CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
CASE WESTERN RESERVE UNIVERSITY, CLEVELAND, OHIO 44106

Square-Planar Sulfur Complexes. VI.[1a] Reactions of Bases with Xanthates, Dithiocarbamates, and Dithiolates of Nickel(II)

BY D. COUCOUVANIS[1b] AND J. P. FACKLER, JR.

Received June 12, 1967

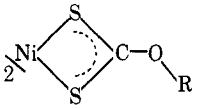
Nitrogenous bases are found to interact strongly with nickel(II) complexes of 1,1-dithio ligands of the type $S_2CCR_3^-$, S_2COR^- and $S_2CNH_2^-$ to form high-spin adducts. Little or no interaction is observed with nickel(II) complexes of the ligands $S_2CNR_2^-$, S_2CS^{2-}, S_2CNR^{2-}, or $S_2CCR_2^{2-}$. The extent of metal–base interaction appears to be directly related to the ability of the ligand to mesomerically shift electron density onto the metal through its π system. Several new sulfur chelates of the 1,1-dithio type are reported in this study.

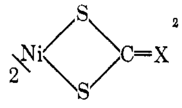
Introduction

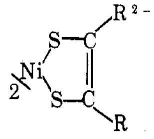
Often metal complexes expand their coordination number by interaction with a Lewis base. This may take place by intermolecular association[2a] or by adduct[2b] formation[3-5] with solvent or other available ligands. The physical properties of the resulting complex often are significantly different from those of the complex not having the expanded coordination number.

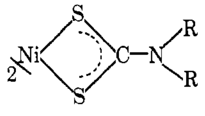
A well-studied class of chalcogenide complexes exhibiting this behavior is the metal β-ketoenolates.[2] For example, a planar, diamagnetic β-ketoenolate complex[3] of nickel(II) such as bis(dipivaloylmethane)-nickel(II) becomes a paramagnetic, presumably *trans*-octahedral species on adduct formation with a Lewis base such as pyridine.[5a] The ability to form adducts also is reflected in the tendency of these complexes to polymerize in noninteracting solvents or in the solid state, that is when the best available Lewis base is another molecule of the complex. Thus acetylacetonates of many bivalent metals and some trivalent metals associate in noncoordinating solvents or in the solid state and readily interact with Lewis bases. With the β-ketoenolates, it was observed[2] that changes in the electronic properties of the ligand have considerably less effect on adduct formation than do changes in the stereochemistry of the ligand. To our knowledge all nickel(II) complexes of the type NiO_4 interact with bases to expand the coordination about the metal ion except when the ligand stereochemically blocks the addition to a fifth or sixth coordination site on the metal ion.

In contrast to the NiO_4 complexes, NiS_4 complexes[6] vary substantially in their ability to interact with Lewis bases. Furthermore, the ability to interact with bases seems to be related closely to the electronic properties of the ligand as a whole, not just the atoms bonded to the metal. Thus xanthate complexes (Ia)[7,8] of nickel(II) strongly interact with Lewis bases while the electronic spectra of 1,1-dithiolate complexes[9] (Ib, X = S, CR_2, or NR) or 1,2-dithiolate complexes[10] (Ic) are unperturbed even by dissolution in solvents which are good bases.

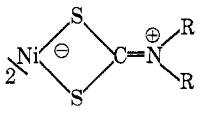

Ia


Ib


Ic


Id

The nickel(II) dithiocarbamates[11,12] (Id) display a behavior toward adduct formation which is intermediate to the extremes mentioned above for the xanthates and dithiolates. In fact, the tendency for adduct formation appears to be related to the degree to which a canonical structure of type II is important[13] in describing these complexes.


II

Experimental Section

Except for the heterocyclic bases which were distilled, chemicals were used as purchased.

Analyses were performed by Galbraith Microanalytical Laboratories, Knoxville, Tenn. Melting points recorded are uncorrected. Complexes were checked for purity by thin layer chromatography.

---

(1) (a) Part V: D. Coucouvanis and J. P. Fackler, Jr., *J. Am. Chem. Soc.*, **89**, 1346 (1967). Abstracted from the Ph.D. thesis of D. Coucouvanis. (b) Petroleum Research Fund Predoctoral Fellow, 1965–1966.

(2) (a) J. P. Fackler, Jr., *Progr. Inorg. Chem.*, **7**, 361 (1966). (b) We assume in this paper that adduct formation means coordination to the metal.

(3) J. T. Hashagen and J. P. Fackler, Jr., *J. Am. Chem. Soc.*, **87**, 2821 (1965).

(4) R. W. Kluiber and W. D. Horrocks, *ibid.*, **87**, 5350 (1965).

(5) D. P. Graddon and E. C. Watson, *Nature*, **187**, 1021 (1960).

(5a) NOTE ADDED IN PROOF.—W. D. Horrocks, private communication, finds the pyridine N-oxide adduct of nickel(II) acetylacetonate to have a *cis* configuration.

(6) S. B. Livingstone, *Quart. Rev.* (London), 386 (1965).

(7) G. W. Watt and B. J. McCormick, *J. Inorg. Nucl. Chem.*, **27**, 898 (1965).

(8) L. Cambi and L. Szego, *Atti Accad. Lincei*, **13**, 93 (1931).

(9) J. P. Fackler, Jr., and D. Coucouvanis, *Chem. Commun.*, 566 (1965).

(10) H. B. Gray, *Progr. Trans. Met. Chem.*, **1**, 240 (1965).

(11) K. Gleu and R. Schwab, *Angew. Chem.*, **62**, 320 (1950).

(12) M. Delepine, *Bull. Soc. Chim. France*, 5 (1958).

(13) J. Chatt, L. A. Duncanson, and L. M. Venanzi, *Suomen Kemistilehti*, **B29**, 75 (1956).

Physical Measurements.—Magnetic susceptibilities (Table I) were determined at room temperature using a Faraday technique. The calibrant was $Hg[Co(SCN)_4]$.[14]

Table I

Magnetic Properties of Some 1,1-Dithio Complexes and Their Base Adducts

Complex[a]	$10^6\chi_g$, cgs units	μ_{eff}^{cor}, BM[a]
$(n\text{-}C_4H_9N)_2Ni(S_2CNC_6H_5)_2$	. . .	Diamagnetic
$((CH_3)_3C_6H_5)Ni(S_2COC_2H_5)_3$	5.89	3.0
$Ni(S_2CNH_2)_2(\gamma\text{-pic})_2$[b]	8.21	2.9
$Ni(S_2CNHC_6H_4Cl)_2(\gamma\text{-pic})_2$[b,c]	. . .	Paramagnetic[c]
$Ni(S_2COC_2H_5)_2(py)_2$[b]	8.73	3.2
$Ni(S_2COC_2H_5)_2(\gamma\text{-pic})_2$[b]	7.01	3.0

[a] Temperature ≃27°; diamagnetic correction, B. Figgis and J. Lewis, "Modern Coordination Chemistry," Interscience Publishers, Inc., New York, N. Y., 1960. [b] γ-pic = 4-methylpyridine, py = pyridine. [c] The adduct loses base at a rate too fast to allow an accurate Faraday measurement.

