more closely resembles that of CuT^{2-}. Such diverse CD behavior for the copper complexes of a single ligand is without precedent and undoubtedly can be attributed to the many chelation modes available to d-tartrate.

The unique feature of this ligand is its two hydroxyl groups capable of deprotonating and binding to the metal ion. That such deprotonation and metal binding does occur is supported by the fact that basic solutions of copper(II) succinate or malate do not contain complexes analogous to the alkaline copper(II) tartrates. Of the various proposed modes of chelation,[4,5,8,12] three can be shown possible by the molecular models

I

II

III
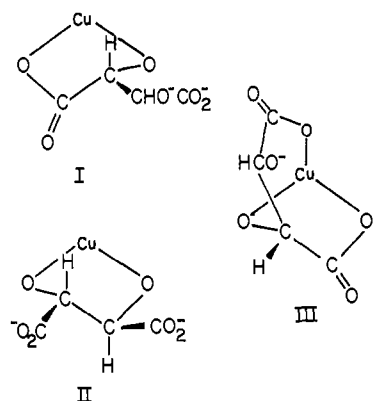
The circular dichroism characteristics of each chelate mode can be predicted from correlations with known copper(II) complexes of optically active amino acids,[9,14] peptides,[10,15] and diamines.[16] The correlations are concerned with the sign and magnitude of the predominant d–d band occurring at 600–700 nm for the present complexes. Because of their empiric nature no theoretical model for optical activity need be assumed.[9,15,17] Chelate mode I can be expected to display a prominent positive CD band since it is structurally related to the common copper(II) chelates of simple L-amino acids but is of opposite absolute configuration. Similarly, III is enantiomerically related to the tridentate L-histidine complexes; it is predicted to display a negative CD band of greater magnitude than the bidentate structures.[9] A negative band can be expected for II on the basis of its correlation with L-amino acid or d-propylenediamine chelates.

Chelate mode I enables a bridging d-tartrate ion to bind two copper ions equivalently with a positive visible-region CD band resulting. In keeping with its observed spectrum Cu_2TOH^- is assigned this structure. Apparently one coordinated water molecule of the complex is deprotonated; the position of this bound OH^- cannot be determined from the present data. Molecular models indicate it may form a second bridge between the two copper ions. With chelate mode II a single copper ion can be bound by two d-tar-

trate ions in a square-planar fashion. A negative CD band should result. Based on its CD behavior CuT_2^{6-} is assigned this tetracoordinate structure. A more difficult situation arises in the case of CuT^{2-} since the continuous variations and other results[5–8] imply a polynuclear complex. Its negative CD band indicates either chelate mode II or III. The intensity, however, is less than expected for tridentate chelation. Therefore, the structure proposed is one employing mode II with the carboxylate groups forming the bridges for polymerization.

Acknowledgment.—The technical assistance of Mr. N. E. Gilman is gratefully acknowledged.

Observations on Some Cobalt(III) Complexes with Aminopolycarboxylic Acids and Nitrite Ion

By B. B. Smith* and R. H. Betts

Earlier studies of the complexes formed by ethylenediaminetetraacetic acid (EDTA)[1] and similar potentially sexadentate ligands (*e.g.*, propylenediaminetetraacetic (PDTA), *trans*-1,2-cyclohexanediaminetetraacetic acid (CyDTA), and hydroxyethylethylenediaminetriacetic acid (HOEDTA)) with cobalt(III) have shown that the ligands can occupy five or six coordination sites of the metal ion.[2–12] Thus, complexes of the types CoY^- and $Co(HY)X^-$, where Y^{4-} denotes the full ligand anion, HY^{3-} the monoprotonated anion, and X a monodentate ligand (H_2O, OH^-, Cl^-, Br^-, NO_2^-) have been identified in aqueous solution and several have been isolated. For $X^- = NO_2^-$, pentadentate complexes $Co(HY)NO_2^-$ and $Co(Y)NO_2^{2-}$ have been isolated for EDTA, PDTA, and HOEDTA and studied in solution by infrared and spectrophotometric methods.[2–5,7–10] Their general method of preparation[2] is *via* the oxidation of the corresponding Co(II) complex with nitrous acid. $Co(HEDTA)NO_2^-$ has also been obtained by treating sodium cobaltinitrite (Na_3Co-

* To whom correspondence should be addressed.

(1) In representations of complexes, EDTA and CyDTA denote the tetranegative ions, while HEDTA, HOEDTA, and HCyDTA denote the trinegative ions.

