made since the previous work was carried out in the gas phase.[17]

The good concordance (1) verifies the validity of the esr method for determining the enthalpy of homolytic thermal cleavage of neat liquids[15] and (2) confirms that the O–O peroxy bond in $S_2O_6F_2$ is quite weak, having a bond dissociation energy of 22–24 kcal/mole.[18]

Acknowledgments. We wish to thank Professor George H. Cady for suggesting an investigation of this system and for helpful discussions. We also wish to thank Professor D. D. DesMarteau and Professor F. B. Dudley for supplying the $S_2O_6F_2$ used.

[17] From (1) our value of $\Delta H°$ in the liquid phase, (2)$\Delta H_{vap}(S_2O_6F_2)$ = 7.6 kcal/mole (67°, ref 7), and (3) a *crude* estimate of $\Delta H_{vap}(SO_3F\cdot) \approx$ 5 kcal/mole, we compute an approximate value $\Delta H°(g) \approx 25$ kcal/mole, which is in fairly good agreement with the enthalpy changes previously measured.

[18] NOTE ADDED IN PROOF. An esr study of the $S_2O_6F_2$–$SO_3F\cdot$ equilibrium in the gas phase has been reported [R. A. Stewart, S. Fujiwara, and F. Aubke, *J. Chem. Phys.*, **48**, 5524 (1968)]. It is not possible to compare our $\Delta H°$ with the results obtained by these workers because they employed an incorrect statement of the van't Hoff equation in their analysis.

Chemistry of Metal Complexes with Polydentate Ligands. Complexes of N-Hydroxyethylethylenediamine

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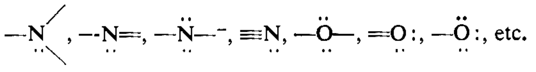
Abstract: It has been found that N-hydroxyethylethylenediamine can act either as a bidentate or a tridentate ligand, coordinating, in the first case, through the amino nitrogens, and in the second case, by the hydroxyl oxygen also. When the hydroxyl group coordinates, the hydrogen atom becomes more acidic, so that, in the presence of a proton acceptor, the ligand becomes a tridentate oxyethylethylenediamine ion. This behavior has been shown to explain the formation of different types of complexes with Co(III), Pt(II), Pd(II), and Ni(II). The nature of these complexes has been studied through their electrical conductivities and their electronic, ir, and nmr spectra. Tentative arguments for the absence of any tris complex and the reason for the apparent inactivity of the noncoordinated hydroxyethyl group have been presented. It has been shown that the uncoordinated hydroxyl group is not inactive and it can be acetylated even under mild conditions.

The formation of a coordinatively saturated complex, Ml_n, where l is a unidentate ligand, statistically involves n steps. If the ligand (L) is a polydentate one, with m coordination sites sterically available to one metal ion M, the complex formed in presence of excess of ligand is $ML_{n/m}$. Since complex formation or ligand substitution is stepwise even with polydentate ligands, we may expect that polydentate ligands, particularly those with nonequivalent coordinating atoms, will exhibit varying dentate natures. Thus, the normally bidentate ethylenediamine can be monodentate[1] as $NH_2CH_2CH_2NH_3^+$ in the Cr(III) complex $[Cr(NH_2CH_2CH_2NH_3^+)(H_2O)_5]_4^+$, and ethylenediaminetetraacetic acid may coordinate as a bi- to hexadentate ligand.

It may be expected that this variation in the polydonation of a ligand will be especially marked for those ligands that contain donor atoms with quite varying affinities toward the metal ion. Such groups, with N and O as the coordinating elements, may be



$$-\ddot{N}\!<,\ -\ddot{N}=,\ -\overset{..}{\underset{..}{N}}-^{-},\ \equiv\ddot{N},\ -\overset{..}{\underset{..}{O}}-,\ =\ddot{O}:,\ -\overset{..}{\underset{..}{O}}:,\ \text{etc.}$$

It may further be expected that the most important factors affecting the dentate nature of a polydentate ligand will be pH, solvent, the coordinated groups, the relative metal to ligand concentration, and any factors that may affect the mechanism of ligand substitution.

