contributions lead to relatively small weight differences in the Gouy method.

General Conclusions.—Our studies suggest that an important factor in the coordination behavior of NCS^- toward nickel(II) is the tendency of this metal ion to adopt six-coordination in the solid state. This is shown by the formation of $Ni(NCS)_6{}^{4-}$ ions (a property in which Ni(II) resembles Mn(II) and Fe(II)) and by the tetragonal, six-coordination of nickel(II) in anhydrous $NiHg(SCN)_4$ and in many of the solid compounds $(cation)_2Ni(NCS)_4$, where the bridging ability of the NCS group permits association of the anions, especially when the cation is relatively small. In the analogous isocyanate complexes there is no evidence of such association, the anion in, *e.g.*, $[(C_2H_5)_4N]_2Ni(NCO)_4$ having a tetrahedral structure.[8]

As expected, the tendency toward six-coordination is less pronounced for copper(II). No complexes of the type $Cu(NCS)_6{}^{4-}$ were isolated and, although in some compounds of composition $(cation)_2Cu(NCS)_4$ the metal ions have tetragonal environments due to anion association, it is probable that the Cu–S bonding is weaker than the analogous Ni–S bonding. Moreover, some cations, *e.g.*, $(C_6H_5)_4As^+$ and Cat^{2+}, which gave tetragonal complexes for nickel(II) did not do so for copper(II).

The existence of the six-coordinate complexes discussed above is confined predominantly, if not entirely, to the solid state, since solution of $(cation)_4Ni(NCS)_6$ and the tetragonal forms of $(cation)_2M(NCS)_4$ in polar, relatively noncoordinating solvents results in the formation of tetrahedral $M(NCS)_4{}^{2-}$ ions. The formation of solid compounds with tetrahedral anions $M(NCS)_4{}^{2-}$ is favored by higher temperatures and the use of very large cations, as both these factors tend to reduce opportunities for M–NCS–M bridging. However, it appears that the discrete anions so formed are distorted from a regularly tetrahedral structure.

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CONTRIBUTION FROM UNION CARBIDE CORPORATION,
PLASTICS DIVISION, BOUND BROOK, NEW JERSEY

Inner Complexes. V. Copper(II) and Nickel(II) Chelates of N-Alkylthiopicolinamides

BY RUDOLPH W. KLUIBER[1]

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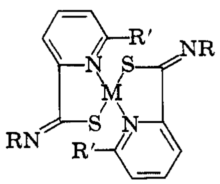
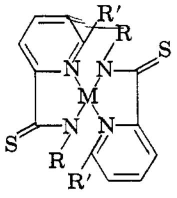
The copper(II) and nickel(II) chelates of a number of N-alkylthiopicolinamides were prepared. These inner complexes are coordinated through the pyridine nitrogen and the thioamide sulfur with a *trans* square-planar configuration around the central metal atom. N-*n*-Butyl-6-methylthiopicolinamide reacts with copper (II) to give a copper(I) chelate.

In the course of studies on mixed chelates we have prepared a number of N-alkylthiopicolinamides and converted these to their copper(II) and nickel(II) inner complexes. As these chelates can have the ligand structure shown in A_1 or A_2 or be a mixture of both ligand structures and each of these can exist in various geometrical configurations around the central metal atom some of which involve aggregation, an effort was made to determine the structure of these materials. Previously, chelates of N-arylthiopicolinamides were prepared and assigned the ligand structure shown in formula A_1.[2] The nickel chelate of N,N′-4,4′-biphenylenebisthiopicolinamide, an insoluble infusible polymer, was assigned a tetrahedral configuration on the basis of its magnetic moment (2.76 B.M.).[3] Octahedral ionic complexes have also been studied and the nickel chelate tentatively assigned nitrogen–sulfur coordination.[4] The present work indicates that the copper(II) and nickel(II) inner complexes of N-alkylthiopicolinamides have the square-planar *trans* structure A_1.



A_1 (M,R,R′)



A_2 (M,R,R′)

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[1] Frick Chemical Laboratory, Princeton University, Princeton, N. J. Correspondence regarding this paper should be sent c/o the Library, Union Carbide Corporation, Plastics Division, Bound Brook, N. J.