Infrared spectra were obtained with Beckman IR-8 and IR-7 recording spectrophotometers, frequency calibrated with polystyrene. Ultraviolet, visible, and near-infrared spectra were obtained with a Cary Model 14 recording spectrophotometer. Reflectance spectra were obtained with a Beckman DK-2 recording spectrophotometer equipped with a reflectance attachment.

Ammonium Dithiocarbamate.—Carbon disulfide, 25 ml, was diluted with 150 ml of tetrahydrofuran (THF). Ammonia was bubbled through the mixture at a vigorous pace. After ~10 min the white crystalline precipitate which formed was filtered off, washed with ether, and dried; yield, 26 g. The filtrate was treated with ammonia for an additional 10 min, whereupon 10 g more of product was obtained. Since the theoretical yield of dithiocarbamate based on carbon disulfide is 28 g, we conclude that the product is a THF adduct. A similar reaction of NH_3 and CS_2 in cyclic ethers has been described.[15]

Bis(dithiocarbamato)bis(4-methylpyridine)nickel(II).—The 4-methylpyridine adduct was prepared by treating a concentrated acetone solution of $Ni(S_2CNH_2)_2$[16] with a twofold excess of 4-methylpyridine. The acetone was evaporated *in vacuo*, whereupon light green crystals of the adduct were isolated. *Anal.* Calcd for $C_{14}H_{18}N_4S_4Ni$: C, 39.60; H, 4.24; N, 13.18. Found: C, 39.55; H, 4.44; N, 12.61.

Bis(dithiocarbamato)bis(pyridine)nickel(II).—A concentrated acetone solution of $Ni(S_2CNH_2)_2$ was treated with a threefold excess of pyridine; upon evaporation of the solvent *in vacuo*, grass green crystals were isolated which were filtered off and dried in a stream of nitrogen. The dried crystals, on standing in a loosely stoppered vial for 24 hr, changed to a blue powder which was found by comparison with an authentic sample to be $Ni(py)_2(SCN)_2$.[17]

Bis(ethylxanthato)bis(pyridine)nickel(II).—A concentrated solution of nickel(II) ethylxanthate was treated with a twofold excess of pyridine. Upon addition of an excess of anhydrous ether and cooling, green crystals were deposited which were washed with ether and dried in a stream of nitrogen. *Anal.* Calcd for $C_{18}H_{20}N_2O_2S_4Ni$: C, 41.80; H, 4.36; N, 6.09. Found: C, 42.6; H, 4.44; N, 5.68.

The 4-methylpyridine adduct was prepared in a manner analogous to the one described above for the bis-pyridine adduct. It is difficult to remove the extra 4-methylpyridine without decomposing the material. *Anal.* Calcd for $Ni(S_2COC_2H_5)_2 \cdot 3C_7H_7N$: C, 49.60; H, 5.45; N, 7.24. Found: C, 49.33; H, 5.52; N, 7.19.

Trimethylphenylammoniumtris(ethylxanthato)nickel(II).—Sodium ethylxanthate, 4.32 g (0.03 mole), was dissolved into 50 ml of water. This solution was added with stirring to a solution of 2.4 g (0.01 mole) of $NiCl_2 \cdot 6H_2O$ and 1.8 g (0.01 mole) of trimethylphenylammonium chloride in 100 ml of water. The green precipitate which formed was redissolved by slowly adding hot acetone, and the solution was filtered. Upon slowly evaporating some of the solvent (in air), green crystals were formed which were isolated, washed with ether, and dried; 4.3 g of product was isolated (77% yield), mp 105°. The crystals on standing in a stoppered vial for ~3 months decomposed to a black, tacky resin. *Anal.* Calcd for $C_{24}H_{29}NO_3S_6Ni$: C, 38.77; H, 6.28; N, 2.51; mol wt, 629.7. Found: C, 39.13; H, 5.53; N, 2.77; mol wt (crystallographic), 632.

Bis(N-phenyldithiocarbamato)nickel(II).—Aniline, 4.7 g (0.05 mole), was added to a solution of 3.8 g (0.05 mole) of CS_2 in 60 ml of methanol. To the yellow solution, an aqueous solution of 7 g of nickel(II) acetate was added with stirring. An olive green precipitate appeared and the suspension was treated with acetone until all of the precipitate dissolved, and the solution was filtered. Upon evaporation of about half of the solvent under reduced pressure, 4.5 g of yellow-green crystals were isolated in 25% yield, mp 196°.

Bis(tetrabutylammonium)bis(N-phenyldithiocarbimato)nickel(II).—Bis(phenyldithiocarbamato)nickel(II), 3 g, was dissolved into 50 ml of hot absolute ethanol saturated with NaOH. An intense green color developed immediately. The solution was filtered and to the filtrate a solution of 7 g of tetrabutylammonium bromide in 50 ml of H_2O was added with stirring. Upon addition of an excess of water, a dark green oil formed which soon crystallized. The product was dissolved in nitromethane and ether was added until the first cloudiness appeared. On cooling, dark green crystals formed which were isolated, mp 151–153°. The aqueous ethanolic filtrate on further standing gave additional crystals; total yield, ~41%. *Anal.* Calcd for $C_{46}H_{84}N_4S_4Ni$: C, 62.9; H, 9.57; N, 6.39. Found: C, 61.9; H, 9.34; N, 6.71.

Bis[N-(*p*-toluidine)dithiocarbamato]nickel(II).—This compound was prepared in exactly the same manner as the phenyldithiocarbamate complex. Seven grams of dark olive green crystals was isolated (35% yield), mp 169–170°. *Anal.* Calcd for $C_{16}H_{16}S_4Ni$: C, 45.40; H, 3.78; N, 6.62. Found: C, 45.70; H, 3.88; N, 6.39.