There has been a number of investigations[2] on the nature of the complexes formed with multidentate ligands containing the N-hydroxyethyl group, particularly on the activity of the noncoordinated hydroxyl group. This paper is concerned with complexes formed with N-hydroxyethylethylenediamine, $NH_2CH_2CH_2NHCH_2CH_2OH$.[3]

It has been found that, depending on the conditions of synthesis and the nature of the coordinated metal, this unsymmetrical and potentially tridentate ligand yields a number of different types of complexes according to the following scheme

$$Ml_n + (x + y + z)\text{etolenH} \longrightarrow$$

$$\left[\begin{array}{c}(\text{etolenH})_x \\ \text{M}(\text{etolen}H)_y(\text{l})_{n-2x-3y-3z} \\ (\text{etolen})_z\end{array}\right] + z\text{H}^+$$

$$\text{M} = \text{Co(III), Pt(II), Pd(II), Ni(II)}$$

$$\text{l} = H_2O,\ NH_3,\ NO_2^-,\ Cl^-$$

$$x = 0, 1, 2;\ \ y = 0, 1;\ \ z = 0, 1, 2$$

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[1] R. F. Childers, Jr., K. G. Vander Zyl, Jr., D. A. House, R. G. Hughes, and C. S. Garner, *Inorg. Chem.*, 7, 749 (1968).

[2] (a) R. A. Krause and S. D. Goldby, Advances in Chemistry Series, No. 37, American Chemical Society, Washington, D. C., 1963, p 143; (b) R. N. Keller and L. J. Edwards, *J. Am. Chem. Soc.*, **74**, 215 (1952); (c) W. C. Drinkard, H. F. Bauer, and J. C. Bailar, Jr., *ibid.*, **82**, 2992 (1960); (d) B. Das Sarma, G. J. Tennenhouse, and J. C. Bailar, Jr., *ibid.*, **90**, 1362 (1968).

[3] Henceforth the expression "etolenH" will be used to indicate the ligand coordinated through only the two nitrogen atoms; "etolen*H*" will indicate the ligand coordinated through the oxygen of the OH in addition to the two N's; "etolen" will represent the tridentate deprotonated ligand, attached through the two N's and oxygen of O^-.

It has been found that in all the complexes so far isolated, etolen is tridentate; etolenH often behaves as a tridentate ligand, but is bidentate (attached through the two N's) when the other coordination sites on the metal are already occupied by strongly coordinating groups (like NO_2^-, tridentate etolen*H*, tetradentate triethylenetetramine, etc.). The tendency of bidentate etolenH to be transformed into tridentate etolen*H* or etolen has been found to account for the formation of a variety of Co(III)–etolenH complexes and the earlier considerable disagreement on the composition and properties of these complexes.

It was reported earlier[4a] that the coordinating tendency of ethanolic oxygen is greatly enhanced by the positive inductive effect of an amino group in the same molecule of ligand, and that ethanolamine behaves as a bidentate chelate in forms corresponding to etolen and etolen*H*. Apparently ethylene glycol forms chelate complexes[4b] also, so the comparatively strong coordinating tendency of the N-hydroxyethyl group in etolenH can be easily understood. However, the proton in any coordinated hydroxy group is readily lost, especially in basic solution. With etolenH, this gives etolen complexes.

Experimental Section

Materials. N-Hydroxyethylethylenediamine (2-(2-aminoethylamino)ethanol) obtained from Matheson Coleman and Bell, was found to be sufficiently pure, on the basis of C, H, N analyses and titration against standard acid, that it was used without further purification.

Sodium hexanitrocobaltate(III), Baker's analyzed (CP) product, was employed.

Activated carbon, Aqua Nuchar A, West Virginia Pulp and Paper Co., New York, N. Y., was used.