(2) G. Schwarzenbach, *Helv. Chim. Acta*, **32**, 839 (1949).

(3) D. H. Busch and J. C. Bailar, Jr., *J. Amer. Chem. Soc.*, **75**, 4574 (1953).

(4) M. L. Morris and D. H. Busch, *ibid.*, **78**, 5178 (1956).

(5) F. P. Dwyer and F. L. Garvan, *ibid.*, **80**, 4480 (1958).

(6) M. L. Morris and D. H. Busch, *J. Phys. Chem.*, **63**, 340 (1959).

(7) F. P. Dwyer and F. L. Garvan, *J. Amer. Chem. Soc.*, **83**, 2610 (1961).

(8) K. Swaminathan and D. H. Busch, *J. Inorg. Nucl. Chem.*, **20**, 159 (1961).

(9) M. Mori, M. Shibata, E. Kyuno, and H. Nakajima, *Bull. Chem. Soc. Jap.*, **29**, 887 (1956).

(10) Y. Shimura and R. Tsuchida, *ibid.*, **29**, 643 (1956).

(11) I. A. W. Shimi and W. C. E. Higginson, *J. Chem. Soc.*, 260 (1958).

(12) R. Dyke and W. C. E. Higginson, *ibid.*, 1998 (1960).

(14) T. Yasui, *Bull. Chem. Soc. Jap.*, **38**, 1746 (1965).

(15) R. B. Martin, J. M. Tsangaris, and J. W. Chang, *J. Amer. Chem. Soc.*, **90**, 821 (1968).

(16) J. P. Mathieu, *Ann. Phys.*, **19**, 335 (1944).

(17) J. R. Gollogly, C. J. Hawkins, and C. L. Wong, *Inorg. Nucl. Chem. Lett.*, **6**, 215 (1970).

$(NO_2)_6$) with the disodium salt of EDTA.[5] There appears to be no report of the isolation of any pentadentate Co^{III}–CyDTA complex, although evidence for the formation of the chloro species $Co(HCyDTA)Cl^-$ in solution has been described.[7]

The objective of the present study was to investigate by nmr spectroscopy the reactions between $Co(NO_2)_6{}^{3-}$ and EDTA, CyDTA, and HOEDTA, to determine which complexes are formed in solution, and (if possible) to isolate the products. It was considered possible that species (*e.g.*, of lower "dentate" number or isomers) other than those reported earlier could be formed in solution but were not isolated or detected by the techniques used. For examples, two geometrical isomers are possible for the pentadentate complex, with the nitrite ligand occupying either a *polar* or *equatorial* site. The previous work has not established which of these

$$N\ N = NCH_2CH_2N$$
$$N\ O = NCH_2CO_2{}^-$$
$$R = CH_2CO_2H \text{ or } CH_2CH_2OH$$

polar   equatorial
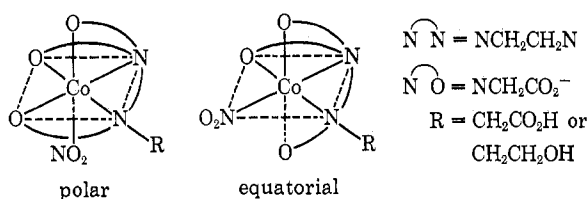
two isomers (or if both) are formed. The present work indicates that the polar isomer is probably formed with EDTA and HOEDTA and that a pentadentate complex is not formed with CyDTA. Nmr studies of Co(III) with EDTA-type ligands and nitrite ion have not been reported previously, although some data for aquo and halo pentadentate Co^{III}– and Rh^{III}–EDTA complexes have been published recently.[13–15]

Experimental Section

Materials.—EDTA and HOEDTA (as the acids and their sodium salts) were obtained from Matheson Coleman, and Bell, and CyDTA (acid form) was obtained from K & K Laboratories Inc. All other materials were reagent grade and were used as supplied.

Procedure.—Equimolar solutions (0.5–0.8 M) of $Na_3Co(NO_2)_6$ and the full sodium salts of the ligands in D_2O were allowed to react at $\sim 40°$ and the reactions were monitored by measuring the nmr spectra of the solutions over a period of several hours for EDTA and HOEDTA and for several days for CyDTA (*i.e.*, reaction completion). The solutions were then concentrated in an air stream and cooled in ice, and the products which separated were collected, recrystallized from water, and dried *in vacuo* (yields 70–80%). Reactions were also carried out using 2:1 and 1:2 $Co(NO_2)_6{}^{3-}$:ligand ratios and at different pD values in the range pD $\sim$ 1–12, the same three compounds being obtained in all cases. Analytical data for C, H, and N indicate that the complexes are $Na_2[Co(EDTA)NO_2]\cdot H_2O$, $Na[Co(HOEDTA)NO_2]$, and $Na[Co(CyDTA)]\cdot 3H_2O$, in agreement with the earlier work;[2–5] $Na[Co(HOEDTA)NO_2]\cdot H_2O$ was also obtained by acidifying a solution of the disodium salt. Samples of the three monosodium salt complexes were also obtained by the Schwarzenbach[2] method (yields 40–50%).