[2] F. Lions and K. V. Martin, *J. Am. Chem. Soc.*, **80**, 1591 (1958); K. V. Martin, *ibid.*, **80**, 233 (1958).

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Experimental

Melting points were taken on a Fisher-Johns melting point apparatus and are uncorrected. Elemental analyses were by Dr. G. Weiler and F. G. Strauss, Oxford, England. Acknowledgment is made to Dr. W. F. Beach and Miss J. C. Engeman for the n.m.r. spectra, to Dr. R. G. Shaw for the e.s.r. spectra, to Mr. K. LaGattuta for the X-ray data, and to the analytical personnel of this laboratory for some of the spectra and molecular weights.

Preparation of N-*n*-Butylthiopicolinamide.—In a 100-ml., round-bottomed flask fitted with a condenser were added 13.9 g. (0.1 mole) of thiopicolinamide (Aldrich Chemical Co.) and 7.31 g. (0.1 mole) of *n*-butylamine. The mixture was gradually heated to 150° over a period of 4 hr. at atmospheric pressure. Distillation of the crude product yielded 16.5 g. (85%) of yellow liquid, b.p. 106–112° (0.2 mm.), which solidified upon standing. Recrystallization from petroleum ether gave yellow crystals, m.p. 44–45°. The other thioamides were similarly prepared except the N-*t*-butyl and N-methyl derivatives were prepared at 150° in a pressure vessel using a 50% excess of amine. Analytical results are given in Table I.

TABLE I

THIOPICOLINAMIDES $(C_5H_4N)CS(NHR)$

		Calcd.		Found	
R	M.p., °C.	% C	% H	% C	% H
CH_3[a]	81–83	55.27	5.30	55.23	5.47
n-C_4H_9[b]	44–45	61.82	7.26	61.96	7.11
i-C_4H_9	Liquid	61.82	7.26	61.99	7.19
s-C_4H_9	51–52	61.82	7.26	61.71	7.00
t-C_4H_9[c]	46–48	61.82	7.26	61.79	6.99
$C_6H_5CH_2$	78–79	68.39	5.26	68.13	5.27

[a] Reported m.p. 75–78°, German Patent 964,142. [b] Calcd.: N, 14.42. Found: N, 14.2. [c] Reported b.p. 112–113° (1 mm.): J. Rainey and R. C. Mansfield, U. S. Patent 2,938,907.

Preparation of Metal Chelates of N-*n*-Butylthiopicolinamide.—To a mixture of 50 ml. of water and 5 ml. of dioxane were added 0.005 mole of metal acetate and 1.94 g. (0.010 mole) of N-*n*-butylthiopicolinamide. The reaction mixture was brought to pH 8 and stirred overnight. The crude chelate was purified by recrystallization from benzene–petroleum ether or heptane.

Pure bis[N-(*n*-butyl)thiopicolinamidato]copper(II) formed dark brown needles, m.p. 156–156.5° dec.

Anal. Calcd. for $C_{20}H_{26}N_4S_2Cu$: mol. wt., 450.10. Found: mol. wt. (osmometric, 1% in chloroform, 37°), 456.

Pure bis[N-(*n*-butyl)thiopicolinamidato]nickel(II) recrystallized from heptane formed yellow needles, m.p. 160–161°.

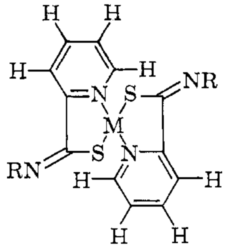
Anal. Calcd. for $C_{20}H_{26}N_4S_2Ni$: mol. wt., 445.25. Found: mol. wt. (osmometric, 1% in chloroform, 37°), 435, 452.

Other chelates were similarly prepared and all are characterized in Table II.