Hexaamminecobalt(III) salts and bisoxyethylethylenediamine cobalt(III) iodide were prepared as reported earlier.[2d]

I. Dinitrobis-N-hydroxyethylethylenediaminecobalt(III) Nitrite, $[Co(etolenH)_2(NO_2)_2]NO_2$. Sodium hexanitrocobaltate(III) (80 g, 0.2 mole) was mixed with 2 g of active carbon. To this was added 400 ml of a 1 *M* solution of etolenH; the mixture was stirred and left overnight. It was filtered and the filtrate concentrated at room temperature under a stream of air. Orange-yellow flakes of the complex nitrite separated. The mother liquor had a pH of ~7. The crystals were filtered under suction and washed twice with cold water followed by 95% alcohol and then by absolute ethanol. The product was dried in air; yield 48 g (60%). *Anal.* Calcd for $CoC_8H_{24}N_7O_8$: C, 23.70; H, 5.93; N, 24.24. Found: C, 23.54; H, 6.01; N, 24.01.

II. Dinitrobis-N-hydroxyethylethylenediaminecobalt(III) Nitrate, $[Co(etolenH)_2(NO_2)_2]NO_3 \cdot H_2O$. To a solution of 30 g of the complex nitrite in 50 ml of water at 55° 5 ml of concentrated nitric acid was added dropwise with constant stirring. Nitrous fumes were evolved and the complex nitrate slowly formed as orange-yellow crystals. More crystals deposited when the solution was cooled in an ice bath. These were filtered and recrystallized from 75 ml of warm water (55°). *Anal.* Calcd for $CoC_8H_{26}N_7O_{10}$: Co, 13.42; C, 21.85; H, 5.92; N, 22.32. Found: Co, 13.74; C, 22.01; H, 6.00; N, 21.76.

III. Dinitrobis-N-hydroxyethylethylenediaminecobalt(III) Iodide, $[Co(etolenH)_2(NO_2)_2]I$. The complex iodide was prepared by adding a saturated solution of sodium iodide to a solution of the complex nitrite. The complex iodide slowly separated as beautiful orange crystals; these were filtered, washed with ice cold water and then with ethanol, and dried in air. *Anal.* Calcd for $CoC_8H_{24}N_6O_6I$: C, 19.74; H, 4.94; N, 17.28; I, 26.13. Found: C, 19.59; H, 5.36; N, 17.52; I, 25.85.

IV. N-Oxyethylethylenediamine-N-hydroxyethylethylenediaminecobalt(III) Iodide, [Co(etolen)(etolen*H*)]I_2. To 10.6 g of finely powdered hexaamminecobalt(III) chloride (0.04 mole) was added 1 g of active charcoal, followed by 5 ml of concentrated ammonia and 80 ml (0.08 mole) of a 1 *M* solution of etolenH. The mixture was heated on the steam bath until the odor of ammonia could no longer be detected. The precipitate which formed was separated from the carbon by heating the mixture with 80 ml of hot water and filtering. The filtrate was concentrated to about 50 ml and 18 g of sodium iodide dissolved in the minimum quantity of water was added to it. Upon standing overnight, the solution yielded dark brown crystals. The mother liquor had a pH of 6.0.

The product was washed several times with cold water, then with 95% ethanol, and finally with absolute ethanol. It was dried in an oven at 105°. *Anal.* Calcd for $CoC_8H_{23}N_4O_2I_2$: Co, 11.34; C, 18.47; H, 4.42; N, 10.77; I, 48.84. Found: Co, 11.38; C, 18.73; H, 4.60; N, 10.62; I, 48.64.

V. Chloro-N-hydroxyethylethylenediaminepalladium(II) Chloride, [Pd(etolen*H*)Cl]Cl. Ten grams of palladium chloride (60% Pd, *ca.* 0.04 mole) was dissolved in 100 ml of water containing 10 g of potassium chloride by heating on the steam bath. To the filtered solution 40 ml of a 1 *M* solution of etolenH (0.04 mole) was added dropwise with constant stirring. The mixture was cooled in an ice bath. The light yellow needles that separated were filtered, washed four times with cold water, and then with ethanol. The sample was dried in an oven at 105°, yield 13 g (80%). *Anal.* Calcd for $PdC_4H_{12}N_2OCl_2$: C, 17.06; H, 4.26; N, 9.95; Cl, 25.23. Found: C, 17.26; H, 4.45; N, 9.77; Cl, 25.05.