The reactions were also followed by observation of the absorption spectra of dilute ($\sim 2 \times 10^{-3}$ M) aqueous solutions of $Co(NO_2)_6{}^{3-}$ and the ligands.

Instrumentation.—Nmr spectra were measured with a Varian Model A-56/60A instrument operating at $\sim 40°$. Some mea-

surements were also made on a Varian Model HA-100 instrument to confirm the assignments. *tert*-Butyl alcohol (TBA) was used as an internal reference and the chemical shifts are referred to TMS* (3-(trimethylsilyl)-1-propanesulfonic acid, sodium salt) as zero. (TBA resonates at 1.233 ppm on the low-field side of TMS*.) Anhydrous sodium carbonate and nitric acid were used to vary the pD of the D_2O solutions. Absorption spectra were measured with a Perkin-Elmer 450 instrument; infrared spectra (*via* KBr disks) were recorded on a Perkin-Elmer 337 instrument.

Results

Nmr spectra of the mixtures initially show only the resonances of the free ligands.[16] As the reactions proceed, the free ligand resonances diminish in intensity and new resonances appear. These latter resonances appear to represent only one new species in each case. All of the resonances are somewhat broadened probably because of the presence of NO_2 (and possibly traces of Co(II)); however, the product and free ligand resonances can be clearly seen, with no evidence for the presence of any species other than the aforementioned complexes. At reaction completion the spectra consist of the product resonances plus some free ligand. Variation of the $Co(NO_2)_6{}^{3-}$: ligand ratios and the pD of the solutions, while affecting the reaction rates, still produced only the same three products. Similar results were obtained in the measurement of the absorption spectra of the reaction mixtures; *i.e.*, bands attributable to only one new species were observed in each case; the spectra obtained agreed with those reported previously.[9,10]

The compounds isolated at reaction completion are mononitro pentadentate species for EDTA and HOEDTA ($Co(EDTA)NO_2{}^{2-}$ or $Co(HEDTA)NO_2{}^-$ and $Co(HOEDTA)NO_2{}^-$) and the sexadentate complex $Co(CyDTA)^-$ for CyDTA. Nmr studies of the latter complex have been described elsewhere,[13] and the present work is in good agreement with these earlier results. The spectrum of the EDTA complex $Co(EDTA)NO_2{}^{2-}$ (Figure 1A) consists of three acetate AB patterns (due to the nonequivalent coupled CH_2 protons), an acetate singlet, and a complex ethylenic ABCD resonance. This is consistent with the presence of pentadentate EDTA, as stereomodels indicate that four separate acetate AB patterns are expected. When the pD of the solution is decreased from pD 7 to ~ 1, the highest field AB pattern shifts downfield approximately 0.32 ppm and is consequently assigned to the uncoordinated acetate CH_2 group. The spectrum of $Co(HEDTA)NO_2{}^-$, which is not very soluble in D_2O, slowly undergoes changes at $\sim 25°$ over a period of several days; these are consistent with the formation of the sexadentate complex $Co(EDTA)^-$. In more acidic solution (pD ~ 0) the spectra indicate that another species is slowly formed from $Co(HEDTA)NO_2{}^-$; this appears to be the monoaquo complex $Co(HEDTA)(OH_2)$ because its spectrum is similar to that reported previously for this complex.[14]

At pD values >7 the acetate singlet in the spectrum of $Co(EDTA)NO_2{}^{2-}$ diminishes in intensity to an area