Infrared Spectra.—All infrared spectra were taken using a Perkin-Elmer Model 21 spectrophotometer. Typical maxima in cm.$^{-1}$ and intensities observed for the N-alkylthiopicolinamides in bromoform are 3225 (w) (N–H stretching), 1590 (w), 1515 (s), (amide II),[5,6] 1490 (m), 1330 (m) (thioamide), 1265 (w), 1043 (m), 970 (m), 795 (m) (out of plane hydrogen wagging), 742 (m); for the copper chelates A, 1600 (w), 1560 (s) (C=N stretching),[7] 1520 (m), 1430 (m), 1260 (ms), 1017 (mw), 780 (out of plane wagging), 752 (m); for the nickel chelates A, 1590 (sh), 1570 (s) (C=N stretching), 1470 (m), 1440 (m), 1265 (m), 1025 (m), 775 (s) (hydrogen wagging), 752 (m); for A (Pd, s-C_4H_9, H) 1600 (w), 1553 (s) (C=N stretching), 1470 (m), 1438 (m), 1258 (m), 1029 (w), 775 (s), 748 (m).

TABLE II

METAL THIOPICOLINAMIDES A



			Calcd.		Found	
R	M	M.p., °C.	% C	% H	% C	% H
CH_3	Cu	223–225 dec.	45.95	3.86	46.07	3.96
n-C_4H_9	Cu	156–157 dec.	53.37	5.82	53.08	5.82
i-C_4H_9	Cu	168–169	53.37	5.82	53.43	6.06
s-C_4H_9	Cu	145–146	53.37	5.82	53.47	5.73
t-C_4H_9	Cu	202–203 dec.	53.37	5.82	53.19	5.97
$C_6H_5CH_2$	Cu	170–172 dec.[a]	60.27	4.28	60.14	4.38
n-C_4H_9	Ni	160–161	53.95	5.89	54.11	6.25
i-C_4H_9	Ni	194–196	53.95	5.89	53.79	5.92
s-C_4H_9	Ni	131–132	53.95	5.89	54.05	5.95
t-C_4H_9	Ni	248–250	53.95	5.89	53.77	5.93
s-C_4H_9	Pd	181–183	48.70	5.31	48.52	5.11

[a] Upon melting a yellow solid is formed which decomposes above 220°.

Ultraviolet and Visible Spectra.—The ultraviolet (Table III) and visible spectra were obtained using a Cary Model 14 recording spectrophotometer. Chelate concentrations of 10^{-3} to 10^{-4} M in chloroform were used for the ultraviolet spectra and the visible and near-infrared spectra were obtained using approximately 10^{-2} M solutions. For the nickel chelates, d–d transitions are found around 660 mμ (ε ~90 l. mole^{-1} cm.$^{-1}$), in agreement with a square-planar structure.[8] In pyridine the nickel chelates form green solutions and two low-intensity absorptions appear at 945 mμ (ε 19 l. mole^{-1} cm.$^{-1}$) and 613 mμ (ε 33.1 mole^{-1} cm.$^{-1}$) for A_1 (Ni, n-C_4H_9, H) and at 945 mμ (ε 18 l. mole^{-1} cm.$^{-1}$) and 630 mμ (ε 33 l. mole^{-1} cm.$^{-1}$) for A_1 (Ni, t-C_4H_9, H). These bands are in reasonable agreement with the two lowest frequency absorptions of an octahedral complex.[9] A third band predicted to occur at 360–370 mμ is not observed due to other strong absorptions in this region. The copper chelates in chloroform solutions show shoulders in the 775–800 mμ region (ε 60 l. mole^{-1} cm.$^{-1}$).

N.m.r. Spectra.—The proton n.m.r. spectra were obtained using a Varian A-60 spectrometer. All reported shifts are for chloroform-*d* solutions and are downfield from an internal tetramethylsilane standard. In the aromatic region the chemical shifts for the protons attached to the pyridine carbons 3, 4, 5, and 6 are, respectively, in the ligands 520, 465, 440, and 505 c.p.s., and in the nickel chelates 475, 460, 430, and 505 c.p.s. These values were obtained by center of gravity measurements of various multiplets. The proton assignments were made by comparison with the spectrum of pyridine[10] and thiopicolinamide[11]

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[5] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, New York, N. Y., 1958.

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[9] A. D. Liehr and C. J. Ballhausen, *Ann. Phys.* (N. Y.), **2**, 134 (1959).

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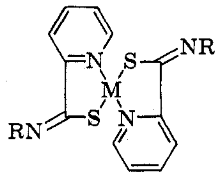
[11] W. Bruegel, *Z. Elektrochem.*, **66**, 159 (1962).

