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Thiocarboxylates of Nickel(II)

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The reaction between nickel(II) and thioacetic, thiopropionic, and thiobenzoic acids in basic ethanolic solution results in the isolation of the compounds $Ni(RCOS)_2 \cdot 0.5C_2H_5OH$ (R = CH_3, C_2H_5, C_6H_5). These compounds have temperature-independent magnetic moments in the range 2.3–2.4 BM/nickel(II) ion. Evidence is presented to show that these compounds are dimeric and contain the nickel(II) ions in both square-planar and square-pyramidal environments within the dimer. The reaction of these compounds with unidentate heterocyclic nitrogen donor ligands (L) breaks up the dimeric structure and compounds of the type $Ni(RCOS)_2 \cdot 2L$ are obtained, with magnetic moments of approximately 3.2 BM/nickel(II) ion.

Introduction

The compounds formed between carboxylic acids and transition metal ions have received considerable attention during the last few years.[2a] Particular interest has been focused on those compounds which have binuclear structures with bridging carboxylate groups and metal–metal bonds of varying strengths.[2b]

However, there have been few studies of the compounds formed between thiocarboxylic acids and transition metal ions. Tarugi,[3] in 1895, prepared several metal salts with thioacetic acid, and more recently Nortia[4] studied the spectral and magnetic properties of bis(thioacetato)copper(II). Hieber and Bruck[5] prepared a bis(thiobenzoato)nickel(II) and Furlani, *et al.*,[6] concluded that tris(thiobenzoato)chromium(III) is monomeric and contains three bidentate thiocarboxylate groups.

This study was undertaken to investigate the effect of the sulfur atom of the $-COS^-$ group on the structures of various transition metal thiocarboxylates. We report here nickel(II) complexes obtained from thioacetic (CH_3COSH), thiopropionic (C_2H_5COSH), and thiobenzoic (C_6H_5COSH) acids.

Experimental Section

Materials.—Thioacetic acid (BDH), thiopropionic acid (Aldrich), and thiobenzoic acid (Koch-Light) were used as supplied. All other chemicals used were of reagent grade or equivalent.

Reaction of Nickel(II) with Thioacetic Acid.—Basic nickel carbonate [$NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$] was added a little at a time to a warm ethanolic solution of thioacetic acid until no more dissolved. The solution was then filtered and the filtrate was allowed to stand at 0° overnight. The resultant dark red crystals were removed by filtration, washed with ice cold ethanol, and dried under vacuum at room temperature over $Mg(ClO_4)_2$. *Anal.* Calcd for $Ni(CH_3COS)_2 \cdot 0.5C_2H_5OH$: C, 25.8; H, 3.9; S, 27.6. Found: C, 25.0; H, 3.9; S, 27.9.

Reaction of Nickel(II) with Thiopropionic Acid.—A similar procedure to that described above was employed. The resultant dark red crystals were dried as above. *Anal.* Calcd for $Ni(C_2H_5COS)_2 \cdot 0.5C_2H_5OH$: C, 32.3; H, 5.0; S, 24.6. Found: C, 31.7; H, 5.1; S, 23.8.

Reaction of Nickel(II) with Thiobenzoic Acid.—A warm solution of nickel chloride hexahydrate (0.01 mol) in ethanol (50 ml) was added to a warm solution of thiobenzoic acid (0.02 mol) and sodium hydroxide (0.02 mol) in ethanol (50 ml). After stirring for a few minutes, fine red-brown crystals were deposited. The solution was allowed to stand at room temperature for approximately 1 hr and then filtered. The residue was washed with ethanol and dried as previously described. *Anal.* Calcd for $Ni(C_6H_5COS)_2 \cdot 0.5C_2H_5OH$: C, 50.6; H, 3.6; S, 18.0. Found: C, 50.7; H, 3.8; S, 17.9.