(13) R. J. Day and C. N. Reilley, *Anal. Chem.*, **37**, 1326 (1965).
(14) J. B. Terrill and C. N. Reilley, *Inorg. Chem.*, **5**, 1988 (1966).
(15) B. B. Smith and D. T. Sawyer, *ibid.*, **7**, 2020 (1968).
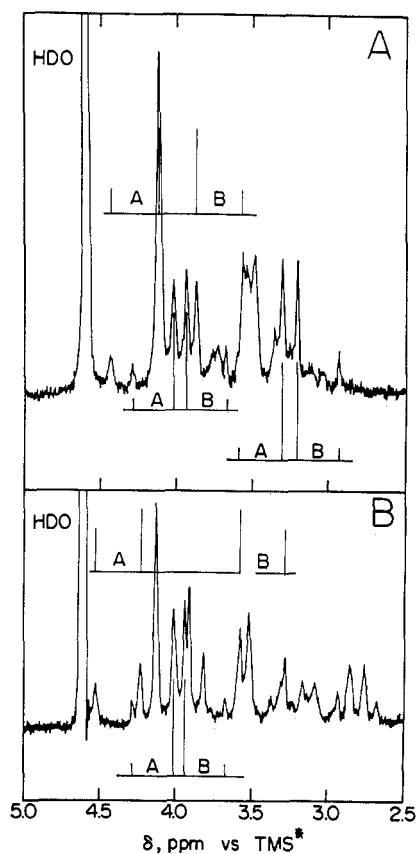(16) J. L. Sudmeier and C. N. Reilley, *Anal. Chem.*, **36**, 1698, 1707 (1964).

Figure 1.— (A) The 60-Mc proton nmr spectrum of Co(EDTA)-NO_2^{2-} in D_2O. Chemical shifts (δ, ppm *vs.* TMS*) and coupling constants (J, cps) for the acetate resonances are as follows: singlet, δ_{CH_2} 4.12; upper AB pattern, δ_A 4.26, δ_B 3.78, J_{AB} = 18.0; middle AB pattern, δ_A 4.11, δ_B 3.86, J_{AB} = 16.0; lower AB pattern, δ_A 3.39, δ_B 3.13, J_{AB} = 16.5. (B) The 60-Mc proton nmr spectrum of Co(HOEDTA)NO_2^- in D_2O: singlet, δ_{CH_2} 4.13; upper AB pattern, δ_A 4.36, δ_B 3.46, J_{AB} = 18.0; lower AB pattern, δ_A 4.09, δ_B 3.87, J_{AB} = 16.0.

approximately equal to that of each of its adjacent higher field resonances; the other resonances are unchanged, although the whole spectrum is broadened, presumably due to the formation of Co(II). Addition of more base (pD >10) causes very severe broadening of the resonances. The disappearance of the singlet is ascribed to isotopic exchange of CH_2 protons with solvent deuterium. Exchanges of this type have recently been reported for several Co^{III}–EDTA type complexes.[14,17,18]

The spectrum of the complex Co(HOEDTA)NO_2^- (Figure 1B) is qualitatively similar to that of the EDTA complex; it contains two acetate AB patterns, an acetate singlet, and two complex ethylenic resonances. The singlet disappears at pD ~10 due to isotopic exchange, while the remaining resonances are unaffected, apart from some broadening. At higher pD values decomposition of the chelate occurs. In acid solution (pD ~0-1) a new species is slowly formed which is probably the monoaquo pentadentate complex;[6] a complete interpretation of the acetate portion of the spec-

trum was not possible because of the superimposition of resonances.

The infrared spectra of the solid complexes were measured to confirm the presence of complexed or free (protonated) carboxylate groups.[19] The results indicate that, except for Co(HEDTA)NO_2^- which contains both types, all of the complexes contain only complexed carboxylates. (Co(EDTA)NO_2^{2-} also contains one –COONa group whose asymmetric stretching frequency is, however, not readily distinguished from those due to –COOCo.)

Discussion

The nmr data indicate that the reactions between Co-$(NO_2)_6^{3-}$ and the ligands produce only one complex in each case; these are pentadentate species for EDTA and HOEDTA and sexadentate species for CyDTA. The previous deuteration studies of sexadentate Co^{III}–EDTA type complexes [14,17,18] have established that the out-of-plane (*i.e.*, polar) acetate protons readily undergo isotopic exchange, while the in-plane (equatorial) ones do so only with difficulty or not at all. This may result from a shorter out-of-plane Co–O bond. The complete deuteration observed here for the singlet acetate CH_2 protons in the pentadentate complexes indicates that these resonances represent out-of-plane acetate groups and that, consequently, each complex appears to contain only one out-of-plane group and is therefore the polar isomer. Two forms of the polar isomer are possible, with the free "arm" and the nitro group either on the same side or on opposite sides of the coordination plane; space-filling models suggest that the latter form would be sterically favored, in agreement with earlier conclusions[14] about the formation of a polar monoaquo pentadentate Co^{III}–EDTA complex upon protonation of Co(EDTA)$^-$. This conclusion is at variance with the X-ray analysis[20] of the complex Ni(HEDTA)-$(OH_2)^-$, which shows the coordinated water molecule occupying an equatorial site. There appear to be no reports of the isolation of both isomers for pentadentate Co^{III}–EDTA type complexes, although the formation of both of the monoaquo isomers in solution has been described.[11,12] There is no evidence in the present study to suggest that both mononitro isomers are formed in solution.[21]