Bis[N-(*p*-chlorophenyl)dithiocarbamato]nickel(II).—*p*-Chloroaniline, 6.9 g (0.05 mole), was added to a solution of 3.8 g (0.05 mole) of CS_2 in 60 ml of methanol. To the dark orange solution, a solution of 7 g of $Ni(OCOCH_3)_2 \cdot 4H_2O$ was added with stirring. A yellow-green precipitate appeared which was filtered off and dried. On recrystallization from tetrahydrofuran (THF), 5.5 g of yellow-green crystals was isolated, mp 203° dec. *Anal.* Calcd for $C_{14}H_{10}Cl_2S_4Ni$: C, 36.23; H, 2.16; N, 6.04. Found: C, 36.65; H, 2.32; N, 6.09.

Bis[N-(*p*-chlorophenyl)dithiocarbamato]bis(4-methylpyridine)nickel(II).—The 4-methylpyridine adduct was prepared by treating a concentrated acetone solution of the bis(*p*-chlorophenyldithiocarbamato)nickel(II) complex with 4-methylpyridine. Upon addition of an excess of water, a light green precipitate formed which was filtered off and washed with a 1:1 mixture of pentane–4-methylpyridine. On heating under vacuum the base adduct loses two molecules of 4-methylpyridine per molecule of complex as determined by weight loss.

Results

Complexes of nickel(II) with dithiocarbamates[12] and xanthates[7] were prepared according to literature methods. To our knowledge the dithiocarbamates of *p*-chloroaniline and *p*-toluidine and the anilinedithiocarbimate of nickel(II) are new compounds.

When the bis(diethyldithiocarbamato)nickel(II) complex is dissolved in pyridine or 4-methylpyridine, it gives a room-temperature absorption spectrum identi-

---

(14) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4190 (1958).

(15) R. A. Mathes, U. S. Patent 2,123,370 (1938); *Chem. Abstr.*, **32**, 6672[7] (1938).

(16) M. Delepine, *Compt. Rend.*, **146**, 981 (1908).

(17) S. M. Nelson and T. M. Shepherd, *Inorg. Chem.*, **4**, 813 (1965).

cal with the spectrum in a noncoordinating solvent such as $CHCl_3$. Upon cooling the pyridine or γ-picoline solutions of the complex to liquid nitrogen temperatures, the color changes from dark olive green to grass green. A similar behavior is observed for acetone solutions of $Ni(S_2CNH_2)_2$ on addition of a nitrogenous heterocyclic base. The absorption band at $\sim$10,000 cm^{-1} associated with the spin-free adduct increases or decreases in intensity as the temperature is lowered or raised, respectively. Solutions of this complex in pyridine at different temperatures are nonconducting.

Solid base adducts of $Ni(S_2CNH_2)_2$ could be obtained with pyridine or 4-methylpyridine. The crystalline compounds were characterized as 2:1 adducts by their elemental analyses. The pyridine 2:1 adduct decomposed in 24 hr into a blue solid which was found to be $Ni(py)_2(SCN)_2$ by comparison with a directly prepared sample. Ammonium dithiocarbamate has been reported to decompose to thiocyanate and ammonium sulfide.[18]

While cyclic tertiary amines add to the unsubstituted dithiocarbamatonickel(II) complex to give the above-mentioned base adducts, cyclic secondary amines like morpholine or piperidine replace the NH_2 group of the ligand. (This very interesting transamination reaction will be reported fully elsewhere.) The *p*-chloroaniline, *p*-toluidine, and aniline dithiocarbamates of nickel(II) dissolve in cyclic aromatic nitrogenous bases to give an intense green color. The bis(N-phenyldithiocarbamato)nickel(II) complex when treated with base in ethanol gives the corresponding dithiocarbimate complex anion[19] which can be isolated as its tetrabutylammonium salt. The infrared spectra of the various dithiocarbimate complexes (Figure 1) clearly show the absence of the N–H stretch which is present in the parent dithiocarbamate complex. The diamagnetic compound is a 2:1 electrolyte in nitromethane. Its electronic spectrum (Table II) is similar to spectra of other square-planar nickel(II) sulfur complexes. No change in the spectrum is observed when the dithiocarbimates are dissolved in 4-methylpyridine or pyridine.

The solution and reflectance, visible, and near-infrared spectra of some of the dithiocarbamate and xanthate adducts are shown in Figure 2.

The room-temperature magnetic susceptibilities of the compounds of interest are given in Table I. The N-phenyldithiocarbimate complex is diamagnetic, as are the base-free dithiocarbamate and xanthate complexes of nickel(II). The adducts are paramagnetic and exhibit moments typical of octahedral or pseudo-octahedral complexes of nickel(II).

When aqueous nickel(II) is treated with an excess of ethylxanthate, the tris(ethylxanthato)nickelate(II) anion is formed.[20] It can be isolated with a large cation such as $(CH_3)_3C_6H_5N^+$. The compound is paramagnetic and has an electronic spectrum similar to those of the octahedral adducts with neutral bases. Its infrared spectrum (Table III, Figure 3) is similar to that of the xanthate complexes with some shifting of band positions.

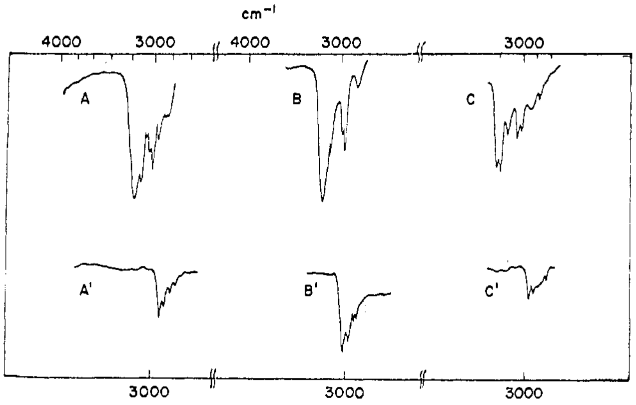


Figure 1.—Infrared NH stretching region of (A) $Ni(S_2CNHC_6H_5)_2$, (B) $Ni(S_2CNHC_6H_4CH_3)_2$, (C) $Ni(S_2CNHC_6H_4Cl)_2$, (A′) $Ni(S_2CNC_6H_5)_2^{2-}$, (B′) $Ni(S_2CNC_6H_4CH_3)_2^{2-}$, and (C′) $Ni(S_2CNC_6H_4Cl)_2^{2-}$. Hexachlorobutadiene mull: 4000–2000 and 1500–1300 cm^{-1}; Nujol mull: 2000–1500 and 1300–625 cm^{-1}