TABLE III

ULTRAVIOLET ABSORPTION MAXIMA OF N-ALKYLTHIOPICOLINAMIDES AND THEIR CHELATES A  IN CHLOROFORM

Compound	$\lambda_{\max}$ (log ϵ, l. mole^{-1} cm.$^{-1}$)			
Thiopicolinamide	406 (2.06)	321 (3.93)	...	272 (3.72)
N-Methylthiopicolinamide	405 (2.08)	317 (3.92)	...	274 (3.91)
N-n-Butylthiopicolinamide	402 (2.13)	320 (3.86)	...	275 (3.90)
N-t-Butylthiopicolinamide	415 (2.11)	321 (3.83)	...	275 (3.86)
A (Cu, CH_3)	431 (3.81)	333 (3.94)	...	272 (4.23)
A (Cu, n-C_4H_9)	438 (3.79)	334 (3.91)	...	274 (4.32)
A (Cu, i-C_4H_9)	439 (3.79)	334 (3.91)	...	274 (4.17)
A (Cu, s-C_4H_9)	440 (3.79)	338 (3.91)	...	273 (4.16)
A (Cu, t-C_4H_9)	456 (3.78)	338 (3.88)	...	273 (4.15)
A (Pd, s-C_4H_9)	397 (3.64)	303 (4.25)	...	269 (4.37)
A (Ni, n-C_4H_9)	447 (3.45)	340 (4.22)	302 (4.06)	267 (4.30)
A (Ni, i-C_4H_9)	447 (3.41)	340 (4.23)	300 (4.06)	267 (4.33)
A (Ni, s-C_4H_9)	450 (3.45)	341 (4.25)	301 (4.07)	267 (4.34)
A (Ni, t-C_4H_9)	455 (3.43)	349 (4.24)	300 (4.03)	268 (4.33)

and by the observation that the absorption for the proton on C-3 is principally a doublet split by 7.5 c.p.s., the proton on C-4 is a distorted triplet split by about 7.3 c.p.s., the proton on C-5 is a complex multiplet, and the proton on C-6 is a doublet with splitting of 5 c.p.s. and with some loss of fine structure apparently due to the nitrogen quadrupole. (Additional splittings of these peaks of about 1 c.p.s. due to *meta* interactions were also noted.)

The relative insensitivity of the resonance peaks due to the protons *ortho* and *para* to the ring nitrogen to coordination suggests that upon coordination the ring nitrogen does not acquire a large positive charge in keeping with the principle of electroneutrality.[12] Aliphatic absorptions are observed at the following frequencies (recorded as c.p.s. downfield from tetramethylsilane; multiplicity where resolved in parentheses): N-n-butylthiopicolinamide, 231 (4), 97, 81, 55.6 (3); A_1 (Ni, n-C_4H_9, H), 224 (3), 100, 60 (3); N-isobutylthiopicolinamide, 222 (3), 121 (9), 59 (2); A_1 (Ni, i-C_4H_9, H), 213 (2), 120–130, 63 (2); N-*sec*-butylthiopicolinamide, 285 (7), 105 (5), 80 (2), 59 (3); A_1 (Ni, s-C_4H_9, H), 245 (6), 100 (5), 74 (2), 57 (3); N-t-butylthiopicolinamide, 100 (1); A_1 (Ni, t-C_4H_9, H), 92 (1). The palladium chelate (Pd, s-C_4H_9, H) absorbed at 517 (2), 493 (2), 468 (3), 440, 247 (6), 100 (5), 74 (2), 57 (3). The spectra of A_1 (Ni, n-C_4H_9, H) in deuteriochloroform taken at various temperatures from 25 to −50° varied little from each other except for a small downfield shift in the center of gravity of the multiplet due to the C-5 pyridine proton and a general broadening of the spectral lines at the lower temperatures. In the presence of small amounts of coordinating materials, such as a tertiary amine, all of the n.m.r. absorptions of the nickel chelates due to the pyridine ring protons and the protons on the carbon adjacent to the thioamide nitrogen are shifted downfield in agreement with the presence of a paramagnetic compound. This shift is largest for the C-6 pyridine proton and diminishes in the order C-6 > C-3, C-5 > C-4, in agreement with a system in which the unpaired electrons on the central metal atom interact mainly with the σ system of the pyridine ring.[13]