The formation of only the sexadentate complex Co(CyDTA)$^-$ with CyDTA is interesting. Model studies indicate that the pentadentate polar isomer is sterically crowded and that the arrangement would probably be unfavorable; the sexadentate complex appears to be much less "congested." For the pentadentate EDTA and HOEDTA complexes the crowding is much less severe. Pentadentate Co^{III}–CyDTA complexes have not been isolated to date, although evidence has been obtained for the formation of a chloro species.[7]

(17) J. L. Sudmeier and G. Occupati, *Inorg. Chem.*, **7**, 2524 (1968).

(18) D. H. Williams and D. H. Busch, *J. Amer. Chem. Soc.*, **87**, 4644 (1965).

(19) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, N. Y., 1963, p 205.

(20) G. S. Smith and J. L. Hoard, *J. Amer. Chem. Soc.*, **81**, 556 (1959).

(21) The authors in ref 6 cited preliminary evidence for the formation of isomers of Na[Co(HOEDTA)NO_2]$^-$; they also interpreted their kinetic data in terms of the presence of isomers of the monobromo complex Co-(HEDTA)Br$^-$.

No evidence is obtained for the formation of the pentadentate complex here, although it is possible that small amounts of other complexes could be formed in solution and remain undetected.

**Acknowledgment.**—This work was supported by the National Research Council of Canada.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
EARLHAM COLLEGE, RICHMOND, INDIANA 47374

Metal Complexes with Azine Ligands. III. Biacetyl Oxime Azine with Nickel(II)[1]

BY WILMER J. STRATTON* AND PAUL J. OGREN[2]

Received December 15, 1969

2-Pyridinecarbaldazine (abbreviated PAA) and 2-pyridyl methyl ketazine have been shown[1,3,4] to form an unusual series of complexes of the general formula $[M_2L_3]X_4$. Much evidence has been accumulated to show that these compounds contain a bridged dinuclear complex cation with symmetric bis-bidentate bonding of each ligand to the two metal ions. Recently, Ball and Blake[5] have reported magnetic studies of Ni_2-$(PAA)_3X_4$ salts which demonstrate spin–spin interaction between the two metal ions, thus lending further support to the proposed structure. Exploratory work with a nonaromatic analog of 2-pyridinecarbaldazine and 2-pyridyl methyl ketazine, biacetyl hydrazone azine (I, "BHA"), demonstrated that it likewise forms 2:3 complexes of the formula $M_2(BHA)_3X_4$.[3c]

I, R = NH₂
II, R = OH
III, R = OCH₃

IV, R = OH
V, R = NH₂
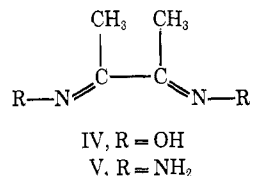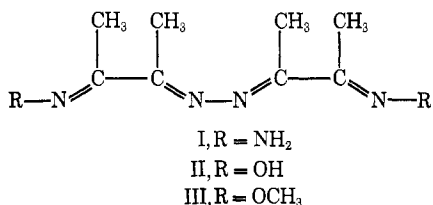
As part of a continuing study of tetrafunctional azine ligands, we report here the synthesis of two new ligands related to I and a brief study of their complexing ability. Biacetyl oxime azine (II, "H₂BOA") was of interest because of its structural relationship to the well-known nickel reagent, dimethylglyoxime (IV, HDMG)

* To whom correspondence should be addressed.
(1) For the previous paper in this series, see W. J. Stratton, *Inorg. Chem.*, **9**, 517 (1970).
(2) Undergraduate research assistant, 1963.
(3) (a) W. J. Stratton and D. H. Busch, *J. Amer. Chem. Soc.*, **80**, 1286 (1958); (b) *ibid.*, **80**, 3191 (1958); (c) *ibid.*, **82**, 4834 (1960).
(4) W. J. Stratton, M. F. Rettig, and R. F. Drury, *Inorg. Chim. Acta*, **3**, 97 (1969).
(5) P. W. Ball and A. B. Blake, *J. Chem. Soc. A*, 1415 (1969).