TABLE II

NEAR-INFRARED AND VISIBLE SPECTRA OF SOME 1,1-DITHIO COMPLEXES AND THEIR BASE ADDUCTS

Complex	$\bar{\nu}_{max}$, cm^{-1}	ϵ, M^{-1} cm^{-1}
$Ni(S_2COC_2H_5)_2(\gamma\text{-pic})_2$[a]	9,250 sh	50
	10,350	65
$[(CH_3)_3C_6H_5N]Ni(S_2COC_2H_5)_3$[b]	15,850	75
	8,650 sh	88
	9,550	110
	14,850	165
$Ni(S_2CNHC_6H_4Cl)_2(\gamma\text{-pic})_2$[a]	9,000 sh	110
	10,050	145
	15,950	278
$Ni(S_2CNHC_6H_5)_3$[c]	15,560	129
	18,000 sh	94
$[(C_4H_9)_4N]_2Ni(S_2CNC_6H_5)_2$[c,d]	16,250	170

[a] Spectrum in γ-picoline. [b] Spectrum in acetonitrile. [c] Spectrum in acetone. [d] Position independent of solvent, pyridine.

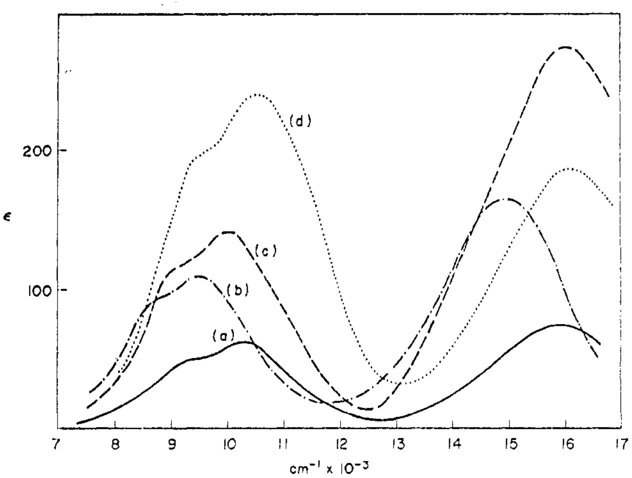


Figure 2.—Electronic spectra of (a) $Ni(S_2COC_2H_5)_2(py)_2$ in pyridine, (b) $[(n\text{-}C_4H_9)_4N]Ni(S_2COC_2H_5)_3$ in CH_3CN, (c) $Ni(S_2CNHC_6H_4Cl)_2(\gamma\text{-pic})_2$ in γ-picoline, and (d) $Ni(S_2CNH_2)_2(\gamma\text{-pic})_2$ diffuse reflectance.

---

[18] R. A. Mathes, *Inorg. Syn.*, **3**, 48 (1950).

[19] J. P. Fackler, Jr., and D. Coucouvanis, *J. Am. Chem. Soc.*, **88**, 3913 (1966).

[20] R. L. Carlin and co-workers, private communication, have studied the formation of this species in solution.

TABLE III

INFRARED SPECTRA ($\bar{\nu}$, CM^{-1}) OF SOME 1,1-DITHIO COMPLEXES AND THEIR BASE ADDUCTS

$Ni(S_2CNH_2)_2(\gamma\text{-pic})_2{}^{a,b}$

1717 m, 1660 w, 1615 s, 1563 w, 1500 m, 1467 s, 1418 m, 1378 s, 1328 w, 1365 s, 1230 w, 1223 w, 1211 m, 1103 m, 1069 m, 1020 m, 990 w, 872 s, 860 s, 813 s, 804 s, 723 s, 667 s

$Ni(S_2CNH_2)_2(py)_2{}^{a,b}$

1620 s, 1600 s, 1480 m, 1450 m, 1350 s, 1235 w, 1205 m, 1145 m, 1065 s, 1035 s, 1025 s, 1010 s, 998 s, 945 w, 858 s, 750 s, 695 s

$Ni(S_2COC_2H_5)_2(\gamma\text{-pic})_2{}^{a,b}$

1715 m, 1620 s, 1608 s, 1504 s, 1465 s, br, 1420 m, 1380 s, 1360 m, 1295 w, 1270 w, 1195 vs, 1150 m, 1125 m, 1064 m, 1042 s, 1019 m, 995 w, 895 m, 804 vs, 797 s, 723 s

$Ni(S_2COC_2H_5)_2(py)_2{}^{a,b}$

1925 vw, 1600 s, 1480 m, 1450 m, 1442 s, 1370 w, 1355 w, 1218 m, 1190 vs, 1145 m, 1120 s, 1065 m, 1038 vs, 1010 m, 945 vw, 876 vw, 813 sh, 807 vs, 795 s, 723 s

$Ni(S_2CNHC_6H_5)_2{}^{a}$

3150 s, 3100 m, 3000 m, 2900 s, 2860 s, 1600 m, 1525 s, 1490 m, 1445 s, 1390 s, 1335 sh, 1285 w, 1220 w, 1155 w, 1075 w, 1028 w, 995 s, 900 w, 751 s, 691 s, 672 m

$[(n\text{-}C_4H_9)_4N]_2Ni(S_2CNC_6H_5)_2{}^{a}$

2940 s, 2850 m, 1600 w, 1580 w, 1500 vs, 1380 s, 1200 w, 1165 m, 1150 m, 1065 w, 1055 w, 1020 w, 923 s, 888 m, 765 s, 731 m, 700 s

$Ni(S_2CNHC_6H_4Cl)_2{}^{a}$

3120 s, 3075 m, 2950 m, 2850 w, 1900 w, 1590 m, 1520 m, 1490 m, 1450 s, 1390 s, 1300 sh, 1280 sh, 1220 w, 1175 w, 1096 s, 1117 m, 1005 s, 835 w, 820 s, 710 s, 678 m, 667 w

$Ni(S_2CNHC_6H_4Cl)_2(\gamma\text{-pic})_2{}^{a,b}$

3120 m, 3075 w, 2900 s, br, 1600 s, 1585 m, 1520 m, 1475 m, 1450 s, 1425 w, 1370 m, 1310 vs, 1205 m, 1170 w, 1085 s, 1070 w, 1007 s, 975 w, 838 m, 830 s, 813 m, 803 s, 712 s, 676 m, 670 w

$[(n\text{-}C_4H_9)_4N]_2Ni(S_2COC_2H_5)_3{}^{a}$

2930 m, 2850 m, 1480 w, 1450 s, 1380 w, 1260 w, 1180 s, 1115 s, 1032 s, 1015 s, 950 w, 843 w, 768 s, 695 m

[a] Spectrum taken in Nujol mull ($\bar{\nu}$ cm^{-1} between salt plates).
[b] γ-pic = 4-methylpyridine, py = pyridine.