E.s.r. Spectra.—These were recorded using a modified Varian instrument. A qualitative electron spin resonance spectrum of the copper(II) chelate (A, R = n-C_4H_9, R′ = H) in chloroform shows four equally spaced peaks of apparently different widths characteristic of the copper atom (Cu^{63}, Cu^{65} $I = {}^3/_2$).[14] Each of these peaks is further split into five peaks having a splitting constant 0.234 that of the copper nucleus splitting. Such splitting is in agreement with the interaction of the unpaired electron with two equivalent nitrogens (N^{14} $I = 1$) as well as the copper atom.

Magnetic Moments.—Using the n.m.r. method of Evans[15] (uncorrected for density) all the nickel chelates of Table II were found to be diamagnetic. A crude Gouy determination on powdered A (Ni, t-C_4H_9) gave $\mu_{\text{eff}} = 0.38 \pm 0.5$ B.M.

X-Ray Diffraction Powder Patterns.—X-Ray diffraction patterns were obtained on finely ground samples using the Kα copper line and a 57.3-mm. radius camera with a 3-hr. exposure. The principal d-spacings in Å. and intensities are for A (Cu, t-C_4H_9) 8.5 (w), 6.8 (s), 5.7 (s), 4.75 (ms), 4.25 (s), 3.80 (w), 3.65 (w), 3.4 (w), 3.2 (m), 3.10 (w), 2.95 (w); for A (Ni, t-C_4H_9) 8.4 (w), 6.7 (ms), 5.6 (ms), 4.8 (m), 4.3 (s), 3.7 (w), 3.2 (w), 3.0 (w); for A (n-C_4H_9, Cu) 8.2 (ms), 7.1 (ms), 5.6 (ms), 4.9 (vw), 4.3 (m), 4.0 (ms), 3.8 (w), 3.55 (s), 3.40 (vw), 3.20 (m), 3.10 (vw); for A (n-C_4H_9, Ni) 7.1 (ms), 6.9 (m), 6.3 (s), 5.7 (ms), 5.2 (vw), 4.5 (ms), 4.0 (ms), 3.65 (s), 3.40 (s), 3.20 (vw), 3.05 (vw); for A (i-C_4H_9, Cu) 6.5 (m), 6.0 (s), 5.3 (mw), 4.9 (m), 4.5 (mw), 4.3 (m), 4.0 (s), 3.8 (m), 3.65 (mw), 3.45 (s), 3.30 (vw), 3.18 (m), 3.05 (w); for A (i-C_4H_9, Ni) 6.1 (s), 4.9 (m), 4.6 (mw), 4.3 (mw), 4.0 (s), 3.85 (s), 3.5 (vw), 3.25 (m).

Bis(thiopicolinamidato)nickel(II).—Stoichiometric amounts of thiopicolinamide and nickel acetate were mixed in 30 ml. of dioxane–water and the mixture brought to pH 7. A red-brown precipitate of bis(thiopicolinamidato)nickel(II), which did not melt below 300° and was only sparingly soluble in chloroform, was obtained.

Anal. Calcd. for $C_{12}H_{10}N_4S_2Ni$: C, 43.27; H, 3.02; N, 16.82. Found: C, 43.11; H, 3.10; N, 16.7.

The infrared spectrum of this chelate in a potassium bromide disk showed significant absorptions at about 3300 cm.$^{-1}$, in the 6–7 μ region at 1610 cm.$^{-1}$, and a very strong band split into absorptions at 1492, 1470, and 1438 cm.$^{-1}$. Thiopicolinamide absorbs in this latter region at 1602, 1588, and 1447 cm.$^{-1}$ in a KCl pellet and at 1577, 1561, and 1440 cm.$^{-1}$ in a bromoform solution. The magnetic moment of this nickel chelate was found to be 3.21 B.M. by the Gouy method. The ultraviolet spectrum in chloroform shows peaks at 475, 372, 328, and 261 mμ. As a Nujol mull this chelate absorbs at 417 and 275 mμ and in a potassium chloride disk it absorbs maximally above 300 mμ at 400 mμ.