which forms a highly stable 2:1 neutral complex with nickel(II) [Ni(DMG)₂]. This compound has been shown by X-ray crystallography to be planar with two hydrogen bonds between the ligands[6] and is diamagnetic as expected for a square-planar d^8 ion. Dimethylglyoxime also forms a paramagnetic 2:1 octahedral complex with nickel(II) involving two coordinated chloride ions and no hydrogen bonds [Ni(HDMG)₂Cl₂].[7] Biacetyl oxime azine (II) is potentially capable both of forming hydrogen bonds and of bridging two metal ions.

A second new ligand, biacetyl methoxime azine (III), was of interest both because this ligand precludes the possibility of hydrogen bonding and because we wanted to investigate the steric effect of terminal methyl groups on complexing ability.

Experimental Section

Biacetyl Oxime Azine (II).—Eighteen grams of 2,3-butanedione 2-oxime (0.18 mol) (Eastman Chemical Co.) and 2.5 g of 97% hydrazine (0.08 mol) were added to 100 ml of ethanol and the solution was heated under reflux for 20 min. Upon cooling in ice, yellow crystals were deposited in 85% yield. The product was recrystallized in high yield from hot ethanol; mp 250–251°. *Anal.* Calcd for $C_8H_{14}N_4O_2$: C, 48.5; H, 7.1; N, 28.2. Found: C, 48.3; H, 6.9; N, 28.4.

Tetraaquobis(biacetyl oxime azine)dinickel(II).—Six-tenths gram of nickel(II) chloride hexahydrate (0.0026 mol) and 0.50 g of biacetyl oxime azine (0.0025 mol) were added to 50 ml of water. A 0.1 *N* sodium hydroxide solution was added slowly with rapid mechanical stirring until pH 11 was reached. The resulting brown solid was filtered, washed well with water, and dried; yield 0.40 g. The product has a very low solubility in water. *Anal.* Calcd for $Ni_2(C_8H_{12}N_4O_2)_2 \cdot 4H_2O$: C, 33.0; H, 5.5; N, 19.3; Ni, 20.2. Found: C, 33.4; H, 5.3; N, 19.7; Ni, 19.3, 19.8. The analysis also fits bis(dimethylglyoxime)nickel(II) equally well. *Anal.* Calcd for $Ni(C_4H_7N_2O_2)_2$: C, 33.3; H, 4.9; N, 19.4; Ni, 20.3. The magnetic susceptibility was 2.9 BM per nickel ion.

Biacetyl Methoxime Azine (III).—This compound was prepared from 2,3-butanedione 2-methoxime (Eastman Chemical Co.) and hydrazine in ethanol. Recrystallization from hot ethanol gave yellow needles; mp 106–108°. *Anal.* Calcd for $C_{10}H_{18}$-N_4O_2: C, 53.1; H, 8.0; N, 24.7. Found: C, 53.2; H, 8.1; N, 24.9. The compound gives no color change or other evidence of reaction when mixed with iron(II) or nickel(II) salts under a variety of conditions.

Equipment.—Magnetic susceptibility measurements were made with a Gouy balance, calibrated with Hg[Co(NCS)₄]. Infrared spectra were recorded on a Perkin-Elmer Model 137 spectrometer, calibrated with polystyrene film. A diffuse-transmission spectrum of the solid complex was recorded on a Beckman Model DB spectrophotometer, using a Nujol mull on filter paper.

pH Titrations.—These were carried out with an Orion 801 digital pH meter and a Corning combination glass–calomel electrode. Weighed samples of ligand (0.0100 mol) along with 25 ml of water and 15 ml of ethanol were placed in a small bottle, fitted with a four-hole stopper containing the electrode, the buret tip, and a nitrogen inlet tube. The bottle was also arranged for magnetic stirring. Nitrogen was swept through the mixture continuously to exclude CO₂. The mixtures were titrated with 4.88 *M* NaOH using a microburet. Similar titrations were carried out under the same conditions with appropriate amounts of nickel chloride added. In all four cases equilibration was slow in the region before the equivalence point, being especially bad for the titrations with nickel ion present. Readings were recorded after they had stabilized to ±0.01 pH unit

(6) L. E. Godyski and R. E. Rundle, *Acta. Crystallogr.*, **6**, 487 (1953).
(7) A. G. Sharpe and D. B. Wakefield, *J. Chem. Soc.*, 496 (1957).