With the $Ni(S_2CNH_2)_2$ complex, the 1438-cm^{-1} band present in the base-free complex is absent in the adduct, and a strong new band near 1360 cm^{-1} (Figure 3) is observed. A band at 822 cm^{-1} in the base-free complex, assigned by Nakamoto, *et al.*,[21] to the C=S stretching vibration, is shifted to 860 cm^{-1} in the base adducts.

With the bis[N-(*p*-chlorophenyl)dithiocarbamato]-nickel(II) complex, a strong band is found at 1390 cm^{-1} which is absent in the 4-methylpyridine adduct and a strong new band is found at 1310 cm^{-1}.

The infrared spectra of the adducts of the bis(ethylxanthato)nickel(II) complex were compared with the infrared spectrum of the base-free complex (Figure 3, Table III). The strong band at 1240 cm^{-1} in the xanthate complex shifts to 1195 cm^{-1} in the bis(4-methylpyridine) adduct and to 1190 cm^{-1} in the bis(pyridine) adduct. The strong band at 1112 cm^{-1} in the base-free complex was found at 1125 and 1120 cm^{-1} in the 4-methylpyridine and pyridine adducts, respectively.

The magnetic susceptibility of the 4-methylpyridine adduct of $Ni(S_2CNH_2)_2$ showed a normal Curie–Weiss behavior from 70 to 300°K with $\theta = -10°$.

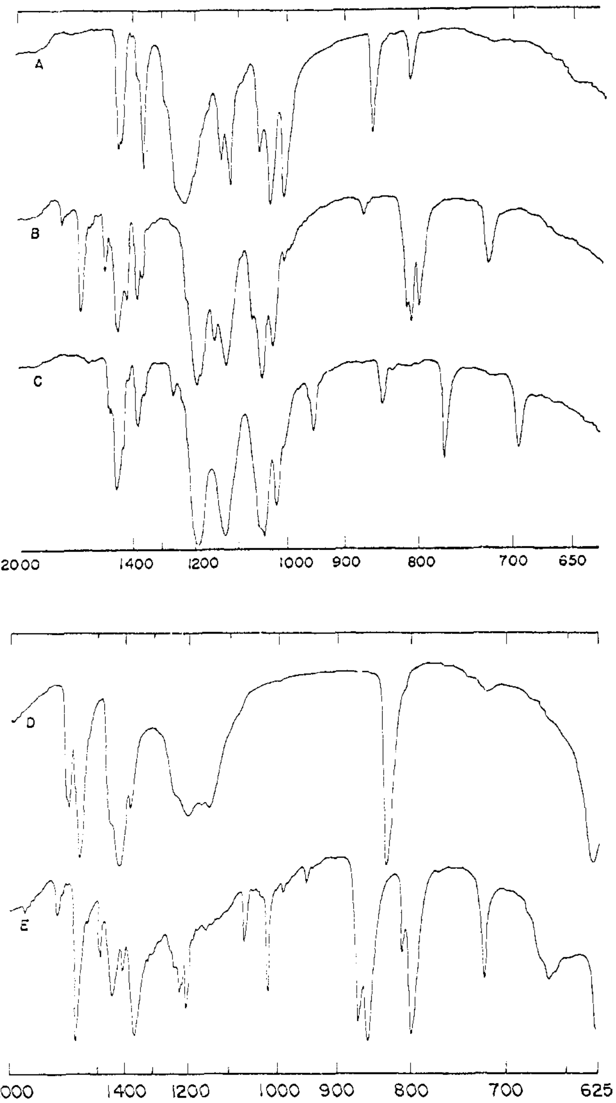


Figure 3.—Infrared spectra (cm^{-1}) (Nujol mulls) of (A) $Ni(S_2COC_2H_5)_2$, (B) $Ni(S_2COC_2H_5)_2(\gamma\text{-pic})_2$, (C) $[(C_4H_9)_4N]_2Ni(S_2COC_2H_5)_3$, (D) $Ni(S_2CNH_2)_2$, and (E) $Ni(S_2CNH_2)_2(\gamma\text{-pic})_2$.

Discussion

General Properties.—During our investigation of the metal complexes[9,19,22] of 1,1-dithiolate ligands, we have found that these ionic products with nickel(II) do not form base adducts with nitrogenous bases. By contrast, other neutral sulfur chelates of nickel(II) such as the xanthate,[7] dithiocarboxylic acid,[23] and dithiophosphate complexes[24,25] readily form adducts.

Apparently conflicting reports have appeared in the literature concerning the adduct-forming ability of dithiocarbamate complexes of nickel(II). Krebs, *et al.*,[23] have found that the bis(N-phenyldithiocarbamato)-nickel(II) complex interacts with Lewis bases while Carlin, *et al.*,[25] have stated that bis(diethyldithiocarbamato)nickel(II) does not interact with similar bases.

We have observed that the diethyldithiocarbamate

---

[21] K. Nakamoto, J. Fujita, R. A. Condrate, and Y. Morimote, *J. Chem. Phys.*, **39**, 423 (1963).

[22] D. Coucouvanis and J. P. Fackler, Jr., *J. Am. Chem. Soc.*, **89**, 1346 (1967).

[23] H. Krebs, E. F. Weber, and H. Fassbender, *Z. Anorg. Allgem. Chem.*, **276**, 128 (1954).

[24] C. K. Jørgensen; *Acta Chem. Scand.*, **17**, 533 (1963).

[25] R. L. Carlin, J. S. Dubnoff, and W. T. Huntress, *Proc. Chem. Soc.*, 228 (1964).

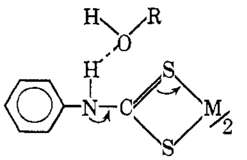
complex of nickel(II) interacts with nitrogenous bases at liquid nitrogen temperatures and have isolated crystalline base adducts of several other dithiocarbamates. It appears that the substituents on the nitrogen of the ligand are important in determining the formation and stability of these adducts (*vide infra*). With the bis(xanthato)nickel(II) complexes, crystalline base adducts were isolated without difficulty.