Chelate from N-n-Butyl-5-methylthiopicolinamide.—6-Methylthiopicolinamide, 30.4 g., and 14.6 g. of n-butylamine were heated to 150° and maintained at that temperature for 3 hr.

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[12] L. Pauling, *J. Chem. Soc.*, 1461 (1948).

[13] J. A. Happe and R. L. Ward, *J. Chem. Phys.*, **39**, 1211 (1963).

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Distillation yielded 24 g. of N-*n*-butyl-6-methylthiopicolinamide, m.p. 12°, b.p. 120–125° (1 mm.).

Anal. Calcd. for $C_{11}H_{16}N_2S$: C, 63.41; H, 7.74. Found: C, 63.23; H, 7.64.

The n.m.r. spectrum has absorptions at (in c.p.s. downfield from tetramethylsilane) (multiplicity) (assignment) 59 (3) ($-CH_3$), 100 (very broad) ($-CH_2CH_2-$), 152 (1) (pyridine C-6–CH_3), 331 (4) (N–CH_2–), 432 (2) (pyridine C-5–H), 458 (3) (pyridine C-4–H), 508 (2) (pyridine C-3–H). The areas under the peaks are in the correct proportion. The region in which N–H protons absorb was not investigated.

Copper acetate, 10 g., dissolved in 100 ml. of water and 7 g. of N-*n*-butyl-6-methylthiopicolinamide in 10 ml. of dioxane were mixed together and neutralized with 4 *N* sodium hydroxide solution. The crude red-brown precipitate was recrystallized from large volumes of heptane to yield 3.4 g. of a yellow solid. This yellow solid was converted to a red solid by heating to 120° or by grinding. The yellow form is immediately soluble in chloroform, whereas the red form dissolves slowly to give the yellow form recoverable by precipitation with petroleum ether. Although indefinitely stable as the crystalline solid, in solution this compound slowly decomposed to give a black amorphous solid containing Cu(II) (by e.s.r.). Magnetic susceptibility measurements by the Gouy method indicate both the yellow and red forms to be diamagnetic solids. The n.m.r. spectrum has peaks centered at 56, 98, 139, 334, 406, 440, and 479 c.p.s. of comparable intensity and splitting to the uncoordinated ligand except for the peak at 334 c.p.s. which is a triplet.

Anal. Calcd. for $(C_{11}H_{15}N_2SCu)_x$: C, 48.77; H, 5.58; N, 10.34; mol. wt. ($x = 4$), 1083. Found (yellow form): C, 48.87; H, 5.64; N, 10.31, mol. wt. (osmometric, 1% in benzene, 37°), 990. Found (red form): C, 48.89; H, 5.35; N, 10.54.

The infrared spectrum in bromoform shows relatively strong absorption peaks at 1587, 1451, 1005, 798, and 741 cm.$^{-1}$, whereas the starting ligand absorbs relatively strongly at 3250, 1520, 1450, 1325, 1081, 805, and 743 cm.$^{-1}$.

The ultraviolet spectrum has maxima at 348 and 283 mμ in chloroform.

Discussion

The most likely structure for bis(N-alkylthiopicolinamidato)copper(II) or -nickel(II) is the square-planar *trans* structure A_1. The n.m.r. spectra are compatible with this structure and show no evidence for the presence of more than one ligand structure. The molecular weight measurements in solution and the near invariance of the n.m.r. spectrum of the nickel chelates at ambient and low temperature indicate these materials are monomeric with little tendency to associate in solution. The similarity of the ultraviolet and infrared spectra of a variety of these chelates indicates that the ligand to metal bonds are formed from the same group of donor atoms in all cases. The infrared spectra further suggest the presence of a C=N– bond in all of these chelates. That the geometrical arrangement of the ligands about the nickel(II) ion is square-planar is supported by the magnetic data and the visible spectra. The geometry of the copper(II) chelates is indicated to be square-planar as the crystalline A (Cu, *t*-C_4H_9, H) compound is isomorphous with the corresponding nickel chelate. The e.s.r. data further require the copper atom to be bonded to two equivalent nitrogens.