VI. Bis-N-hydroxyethylethylenediaminepalladium(II) Chloride, $[Pd(etolenH)_2]Cl_2$. To 7 g of compound V (0.025 mole) was added 24 ml of 1 *M* etolenH (0.024 mole). On warming, most of the yellow crystals dissolved, forming an almost colorless solution. This was filtered and the filtrate was concentrated on the steam bath to an oily, light yellow residue. When the oil was treated with cold absolute ethanol, an almost white solid formed. This was filtered, and the crystals were washed with absolute ethanol, followed by an ethanol–ether mixture, and finally with ether, and dried at 105°. The yield was almost quantitative. The product was somewhat hygroscopic and tended to turn gummy on the filter unless quickly washed with absolute ethanol. *Anal.* Calcd for $PdC_8H_{24}N_4O_2Cl_2$: C, 24.91; H, 6.23; N, 14.53; Cl, 18.42. Found: C, 25.57; H, 6.31; N, 13.98; Cl, 18.20.

VII. Chloro-N-hydroxyethylethylenediamineplatinum(II) Chloride, [Pt(etolenH)Cl]Cl. To a solution (25 ml) of tetrachloroplatinic(II) acid obtained from 5 g of hexachloroplatinic(IV) acid[5] was added 15 ml (0.015 mole) of 1 *M* etolenH. When this was heated on a water bath with stirring, the red solution slowly became light yellow. The complex chloride separated on cooling as light yellow woolly needles. The product was filtered and recrystallized from warm water, yield 2 g. *Anal.* Calcd for $PtC_4H_{12}N_2OCl_2$: C, 12.97; H, 3.24; N, 7.57; Cl, 19.19. Found: C, 13.43; H, 3.41; N, 7.38; Cl, 20.12.

VIII. Bis-N-hydroxyethylethylenediaminenickel(II) Bromide, $[Ni(etolenH)_2]Br_2$. To 8.7 g of nickel bromide (0.04 mole) was added 80 ml of 1 *M* etolenH solution, and the mixture was heated on the water bath. The blue solution was filtered and evaporated to a syrup on the water bath. It was then cooled in ice and the complex bromide was precipitated by the addition of absolute ethanol. The material was purified by dissolving in water, filtering, and reprecipitating with cold ethanol. The blue-violet product was washed with ethanol, then with an ethanol–ether mixture, and finally with ether. It was dried at 105°. *Anal.* Calcd for $NiC_8H_{24}N_4O_2Br_2$: C, 22.51; H, 5.63; N, 13.13; Br, 37.47. Found: C, 22.94; H, 5.75; N, 12.92; Br, 37.28.

IX. Triethylenetetramine-N-hydroxyethylethylenediaminecobalt(III) Chloride, $[Co(trien)(etolenH)]Cl_3 \cdot H_2O$. To a suspension of 6.25 g (0.02 mole) of finely powdered dichlorotriethylenetetraminecobalt(III) chloride[6] in 200 ml of absolute ethanol was added 20 ml of 1 *M* etolenH (0.02 mole). The mixture was stirred and boiled under reflux for 2 hr and cooled. The yellow-orange product which separated was filtered and washed with ethanol and was recrystallized from a minimum quantity of boiling water, washed successively with ethanol and ether, and dried in an oven at 110°; yield 6.1 g. *Anal.* Calcd for $CoC_{10}H_{30}N_6OCl_3 \cdot H_2O$: C, 25.70; H, 7.38; N, 19.38; Cl, 24.56. Found: C, 25.57; H, 7.21; N, 19.12; Cl, 24.60.

