. *Anal.* Calcd for Ni<sub>2</sub>C<sub>11</sub>H<sub>11</sub>NSO: C, 50.05; H, 4.20; N, 5.31; S, 12.15. Found: C, 52.34; H, 4.49; N, 5.46; S, 11.60.

**Bis(2-(2-mercaptoethyl)salicylaldiminato)dinickel(II), Ni<sub>2</sub>(SMA)<sub>2</sub>.**—The same method was employed using 2.36 ml of 2-mercaptoaniline, 2.51 ml of salicylaldehyde, 5.89 g of potassium acetate, and 4.98 g of nickel acetate tetrahydrate. The red-brown complex is sparingly soluble in organic solvents. *Anal.* Calcd for Ni<sub>2</sub>C<sub>13</sub>H<sub>9</sub>NSO: C, 54.65; H, 3.17; N, 4.90; S, 11.21. Found: C, 54.65; H, 3.30; N, 5.11; S, 11.08.

#### Results and Discussion

Magnetic susceptibilities were measured by the Gouy method. The data are summarized in Table I. The small residual paramagnetism may be attributed to

TABLE I  
MAGNETIC SUSCEPTIBILITY DATA FOR SOME NICKEL(II)  
COMPLEXES WITH SULFUR-CONTAINING SCHIFF BASE LIGANDS

Compound	T, °K	10 <sup>3</sup> $\chi_m$ /Ni	$\mu$ /Ni <sup>a</sup>
Ni <sub>2</sub> (AME) <sub>2</sub>	296	12.1	0.17
Ni <sub>2</sub> (SME) <sub>2</sub>	296	22.0	0.22
Ni <sub>2</sub> (AMA) <sub>2</sub>	296	21.6	0.23
Ni <sub>2</sub> (SMA) <sub>2</sub>	296	66.5	0.40

<sup>a</sup>  $\mu = 2.84 (\chi_m T)^{1/2}$ .