Although dipole moments were not measured, the *cis* form of square-planar A_1 or A_2 (*i.e.*, that structure in which the two pyridine rings are attached to *cis* positions of the metal atom) is an unlikely structure due to steric interactions between R′ groups on adjacent pyridine rings.[16,17] Thus, in order for the pyridine rings to lie in the same plane in a stable structure having a *cis* configuration around the central metal atom and normal metal to ligand bonds, the central metal atom must have a radius larger than that found in the first transition series. The *trans* square-planar structure A_2 in which the thioamide nitrogens are trigonal can be ruled out on the basis of steric interaction between the opposed R and R′ groups. This interaction is significant even in the example A_2 (R = CH_3, R′ = H) and is prohibitively large in the square-planar chelate A_2 (R = *t*-C_4H_9, R′ = H). In the less hindered salicylaldimines, as the size of the nitrogen substituent increases, the structures of the nickel(II) chelates change from square-planar to tetrahedral with corresponding changes in spectral and magnetic properties.[18] The similarity of the spectra and magnetic moments in the series A (R = CH_3) to A (R = *t*-C_4H_9) therefore rules out A_2 with a trigonal thioamide nitrogen.

An alternate structure A_2 in which the thioamide nitrogen is tetrahedral cannot be ruled out on steric grounds, but it should be energetically unfavorable as in this configuration the thioamide nitrogen cannot participate in resonance stabilization of the thioamide group.[19] In addition bulky R groups should shield the *z* axis and inhibit the formation of an octahedral complex. However, the spectral data show that both A (R = *n*-C_4H_9) and A (R = *t*-C_4H_9) form octahedral complexes in pyridine solutions indicating the *z* axis to be relatively unhindered, although rearrangements to give other configurations have not been ruled out. The most reasonable structure thus remains the square-planar form A_1. The similarity in the physical properties of the palladium(II) chelate to those of the nickel(II) and copper(II) chelates is in agreement with this conclusion as in nitrogen–sulfur competition palladium(II) generally (though not exclusively) coordinates with the sulfur donor in a square-planar complex.

Exceptions to the general structure A_1 include the copper chelate of N-*n*-butyl-6-methylthiopicolinamide. Here neither the *cis* nor *trans* square-planar A_1 or A_2 is free from strong inter-ligand steric effects involving the 6-methyl group. As chelation of this ligand to give a square-planar copper(II) complex is sterically unfavorable an alternate reaction, the reduction of copper(II) to copper(I), occurs. Similar effects have been reported for the reaction of other sulfur-containing ligands with copper(II).[16,20,21] The n.m.r. spectrum indicates that in this copper(I) chelate considerable back donation of electrons from the copper to the py-

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ridine ring occurs. Unlike the back donation of electrons in pyridine oxide which occurs through the ring π system, the back donation of electrons in this chelate appears to be distributed in the pyridine ring by the σ bonds. Another possible exception to the structure A_1 is bis(thiopicolinamidato)nickel(II), in which the low steric requirements of the hydrogens could allow the formation of structure A_2. Although the solution ultraviolet spectrum of this compound supports structure A_2, the magnetic data and solubility indicate that this material is polymeric in the solid phase, presumably due to interchelate coordination.

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Kinetics of the Substitution Reaction between Copper(II) and Monoiminodiacetatonickelate(II)

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The kinetics of the substitution reaction between the monoiminodiacetatonickelate(II) ion and the hydrated copper(II) ion have been studied from pH 4.9 to 3.4 with ionic strength and temperature variation. The over-all rate of reaction is given by the expression $R = k_{\mathrm{Cu}}{}^{\mathrm{NiL}}[\mathrm{Cu}^{+2}][\mathrm{NiL}] + k^{\mathrm{NiL}}[\mathrm{NiL}] + k_{\mathrm{H}}{}^{\mathrm{NiL}}[\mathrm{H}^+][\mathrm{NiL}]$ where [NiL] refers to the concentration of the monoiminodiacetatonickelate(II) ion. The rate expression is similar to that for copper exchange with the nitrilotriacetatonickelate(II) ion[1] and is quantitatively related to this rate on the basis of proposed reaction intermediates assuming an identical rate step in each system, *i.e.*, the breaking of the nickel–nitrogen bond.