Procedure for the Preparation of Pyridine and Picoline Derivatives. Preparation of Di(thiobenzoato)bis(pyridine)nickel(II). A 1-g sample of $Ni(C_6H_5COS)_2 \cdot 0.5C_2H_5OH$ was suspended in 100 ml of ethanol and 3.5 g of pyridine (py) in 50 ml of ethanol was added. The solution was stirred and warmed gently. A clear bright green solution was obtained. The solution was filtered, concentrated to approximately 50 ml, and allowed to stand at 0° overnight. The resultant bright green crystals were removed by filtration, washed with a little ice-cold ethanol, and dried as previously described. *Anal.* Calcd for $Ni(C_6H_5COS)_2 \cdot py$: C, 58.6; H, 4.1; S, 13.0; N, 5.7. Found: C, 58.1; H, 4.1; S, 13.3; N, 5.7.

All other compounds were obtained using a similar procedure (α-pic, α-picoline; β-pic, β-picoline; γ-pic, γ-picoline). *Anal.* calcd for $Ni(C_6H_5COS)_2 \cdot 2pic$: C, 59.9; H, 5.0; S, 12.3; N, 5.4. Found for $Ni(C_6H_5COS)_2 \cdot 2\alpha$-pic: C, 59.9; H, 5.0; S, 12.1; N, 5.6. Found for $Ni(C_6H_5COS)_2 \cdot 2\beta$-pic: C, 60.1; H, 4.9; S, 12.3; N, 5.7. Found for $Ni(C_6H_5COS)_2 \cdot 2\gamma$-pic: C, 60.1; H, 4.9; S, 12.2; N, 5.3. Calcd for $Ni(CH_3COS)_2 \cdot 2py$: C, 45.8; H, 4.4; S, 17.4; N, 7.6. Found: C, 46.0; H, 4.5; S, 17.2; N, 7.8. Calcd for $Ni(CH_3COS)_2 \cdot 2pic$: C, 48.6; H, 4.6; S, 16.2; N, 7.1. Found for $Ni(CH_3COS)_2 \cdot 2\beta$-pic: C, 48.5; H, 5.0; S, 16.0; N, 7.3. Found for $Ni(CH_3COS)_2 \cdot 2\gamma$-pic: C, 48.5; H, 5.0; S, 16.2; N, 7.0.

Physical Measurements.—Infrared absorption spectra in the range 4000–400 cm^{-1} were obtained using a Perkin-Elmer Model 125 recording spectrophotometer. Nujol and hexachlorobutadiene mull techniques were used. Reflectance spectra were obtained over the range 6000–28,000 cm^{-1} using a Perkin-Elmer Model 450 recording spectrophotometer. The samples were mounted on filter paper. Magnetic measurements, both at room temperature and over a temperature range, were made by the Gouy method, using $Hg[Co(NCS)_4]$ as calibrant. Susceptibilities of ligands and anions were calculated from Pascal's constants.[7]

Molecular weight determinations were carried out in chloroform solutions at 37°, using a Mechrolab vapor pressure osmometer.

Results and Discussion

The reaction between nickel(II) and thioacetic, thio-

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[2] (a) C. Oldham, *Progr. Inorg. Chem.*, **10**, 223 (1968); (b) M. J. Bennett, R. G. Caulton, and F. A. Cotton, *Inorg. Chem.*, **8**, 1 (1969).

[3] N. Tarugi, *Gazz. Chim. Ital.*, **25**, 341 (1895).

[4] T. Nortia, *Suomen Kemistilehti*, **B33**, 120 (1960).

[5] W. Hieber and R. Bruck, *Z. Anorg. Allgem. Chem.*, **269**, 13 (1952).

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

[7] B. N. Figgis and J. Lewis, "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, New York, N. Y., 1960.

propionic, and thiobenzoic acids in basic ethanolic solution results in the isolation of dark red-brown crystalline compounds with the general empirical formula $Ni(RCOS)_2 \cdot 0.5C_2H_5OH$ ($R = CH_3$, C_2H_5, or C_6H_5).

The infrared absorption bands corresponding to ν(C—H), ν(S—H), and ν(C=O) for the free acids and complexes are shown in Table I. The absence of the ν(S—H) band in the complexes and the considerable lowering of the ν(C=O) band suggests that the thiocarboxylic acids are functioning as bidentate or bridging ligands.