A similar reaction with *cis*-dichlorobisethylenediaminecobalt(III) chloride and etolenH in ethanol led to a yellow-orange solid and a red-brown solution. The solid product was shown to be tris-

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(4) (a) H. Yoneda and S. Kida, *J. Am. Chem. Soc.*, **82**, 2139 (1960); (b) see, for example, C. K. Jørgensen, "Inorganic Complexes," Academic Press, New York, N. Y., 1964, p 101.

(5) W. E. Cooley and D. H. Busch, *Inorg. Syn.*, **5**, 208 (1957).

(6) F. Basolo, *J. Am. Chem. Soc.*, 70, 2634 (1948).

ethylenediamine cobalt(III) chloride, $[Co(en)_3]Cl_3$, by chemical and infrared analysis. On addition of ethanol, the mother liquor yielded more $[Co(en)_3]Cl_3$. The filtrate from this treatment was concentrated on a water bath and cooled. A concentrated solution of KI in water was added, whereupon a brown product, identical with compound IV, $[Co(etolen)(etolen\mathit{H})]I_2$, slowly crystallized.

X. Dinitrobis-N-acetatoethylethylenediaminecobalt(III) Iodide, $[Co(etolenCOCH_3)_2(NO_2)_2]I$. A suspension of 2 g of finely ground IV in 100 ml of acetic anhydride was placed in a flask fitted with a reflux condenser. The suspension was stirred with a magnetic stirrer at room temperature (20°) for 24 hr and then filtered. The residue was found to be unreacted starting material (0.42 g). The yellow filtrate was cooled and slowly added to 500 ml of ether. The yellow solid that separated was filtered and washed several times with ether and dried at 90°; yield 1.5 g.

The crude product was dissolved in 5 ml of water and filtered, and a saturated solution of 0.8 g of KI in cold water was added. Beautiful orange-yellow flakes crystallized. These were washed twice with cold water, then with ethanol, and finally with ether, and were dried at 75° under vacuum; yield 1.1 g. The compound was found to be quite stable in aqueous solution at room temperature and to hydrolyze very slowly. *Anal.* Calcd for $CoC_{12}H_{28}N_6O_8I$: C, 25.27; H, 4.95; N, 14.73; I, 22.34. Found: C, 25.13; H, 4.93; N, 14.62; I, 22.40.

Acetylation of Cobalt and Palladium–etolenH Complexes. Because of the reported apparent inactivity of the hydroxyl group of etolenH complexes toward reagents that are reactive to primary alcohols, a strong acetylating agent like ketene was initially employed for acetylation. Ketene was generated by the pyrolysis of acetone in an apparatus identical with that described in the literature.[7] The yield of ketene was 0.126 mole/hr as found by reaction with standard sodium hydroxide solution.

One of the major difficulties in the acetylation was that no solvent that was inert toward acetylating agents would dissolve the etolenH complexes. Solutions of the complexes in dimethyl sulfoxide were studied until it was found that the solvent itself reacts with ketene. Cobalt(III) complexes of ethylenediamine and those of etolenH reacted with equal ease with ketene in DMSO solutions. The reactions were then attempted in acetone suspensions of the complexes (0.005 mole of finely powdered sample in 100 ml of dry acetone). Ketene was passed through the solution for 90 min.

It was observed that there was practically no reaction of ketene with $[Co(etolen)_2]NO_3$, *cis*-$[Co(en)_2(NO_2)_2]NO_3$, and $[Co(etolen)(etolen\mathit{H})]I_2$. Practically all of the starting material could be recovered by filtration after the treatment with ketene. $[Co(etolenH)_2(NO_2)_2]NO_3$ reacted with ketene in acetone forming an orange-red solution. $[Pd(etolenH)_2]Cl_2$ also reacted, forming a deep yellow solution. The reaction mixture was filtered to remove any unreacted starting material. The acetone solution was concentrated in a rotary evaporator and then added to cold ether. A brick red product was obtained from the cobalt complex. The Pd–etolenH complex yielded a yellow product. Infrared spectra of both products exhibited sharp and strong peaks at 1725 cm^{-1}, but the elemental analysis was poor for both the Co(III) and Pd(II) reaction products on the basis of their diesters. Attempts to purify these products were unsuccessful. It was observed, however, that the complexes underwent some reduction during acetylation with ketene. Some Co(II) salts and some black Pd salts were always present in the respective reaction mixtures.