Introduction

The reaction of copper(II) with the nitrilotriacetatonickelate(II) ion[1] has been measured and postulated to proceed through an intermediate possessing an acetate group bonded to copper(II) and a glycinate segment bonded to nickel(II). The rate-determining step involves the breaking of the nickel–nitrogen bond. The third acetate group of the ligand was assumed to be nonbonded but contributed to the stability of the intermediate by electrostatic attraction. The present study investigates the effect of replacing this acetate group by a proton, giving the ligand, iminodiacetate (ImDA or L^{-2}). The copper attack and hydrogen ion dissociation of its nickel complex (Ni–ImDA or NiL) are studied.

The system is

$$\mathrm{NiL} + \mathrm{Cu}^{+2} \xrightleftharpoons[k_{\mathrm{Ni}}{}^{\mathrm{CuL}}]{k_{\mathrm{Cu}}{}^{\mathrm{NiL}}} \mathrm{CuL} + \mathrm{Ni}^{+2} \tag{1}$$

$$\mathrm{NiL} \xrightleftharpoons[k_{\mathrm{Ni}}{}^{\mathrm{L}}]{k^{\mathrm{NiL}}} \mathrm{Ni}^{+2} + \mathrm{L}^{-2} \tag{2}$$

$$\mathrm{NiL} + \mathrm{H}^+ \xrightleftharpoons[k_{\mathrm{Ni}}{}^{\mathrm{HL}}]{k_{\mathrm{H}}{}^{\mathrm{NiL}}} \mathrm{Ni}^{+2} + \mathrm{HL}^- \tag{3}$$

$$\mathrm{Cu}^{+2} + \left[\begin{smallmatrix} & \mathrm{L}^{-2} \\ \mathrm{HL}^- & \end{smallmatrix}\right] \xrightleftharpoons{\text{rapid}} \mathrm{CuL} + [\mathrm{H}^+] \tag{4}$$

Experimental

The experimental procedures were similar to those reported previously.[1,2] Precautions were taken to avoid interferences from other complexes or from trace impurities. No buffer was used and no difficulty was encountered in maintaining constant pH during the reaction in the pH range studied. The pH of the reaction solutions was adjusted with perchloric acid. Sodium perchlorate was used to adjust the ionic strength. Nickel and copper perchlorates were prepared from their carbonates and standardized by direct titration (using murexide indicator) against a standard EDTA solution. Iminodiacetic acid was precipitated by the addition of hydrochloric acid to a solution of the disodium salt (Eastman). The acid was further recrystallized three times from water and standardized as a monoprotic acid[3] by pH titration with standard sodium hydroxide solution. Results of these titrations agreed to within 0.5% of the theoretical value. In the rate studies, solutions of ImDA were prepared just prior to use to avoid possible bacterial decay. Nickel perchlorate was then added in excess to assure the formation of the mono complex[4] and the pH adjusted to 5. The reaction was begun by the addition of an acidic copper perchlorate solution.

The reaction was followed spectrophotometrically at the 725 mμ absorption band of Cu–ImDA. The values of ϵ_{NiL}, ϵ_{Ni}, ϵ_{Cu}, and ϵ_{CuL} are 1.8, 2.1, 8.4, and 70.2 M^{-1} cm.$^{-1}$, respectively, at 725 mμ. The values of ϵ_{NiL} and ϵ_{CuL} are independent of pH in the range 5.0 to 3.4, indicating no evidence for any acid species such as HNi–ImDA.

The concentration of product at any time was calculated from the expression

$$[\mathrm{Cu\text{–}ImDA}] = \frac{A - A_{\mathrm{i}}}{b(\epsilon_{\mathrm{CuL}} + \epsilon_{\mathrm{Ni}} - \epsilon_{\mathrm{NiL}} - \epsilon_{\mathrm{Cu}})} \tag{5}$$

where A is the observed absorbance, A_{i} is the initial absorbance of the reactants, and the cell length, b, is 5 cm. The absorbance measurements were made against a blank solution containing an equivalent copper concentration as the rate solution. Equation 5 assumes that there is no stable mixed complex such as $\mathrm{NiImDACu}^{+2}$. This assumption appears valid since the values of the initial absorbance obtained by extrapolation to zero time agree very well with the theoretical values. All rate solutions

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