TABLE I

CHARACTERISTIC INFRARED ABSORPTION BANDS[a]

Compound	ν(C—H)	ν(S—H)	ν(C=O)
CH_3COSH	2990 w 2920 m	2560 s	1700 s, br
$Ni(CH_3COS)_2 \cdot 0.5C_2H_5OH$	3250 m[b] 2980 m 2920 m	. . .	1540 s, br
$Ni(CH_3COS)_2 \cdot 2py$	2980 m 2920 m	. . .	1600 s, br
$Ni(CH_3COS)_2 \cdot 2\beta$-pic	2960 m 2920 m	. . .	1590 s, br
$Ni(CH_3COS)_2 \cdot 2\gamma$-pic	2960 m 2920 m	. . .	1610 s, br
C_2H_5COSH	2980 s 2940 s 2900 m	2560 s	1700 s, br
$Ni(C_2H_5COS)_2 \cdot 0.5C_2H_5OH$	3250 m[b] 2980 m 2920 m	. . .	1580 s, br
C_6H_5COSH	3050 m	2560 s	1660 s, br
$Ni(C_6H_5COS)_2 \cdot 0.5C_2H_5OH$	3320 m[b] 3050 m	. . .	1520 s, br
$Ni(C_6H_5COS)_2 \cdot 2py$	3050 m	. . .	1600 s, br
$Ni(C_6H_5COS)_2 \cdot 2\alpha$-pic	3050 m	. . .	1610 s, br
$Ni(C_6H_5COS)_2 \cdot 2\beta$-pic	3050 m	. . .	1600 s, br
$Ni(C_6H_5COS)_2 \cdot 2\gamma$-pic	3050 m	. . .	1610 s, br

[a] All values in cm^{-1}. Abbreviations: w, weak; m, medium; s, strong; br, broad. [b] From the ethanol molecule.

The room-temperature magnetic properties of these compounds are listed in Table II. The values of μ_{eff} per nickel(II) ion are independent of field strength but do not correspond to the two extremes usually associated with nickel(II) ions, *viz.*, two unpaired electrons or complete pairing of the electrons.

A study of the temperature dependence of the magnetic susceptibility was carried out for each of the three compounds between 80 and 300°K and the results are presented graphically in Figure 1. It can readily be seen that the Curie–Weiss law is followed over this temperature range for each compound, with only small values of the Weiss constant (θ) being obtained ($R = CH_3$, $\theta = -12°$; $R = C_2H_5$, $\theta = -7°$; $R = C_6H_5$, $\theta = -15°$). Thus possibilities of spin-state isomerism and strong electronic interactions between nickel ions to account for the "anomalous" magnetic moment may be ruled out.

TABLE II

ROOM-TEMPERATURE MAGNETIC PROPERTIES

Compound	T, °K	$10^6\chi_m^{cor}$	μ_{eff}, BM[a]
$Ni(CH_3COS)_2 \cdot 0.5C_2H_5OH$	291	2356	2.33
$Ni(C_2H_5COS)_2 \cdot 0.5C_2H_5OH$	292	2195	2.27
$Ni(C_6H_5COS)_2 \cdot 0.5C_2H_5OH$	291	2380	2.35
$Ni(CH_3COS)_2 \cdot 2py$	292	4160	3.14
$Ni(CH_3COS)_2 \cdot 2\beta$-pic	292	4230	3.17
$Ni(CH_3COS)_2 \cdot 2\gamma$-pic	292	4260	3.18
$Ni(C_6H_5COS)_2 \cdot 2py$	291	4325	3.19
$Ni(C_6H_5COS)_2 \cdot 2\alpha$-pic	292	4190	3.15
$Ni(C_6H_5COS)_2 \cdot 2\beta$-pic	291	4210	3.16
$Ni(C_6H_5COS)_2 \cdot 2\gamma$-pic	291	4260	3.16

[a] Per nickel(II) ion, calculated from $\mu_{eff} = 2.84\sqrt{\chi_m^{cor}T}$.