The electronic spectra of the base adducts of the xanthates and dithiocarbamates, both in solution and in the solid state, are characteristic of nickel(II) complexes (Figure 2) with a distorted octahedral coordination about the nickel(II) ion. The low-energy transition $^3A_{2g} \rightarrow {}^3T_{2g}$ (in O_h) is centered at 10,000 cm^{-1} and is split by ~900 cm^{-1}. Some asymmetry also is evident in the $^3A_{2g} \rightarrow {}^3T_{1g}$ transition at 16,000 cm^{-1}. The $^3A_{2g} \rightarrow {}^3T_{1g}$ (P) transition is hidden under a strong ultraviolet absorption. The spin-forbidden transition $^3A_{2g} \rightarrow {}^1E_g$ (in O_h) similarly could not be observed.

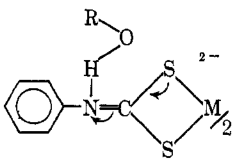
The spectrum of the tris(xanthato)nickel(II) complex is similar to that of the base adducts except that the ligand field transitions for the anion are more intense. This suggests that the base adducts may be *trans* and thus nearly centrosymmetric.[26] Similar intensity results have been obtained with the base adducts of some nickel(II) β-ketoenolates.[3]

As we have pointed out,[19] dithiocarbamates with an electron-withdrawing group and a proton on the nitrogen atom may lose the proton to form dithiocarbimates. Thus strong bases not only may interact with the metal but they may also remove a proton on the nitrogen atom to form the anionic nickel(II) dithiocarbimate. In fact, with R = phenyl, the tetrabutylammonium salt of bis(N-phenyldithiocarbimato)nickel(II) has been isolated using ethanolic sodium hydroxide to remove the proton. However, conductivity measurements on 4-methylpyridine or pyridine solutions of the dithiocarbamate and N-phenyldithiocarbamate nickel(II) complexes indicate that dithiocarbimate formation here is negligible.

In ethanol where hydrogen bonding of types IIIa and b is likely, the electronic spectra of the phenyldithiocarbamate and phenyldithiocarbimate nickel(II) complexes are nearly identical (similar to Figure 4A) while in acetonitrile, where no H bonding occurs, striking differences are observed. This appears to be a rather unusual manifestation of a hydrogen-bonding solvent effect.



IIIa



IIIb

Mesomeric Effects.—Infrared spectral evidence was presented by Chatt, *et al.*,[13,27] which showed a significant contribution of a structure of type II is necessary to describe the electronic structure of alkyl- and aryldithiocarbamate complexes. The strong band found between 1480 and 1550 cm^{-1} in these complexes was assigned to the C$\overset{..}{-}$N stretch. Its frequency lies intermediate to the stretching frequency region associated with C—N single bonds (1250–1350 cm^{-1}) and C═N bonds, (1640–1690 cm^{-1}). Nakamoto, *et al.*,[21] came to a similar conclusion in their normal-coordinate treatment of $M(S_2CNH_2)_2$ complexes. From X-ray crystallographic data now available (Table IV), it is apparent that the C—N bond distance in metal dithiocarbamates generally is intermediate to that of C—N single (~1.46 A) and C═N double (~1.27 A) bonds. A very interesting consequence of the conjugated π system is found[28] in the hyperfine interaction observed in the nmr spectra of alkyl- and aryldithiocarbamate complexes of iron(III).

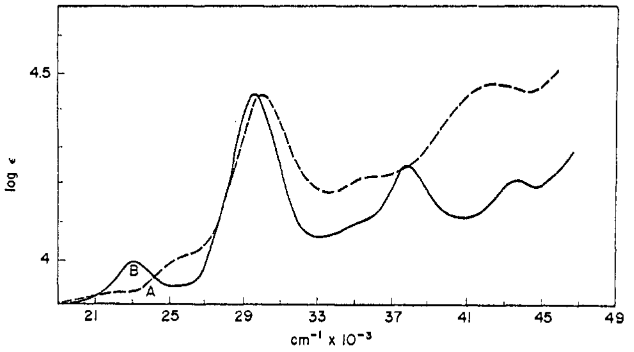


Figure 4.—Electronic spectra of (A) $Ni(S_2CNHC_6H_5)_2$ and (B) $Ni(S_2CNC_6H_5)_2{}^{2-}$ in acetonitrile (ϵ, M^{-1} cm^{-1}).

Cotton and McCleverty[29] have suggested that the very high C$\overset{..}{-}$N frequencies observed in nickel(II) derivatives of the dithiocarbamates might be a result of electron donation by the sulfur atoms into a nonbonding molecular orbital containing the $4p_z$ function of nickel. If this is true, the ability of the ligand to mesomerically shift electron density onto the sulfur atoms should greatly affect the ability of the nickel(II) ion to interact with Lewis bases to form base adducts. A strong interaction between the Ni $4p_z$ (a_{2u}) orbital and the sulfur π orbitals with symmetries a_{2u}, b_{2u}, and e_g decreases the availability of the $4p_z$ orbital for interaction with bases.

With 1,1-dithiol complexes of nickel(II), resonance shifts of electron density toward the metal should increase as the double-bond formation from the X atom to the carbon of the CS_2 unit decreases (IV). With X = CR_2 or NR, $Z = -2$, double-bond formation is expected to be essentially complete, while with X = CH_3, $Z = 0$, the contribution of IVb is expected to be small. Qualitatively a resonance shift of π-electron density might be expected to follow the order for X: $CR_3 < SR \sim OR < NH_2 < NR_2 < S\ (Z = -2) < NR\ (Z = -2) \sim CR_2\ (Z = -2)$. If the electron density shift

---

[26] LaPorte forbidden transitions are no longer strictly forbidden when the symmetry center is removed. Mixing of d with p levels in the noncentrosymmetric molecule can produce the intensity enhancement in the d–d transitions.

[27] J. Chatt, L. A. Duncanson, and L. M. Venanzi, *Nature*, **177**, 1042 (1956).

[28] R. M. Golding, W. C. Tennant, C. R. Kanekar, R. L. Martin, and A. M. White, *J. Chem. Phys.*, **45**, 2688 (1966).

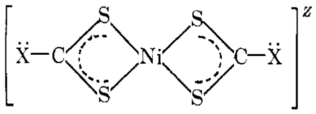
[29] F. A. Cotton and J. A. McCleverty, *Inorg. Chem.*, **3**, 1398 (1964).