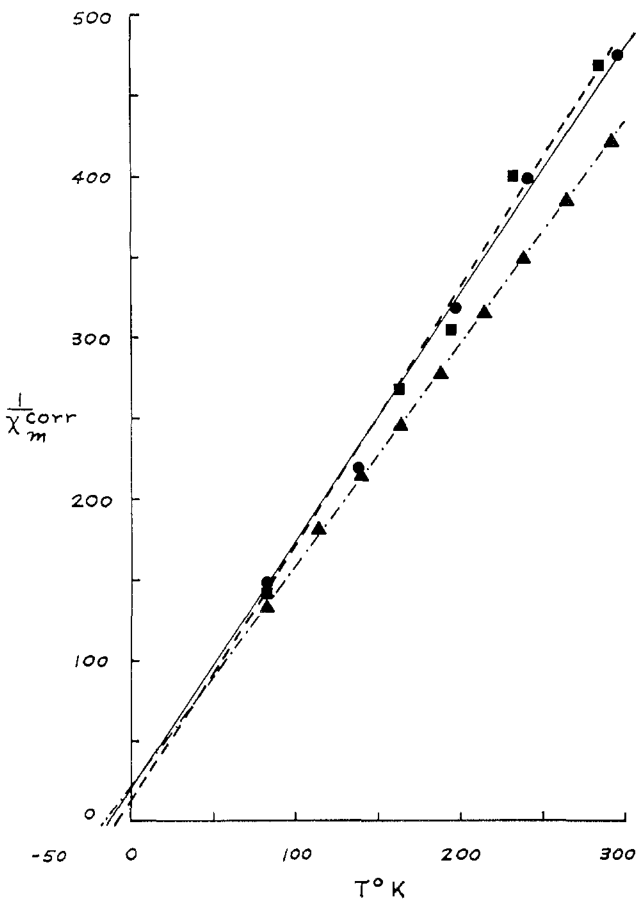

Figure 1.—Variation of the reciprocal of the magnetic susceptibility with temperature: ●, $Ni(CH_3COS)_2 \cdot 0.5C_2H_5OH$; ■, $Ni(C_2H_5COS)_2 \cdot 0.5C_2H_5OH$; ▲, $Ni(C_6H_5COS)_2 \cdot 0.5C_2H_5OH$.

Measurements of the molecular weights of the thioacetate and thiopropionate compounds were made in chloroform solutions at 37° by a vapor pressure osmometer. Molecular weights corresponding to twice the empirical formulas were obtained for each compound, suggesting the presence of a dimeric structure in each case. Owing to the insolubility of the thiobenzoate compound in chloroform, or any suitable solvent, it was impossible to obtain values for the molecular weight of this compound. However, since the formula and magnetic properties of the thiobenzoate compound are very similar to those of the thioacetate and thiopropionate compounds, a similar dimeric structure is also proposed.

Recently, we determined the crystal and molecular structure of the thiobenzoate compound.[8] A general view of the structure is shown in Figure 2. It can be

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[8] G. A. Melson, P. T. Greene, and R. F. Bryan, *Inorg. Chem.*, **9**, 1116 (1970).

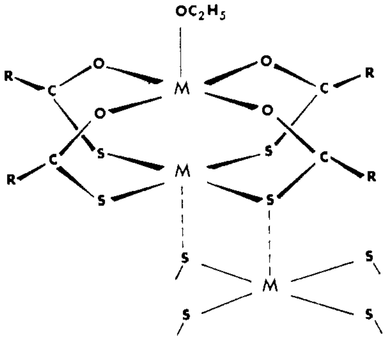

Figure 2.—Structure of the bis(thiocarboxylato)nickel(II) compounds.

seen that four thiocarboxylic acid groups behave as bridging ligands between two nickel(II) ions to form a structure similar to that found for several transition metal carboxylates.[2b] However, due to the unsymmetrical nature of the COS⁻ group, the two nickel(II) ions within the dimer are in different environments. One of the nickel ions is surrounded by four sulfur atoms, whereas the other has five oxygen atoms arranged about it, four from the acid groups in a plane, the fifth position being occupied by the oxygen atom of an ethanol molecule. In the solid state, two of these dimeric units are linked together by weak interactions between a nickel ion of one unit and a sulfur atom of another unit. The separation between the two nickel(II) ions within a dimer was found to be 2.503 Å, in close agreement with the value of 2.49 Å found by Bonamico, *et al.*[9] It is proposed that the above structure is held by all three nickel thiocarboxylates. In chloroform solution, the weak interactions between dimeric units are probably broken, but the dimers themselves remain intact, accounting for the observed molecular weights of the thioacetate and thiopropionate compounds.

The magnetic properties of these compounds can now be accounted for. Calculations of the magnetic moment based on the molecular weight of the dimeric unit result in values corresponding to the presence of two unpaired electrons per dimer. The linear dependence of the reciprocal of the molar susceptibility with temperature suggests there is little or no interaction between the nickel(II) ions within the dimer in spite of the short Ni–Ni distance. Thus, the nickel ion coordinated to the four sulfur atoms is in a square-planar ligand field (D_{4h}) whereas the nickel ion surrounded by five oxygen donors is in a square-pyramidal ligand field (C_{4v}). The square-planar environment of sulfur donor atoms will produce a strong ligand field about the nickel ion and result in complete pairing of all the electrons,[10-12] but for the nickel ion in the relatively weak square-pyramidal ligand field of oxygen donor atoms, two unpaired electrons should be observed.[13,14] The susceptibility of the nickel ions in the high-spin configuration will obey the Curie–Weiss law, with that of the nickel ions in the low-spin configuration making only a small temperature-independent contribution.

Thus it is suggested from consideration of the proposed structures that the magnetic moment of the dimeric unit should correspond to two unpaired electrons and the susceptibility should follow the Curie–Weiss law. This is exactly the observed behavior that was described earlier. The presence of different coordination environments within a crystal has been proposed to account for some apparently anomalous magnetic properties,[15-18] but these are the first examples where a chelating ligand with two different donor atom types produces this effect within a single molecule.

The reflectance spectra recorded in Table III support the conclusions reached concerning the two different environments for the nickel ions by exhibiting absorption bands characteristic of each. Ciampolini[13] and Sacconi, *et al.*,[19] have measured the spectra of some high-spin square-pyramidal nickel(II) complexes. One distinguishing feature of the spectra is a low-energy absorption band, assigned to the transition $^3B_1 \rightarrow {}^3E$ in C_{4v} symmetry, observed in the region of 7700 cm⁻¹. We have observed an absorption band in this region for the three nickel thiocarboxylates. A shoulder in the region of 12,500–13,000 cm⁻¹ is assigned to the transition $^3B_1 \rightarrow {}^3B_2$ and the band at 15,500 cm⁻¹ to $^3B_1 \rightarrow {}^3E$. The band predicted in the region of 10,000 cm⁻¹ ($^3B_1 \rightarrow {}^3A_2$) was not detected, but its intensity is usually much less than that arising from either of the $^3B_1 \rightarrow {}^3E$ transitions.[13] The strong absorption band at approximately 20,000 cm⁻¹ for each compound probably arises from the $^1A_{1g} \rightarrow {}^1A_{2g}$ transition for the nickel ion in D_{4h} symmetry although charge-transfer bands and ligand transitions are expected to complicate this region of the spectrum and contribute mainly to the 27,000-cm⁻¹ band. Similar assignments were made for bis(dithiocarboxylato)nickel(II) compounds which contain nickel(II) ions coordinated by four sulfur donor atoms in a square-planar configuration.[10,20] Furlani, *et al.*,[6] observed an intense band at ~29,000 cm⁻¹ in

TABLE III

REFLECTANCE SPECTRA[a]