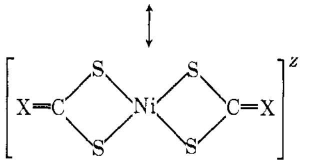
TABLE IV

S—C, C—N, AND N—C DISTANCES IN DITHIOCARBAMATE COMPLEXES

Complex	S┄C, A	C┄N, A	N—C, A	Ref
$[CuS_2CN(C_2H_5)_2]_4$	1.708 ± 0.018	1.408 ± 0.033	1.483 ± 0.025	*a*
$Cu[S_2CN(C_2H_5)_2]_2$	1.717 ± 0.004	1.34 ± 0.01	1.470 ± 0.005	*b, c, d*
$Ni[S_2CN(C_2H_5)_2]_2$	1.727 ± 0.005	1.325 ± 0.009	1.485 ± 0.011	*e*
$Zn[S_2CN(C_2H_5)_2]_2$	1.727 ± 0.005	1.325 ± 0.009	1.473 ± 0.007	*f*
$Zn[S_2CN(CH_3)_2]_2$	1.722 ± 0.010	1.347 ± 0.018	1.472 ± 0.015	*g*
	1.70 ± 0.03	1.37 ± 0.03	...	*h*
$Ni[S_2CNH_2]_2$	1.68 ± 0.03	1.38 ± 0.03	...	*i*
$ClFe[S_2CN(C_2H_5)_2]_2$	...	1.36	...	
$NOCo[S_2CN(C_2H_5)_2]_2$	1.75 1.67 1.78	1.25 1.30	1.5	*j*
$C_6H_5As[S_2CN(C_2H_5)_2]_2$	1.71 1.75	1.34		*k*
H_3CNH_2			1.474 ± 0.005	*l*

[a] R. Hesse, *Arkiv Kemi*, **20,** 481 (1962). [b] R. Bally, *Compt. Rend.*, **257,** 425 (1963). [c] M. Bonamico, G. Dessy, A. Mugnoli, A. Vaciago, and L. Zambonelli, *Acta Cryst.*, **19,** 886 (1965). [d] B. H. O'Connor and E. N. Masten, *ibid.*, **21,** 828 (1966). [e] M. Bonamico, G. Dessy, C. Maniami, A. Vaciago, and L. Zambonelli, *ibid.*, **19,** 619 (1965). [f] M. Bonamico, G. Mazzone, A. Vaciago, and L. Zambonelli, *ibid.*, **19,** 898 (1965). [g] H. P. Klug, *ibid.*, **21,** 536 (1966). [h] L. Capacchi, M. Nardelli, and H. Villa, *Chem. Commun.*, **14,** 441 (1966). [i] B. F. Hoskins, R. L. Martin, and A. H. White, *Nature*, **211,** 627 (1966). [j] P. R. H. Alderman, P. G. Owston, and J. M. Rowe, *J. Chem. Soc.*, 668 (1962). [k] R. Bally, *Compt. Rend.*, **261,** 3617 (1965). [l] "Tables of Interatomic Distances and Configurations in Molecules and Ions," Supplement, 1956–1959.


IVa


IVb

to the metal were primarily inductive, the position of CR_3 relative to NH_2 or NR_2 would be reversed.

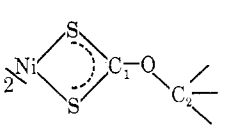
Adduct instability with nickel(II) complexes of 1,1-dithiols qualitatively follows the above order for a resonance shift. Xanthates and dithioacid complexes of nickel(II) readily interact with nitrogenous bases,[30, 31] dithiocarbamate complexes show an intermediate behavior, and the dithiocarbimates, trithiocarbonates, and ethylene-1,1-dithiolates show no adduct-forming ability. The C┄N stretching frequency of the nickel(II) dithiocarbamates decreases on changing R in a manner which parallels the adduct-forming ability of the complex (Table V). The isolated adducts themselves show a considerably lower C┄N frequency than do the planar nickel(II) dithiocarbamates in accord with the decreased double-bond character for the C—N bond.

TABLE V

A CORRELATION AMONG THE NR_2 GROUP, THE C–N STRETCHING VIBRATION, AND THE ADDUCT-FORMING ABILITY IN SOME DITHIOCARBAMATES

Compound	ν_{C-N}, cm^{-1}	Adduct-forming ability
$Ni[S_2CN(CH_3)_2]_2$	1550	No apparent spectral change with pyridine or γ-picoline in acetone at −73°
$Ni[S_2CN(C_2H_5)_2]_2$	1511	Change in color with pyridine or γ-picoline in acetone (Dry Ice)
$Ni(S_2CNH_2)_2$	1438	Isolable base adduct with pyridine or γ-picoline
$Ni[S_2CNHC_6H_5Cl]_2$	1390 (split)	Isolable adduct with γ-picoline

In their study of the infrared spectra of some nickel xanthates, Watt and McCormick[32] have assigned the band between 1114 and 1188 cm^{-1} to the C_2–O stretch and one between 1250 and 1325 cm^{-1} to the C_1–O stretch (V). Considering the short (1.35 A) C_1–O bond distance, as compared to the C_2–O bond length of 1.48 A found in the crystal structure of potassium ethyl xanthate,[33] they concluded that form IVb ($Z = 0$) is of some importance in the xanthate complexes. However the C_1–O and C_2–O bond lengths in the crystal structure of the bis(ethylxanthato)nickel(II) complex[34] have both been reported to be 1.38 A, a result which has been questioned.[32] With $Mo_2O_3(S_2COC_2H_5)_4$, Blake, *et al.*,[35] have found the C_2–O and C_1–O bonds to be ~1.46 and ~1.39 A, respectively. The C_1┄O stretch in the nickel(II) xanthates shifts by ~50 cm^{-1} on adduct formation.


V

The positions of infrared bands associated with the C–X bond in both the xanthate and dithiocarbamate base adduct complexes suggest a smaller contribution of IVb than occurs in the planar complex. This result is to be expected since the base donates electron density to the metal and the complex becomes more ionic in character. The infrared spectra of gold(III) com-

---

(30) J. V. Dubsky, *J. Prakt. Chem.*, **93,** 142 (1916); **103,** 109 (1921).

(31) H. Krebs, E. F. Weber, and H. Fassbender, *Z. Anorg. Allgem. Chem.*, **276,** 128 (1954).

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

(33) F. Mazzi and C. T. Tadini, *Z. Krist.*, **118,** 378 (1963).

(34) M. Frazini, *ibid.*, **118,** 393 (1963).

(35) A. B. Blake, F. A. Cotton, and J. S. Wood, *J. Am. Chem. Soc.*, **86,** 3024 (1964).

plexes[36] of the type $L_2AuS_2CNR_2$ also show an apparent increase in the $\mathrm{C\overset{--}{-}N}$ double-bond character as the electron-withdrawing ability of L is increased.