$Ni(CH_3COS)_2 \cdot 0.5C_2H_5OH$	7700	12,500 sh	15,500 sh	19,800	27,000
$Ni(C_2H_5COS)_2 \cdot 0.5C_2H_5OH$	7700	12,500 sh	15,500 sh	20,000	27,300
$Ni(C_6H_5COS)_2 \cdot 0.5C_2H_5OH$	7700	13,000 sh	15,500 sh	20,000	27,300
$Ni(CH_3COS)_2 \cdot 2py$	9300	11,500 sh	16,500	26,000 br	
$Ni(CH_3COS)_2 \cdot 2\beta$-pic	9500	11,600 sh	16,500	26,000 br	
$Ni(CH_3COS)_2 \cdot 2\gamma$-pic	9300	11,600 sh	16,300	26,000 br	
$Ni(C_6H_5COS)_2 \cdot 2py$	9650	11,400 sh	16,400	25,500 br	
$Ni(C_6H_5COS)_2 \cdot 2\alpha$-pic	9200	11,400 sh	16,400	26,000 br	
$Ni(C_6H_5COS)_2 \cdot 2\beta$-pic	9800	11,700 sh	16,400	26,000 br	
$Ni(C_6H_5COS)_2 \cdot 2\gamma$-pic	9600	11,600 sh	16,200	26,000 br	

[a] All values in cm⁻¹. Abbreviations: sh, shoulder; br, broad.

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(9) M. Bonamico, G. Dessy, and V. Fares, *Chem. Commun.*, 697 (1969).

(10) C. Furlani and M. L. Luciani, *Inorg. Chem.*, **7**, 1586 (1968).

(11) J. P. Fackler and D. Coucouvanis, *J. Am. Chem. Soc.*, **88**, 3913 (1966).

(12) B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, **6**, 37 (1964).

(13) M. Ciampolini, *Inorg. Chem.*, **5**, 35 (1966).

(14) L. Sacconi, P. L. Orioli, and M. Di Vaira, *J. Am. Chem. Soc.*, **87**, 2059 (1965).

(15) M. Kondo and M. Kubo, *J. Phys. Chem.*, **61**, 1648 (1957).

(16) S. C. Nyburg and J. S. Wood, *Inorg. Chem.*, **3**, 468 (1964).

(17) D. Hall and J. M. Waters, *ibid.*, **3**, 615 (1964).

(18) G. R. Brubaker and D. H. Busch, *ibid.*, **5**, 2114 (1966).

(19) L. Sacconi, P. Nanneli, N. Nardi, and U. Campigli, *ibid.*, **4**, 943 (1965).

(20) M. Bonamico, G. Dessy, and V. Fares, *Chem. Commun.*, 324 (1969).

tris(thiobenzoato)chromium(III) and assigned this as excitation to a state arising from both charge transfer and an excited ligand state.

The reaction of bis(thiocarboxylato)nickel(II) compounds with a large excess of pyridine or some picolines resulted in the isolation of bright green crystalline complexes of the general formula $Ni(RCOS)_2 \cdot 2L$, where $R = CH_3$ and L = py, β-pic, or γ-pic; or $R = C_6H_5$ and L = py, α-pic, β-pic, or γ-pic. Reactions involving bis(thiopropionato)nickel(II) resulted in decomposition of the compound to nickel sulfide, and no complexes were obtained. Infrared spectra of the complexes (Table I) suggest that the thiocarboxylic acids are behaving as bidentate or bridging ligands, although, since the lowering of $\nu(C{=}O)$ is not as great as is observed for the bis(thiocarboxylato)nickel(II) compounds, the type of coordination may be different from that found for the latter compounds. Furlani, *et al.*,[6] concluded that tris(thiobenzoato)chromium(III) contains bidentate thiocarboxylates although no infrared data were quoted for this compound. Room-temperature magnetic properties (Table II) suggest the nickel ion is in an octahedral environment, with a triplet ground state. Further evidence to support this conclusion is obtained from the reflectance spectra (Table III). The following transitions are assigned for nickel(II) in O_h symmetry: ν_1, $\sim$9500 cm^{-1}, $^3A_{2g} \rightarrow {}^3T_{2g}$; ν_2 $\sim$11,500 cm^{-1}, $^3A_{2g} \rightarrow {}^1E_g$; ν_3, $\sim$16,500 cm^{-1}, $^3A_{2g} \rightarrow {}^3T_{1g}(F)$; ν_4, $\sim$26,000 cm^{-1}, $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ plus charge transfer.