We have noted that an acceptable correlation exists between the $\mathrm{C\overset{--}{-}N}$ bond order[37] as judged by Bernstein's relationship[38] and the tendency of the nickel(II) dithiocarbamates to form base adducts. The greater the C–N bond order, the less is the tendency of the nickel(II) complex to form a base adduct, providing other factors are maintained constant. This type of an electronic effect and the role it plays in metal-influenced ligand reactions has been little explored to date. It is apparent from the work reported here, however, that base interactions (adduct formation) with the metal can influence properties of the ligand substantially, even properties associated with ligand atoms well removed from the metal.

Acknowledgment.—We acknowledge several stimulating discussions with Professors J. Lewis and A. Wojcicki regarding this work.

(36) H. J. A. Blaauw, R. J. F. Nivard, and G. J. M. Van Der Kerk, *J. Organometal. Chem.* (Amsterdam), **2**, 236 (1964).

(37) J. P. Fackler, Jr., and D. Coucouvanis, submitted for publication.

(38) A. J. Bernstein, *J. Chem. Phys.*, **15**, 284 (1947).

CONTRIBUTION FROM THE CHEMICAL LABORATORY AT NORTHWESTERN UNIVERSITY, EVANSTON, ILLINOIS,
AND THE J. HEYROVSKÝ INSTITUTE OF POLAROGRAPHY, CZECHOSLOVAK ACADEMY OF SCIENCES, PRAGUE, CZECHOSLOVAKIA

Redox Reactions of Cobalt–Cyanide Complexes. II.[1] Reaction of Pentacyanocobaltate(II) with *p*-Benzoquinone. Properties of $[(CN)_5CoOC_6H_4OCo(CN)_5]^{6-}$

BY A. A. VLČEK[2] AND J. HANZLÍK

Received May 17, 1967

Pentacyanocobaltate(II) ion reacts very rapidly with *p*-benzoquinone to form the bridge species $[(CN)_5CoOC_6H_4OCo(CN)_5]^{6-}$ (I). The organic ligand in I is isoelectronic with the dianion of hydroquinone, but owing to the influence of Co atoms, it shows a higher degree of π-electron delocalization, as can be deduced from spectroscopic and electrochemical properties. Compound I is not oxidized electrochemically, but shows a four-electron reduction analogous to that of other cobalt(III)–pentacyano complexes. I undergoes a two-step decomposition in aqueous solution. Both steps show general acid catalysis. The products of the first step are $[Co(CN)_5H_2O]^{2-}$ and $[(CN)_5CoOC_6H_4OH]^{3-}$ (II). The ligand in II resembles hydroquinone in its spectroscopic and electrochemical behavior. II shows a two-electron oxidation, the product of which is an unstable complex, $[Co(CN)_5(\text{quinone})]^{2-}$, which decomposes to quinone and $[Co(CN)_5H_2O]^{2-}$. II also shows a normal cobalt(III)–cyanide complex reduction. II itself decomposes in solution with the formation of $[Co(CN)_5H_2O]^{2-}$ and hydroquinone. The mechanism of reductions by $Co(CN)_5^{3-}$ is discussed and it is deduced that these reactions proceed mostly *via* a redox addition mechanism, the oxidizing agent (or its fragments) being reduced and coordinated to the cobalt atom at the same time. One-electron agents give monomolecular species whereas two-electron agents give bridged complexes.

Solutions of cobaltous pentacyanide catalyze the hydrogenation of several groups of organic compounds or reduce these compounds (see ref 3 for review). However, except for the reaction with organic halides,[4] no other reaction has been studied in detail. In the reactions with some substrates, deviations from the expected course of reaction are observed[3] which indicate that the process might involve several intermediates and complicated steps.

In the course of our systematic study of the oxidation–reduction reactions of cobalt cyanide complexes, the reaction between cobaltous pentacyanide and *p*-benzoquinone has been studied.

Experimental Section

Preparation of $[K_6Co(CN)_5C_6H_4O_2Co(CN)_5]\cdot 2H_2O$.—To 50 ml of a carefully deaerated aqueous solution of 3 g of $CoCl_2\cdot 6H_2O$, 30 ml of a deaerated solution containing 4.1 g of KCN (reprecipitated from aqueous solution by ethanol) is added at 0° under nitrogen. To the resulting deep green solution 100 ml of an ethanolic, deaerated solution of 0.7 g of *p*-benzoquinone (cooled to 0°) is added slowly with strong stirring and cooling in a nitrogen atmosphere. The color changes immediately to deep red. At the end of the addition of the quinone solution, a red-brown precipitate starts to form (in some cases, especially when the addition of quinone solution is rapid, red oil is first formed which becomes crystalline on longer stirring of the solution at 0°). After 5–10 min of stirring, the precipitate is collected on a filter under nitrogen and washed several times with deaerated ethanol and ether. The resulting material (*ca.* 3.6 g, *i.e.*, about 75%) is dissolved rapidly in a very small amount of water at 0° and reprecipitated rapidly with ethanol (precooled to 0°). It is advisable to precipitate only about three-fourths of the material; otherwise contamination with the decomposition products tends to be high. The precipitate is collected on a filter in a nitrogen atmosphere, washed with ethanol and ether, and dried under vacuum over P_2O_5. *Anal.*[5] Calcd for $K_6[(CN)_5CoOC_6H_4OCo(CN)_5]\cdot 2H_2O$: C, 25.39; N, 18.51; H, 1.06. Found: C, 25.8; N, 18.44; H, 1.16.

Potentiometric Titration.—A Beckman Model 9 potentiometer with a bright platinum electrode combined with a commercial

(1) Part I: A. A. Vlček and F. Basolo, *Inorg. Chem.*, **5**, 156 (1966).

(2) This work was started during the leave of absence of A. A. V. from the J. Heyrovský Institute of Polarography, Czechoslovak Academy of Sciences, Prague, Czechoslovakia. He is a recipient of a Senior Foreign Scientist National Science Foundation Fellowship at Northwestern University, 1964–1965.

(3) J. Kwiatek, I. L. Mader, and J. K. Seyler, Advances in Chemistry Series, No. 37, American Chemical Society, Washington, D. C., 1963, p 201.

(4) J. Halpern and J. P. Maher, *J. Am. Chem. Soc.*, **87**, 5361 (1965).

(5) The analysis was performed by Micro-Tech, Skokie, Ill.