Thus the reaction of these nitrogen donor ligands with the bis(thiocarboxylato)nickel(II) compounds breaks down the dimeric structure to produce complexes probably containing bidentate thiocarboxylates Attempts to remove the pyridine ligands by heating under vacuum above the boiling point of the ligand for several hours resulted in a change from bright green to the red-brown characteristic of the original dimeric species. However, reproducible analyses were not obtained for these products and prolonged heating finally led to complete decomposition to nickel sulfide.

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Dissociation Reactions of the Amide Protons of N,N′-Diglycylethylenediaminenickel(II). Kinetics of Octahedral–Square-Planar Conversion[1]

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The kinetics of the transition of nickel(II)–N,N′-diglycylethylenediamine (DGEN) complexes from the paramagnetic octahedral form to the diamagnetic square-planar form, which accompanies the dissociation of the amide hydrogens from the ligand, have been studied spectrophotometrically. The rate is given by $d[NiH_{-2}L]/dt = k[OH^-][NiL^{2+}] + k'[OH^-] \cdot [NiL_2{}^{2+}]$ where L represents the neutral ligand DGEN, $NiH_{-2}L$ is the fully deprotonated yellow complex, and k and k' are 3.3×10^2 and 2.5×10^2 sec^{-1} M^{-1}, respectively, at 25.3° and an ionic strength of 1.0 M. The mechanisms of the reactions are discussed. Evidence is presented for the simultaneous dissociation of the two peptide protons proposed previously on the basis of potentiometric equilibrium studies.

Introduction

The amide hydrogens in polypeptides may be displaced by nickel(II)[2-4] as well as by copper(II)[2,5-7] ions. Direct evidence for amide proton displacement was obtained from aqueous (D_2O) infrared spectra for complexes in solution[4,6,7] and from X-ray crystallographic studies for complexes in the solid state.[8] In these deprotonated peptide complexes, the metal ion is coordinated to the nitrogen of the peptide groups both in solution and in the solid state. The nickel(II) complexes of polypeptides in which the peptide protons are displaced are yellow, diamagnetic, and square planar.[3,4,9,10] The displacement of the peptide hydrogens is slow[3,4] and all of the peptide hydrogens in the ligand seemed to be released simultaneously,[4,10] or nearly simultaneously, to give the final completely deprotonated forms in one-step neutralization reactions.

In a recent publication,[11] the equilibria involved in the formation of N,N′-diglycylethylenediamine (DGEN) complexes of nickel(II) and copper(II) have been described. It was found that this synthetic peptide-like ligand behaves in a manner similar to that

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[2] A. R. Manyak, C. B. Murphy, and A. E. Martell, *Arch. Biochem. Biophys.*, **59**, 373 (1955).

[3] R. B. Martin, M. Chamberlin, and J. T. Edsall, *J. Am. Chem. Soc.*, **82**, 495 (1960).

[4] M. K. Kim and A. E. Martell, *ibid.*, **89**, 5138 (1967).

[5] H. Dobbie and W. O. Kermack, *Biochem. J.*, **59**, 246, 257 (1955).

[6] A. E. Martell in "Recent Topics in Coordination Chemistry," S. Misumi and K. Ueno, Ed., Special Publication No. 84, Nankodo Publishing Co., Japan, 1968, p 47.

[7] M. K. Kim and A. E. Martell, *J. Am. Chem. Soc.*, **88**, 914 (1966).

[8] H. C. Freeman in "The Biochemistry of Copper," J. Peisach, P. A. Isen, and W. E. Blumberg, Ed., Academic Press, Inc., New York, N. Y., 1966.

[9] R. Mathur and R. B. Martin, *J. Phys. Chem.*, **69**, 668 (1965).

[10] M. K. Kim and A. E. Martell, *J. Am. Chem. Soc.*, **91**, 872 (1969).

[11] K. S. Bai and A. E. Martell, *ibid.*, **91**, 4412 (1969).