Table I. Molar Conductance (mhos) at 20° (0.001 *M* Aqueous Solution)

1.	$[Co(trien)(etolenH)]Cl_3$	363
2.	$[Co(etolen)(etolen\mathit{H})]I_2$	225
3.	$[Pd(etolenH)_2]Cl_2$	215
4.	$[Ni(etolenH)_2]Br_2$	209
5.	$[Pt(etolen\mathit{H})Cl]Cl$	90
6.	$[Pd(etolen\mathit{H})Cl]Cl$	79
7.	$[Co(etolenH)_2(NO_2)_2]NO_2$	75
8.	$[Co(etolenH)_2(NO_2)_2]NO_3$	78
9.	$[Co(etolenH)_2(NO_2)_2]I$	82
10.	$[Co(etolenCOCH_3)_2(NO_2)_2]I$	90[a]
11.	$[Co(etolen)_2]I$	128

[a] Slowly increases.

Electrical Conductivity. The molar conductances of the etolenH complexes are tabulated in Table I. Except for $[Co(etolenCOCH_3)_2(NO_2)_2]I$, the conductance values remained reasonably constant for periods of 4 hr or more after the solutions were prepared. The conductances of the first four complexes are those expected for their ion types, but the values for the next six are lower, and that of the last compound somewhat higher than expected.[8]

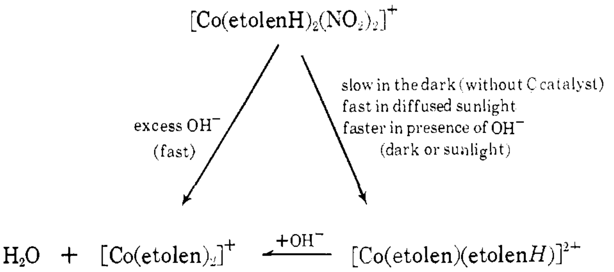
Absorption Spectra. Table II summarizes the absorption bands of the etolenH complexes in water at 20°.

Table II

Compound	Wavelength, mμ	Molar extinction coeff
$[Co(etolenH)_2(NO_2)_2]I$	445	195
	344	3200
$[Co(etolenCOCH_3)_2(NO_2)_2]I$	445	208
	345	3950
$[Co(etolen)(etolen\mathit{H})]I_2$	470	131
$[Co(etolen)_2]I$	512	80
	370	95
$[Ni(etolenH)_2]Br_2$	557	14
	350	50
$[Co(trien)(etolenH)]Cl_3$	480	155
	344	138

The platinum and palladium–etolenH complexes do not have any absorption peaks in the 325–650-mμ region. Concentrating our attention on the Co(III) complexes (Figure 1), the first absorption bands are nearly parabolic curves with wavelength increasing and extinction coefficient decreasing with the replacement of NO_2^- by OH and then by O^-, as predicted by the spectrochemical series. While $[Co(en)_2(NO_2)_2]^+$ is fairly stable in aqueous solution, $[Co(etolenH)_2(NO_2)_2]^+$ slowly hydrolyzes in dilute aqueous solution, unless some acid is present. The hydrolysis is very much accelerated by active carbon, sunlight (direct or diffuse), and more by OH^-, even in the dark (Figure 2). The reaction can be followed spectrophotometrically and can be represented by Scheme I.

Scheme I



The conversion of $[Co(etolenH)_2(NO_2)_2]^+$ into $[Co(etolen)(etolen\mathit{H})]^{2+}$ and $[Co(etolen)_2]^+$ possibly may pass through intermediates like $[Co(etolen\mathit{H})(etolenH)(NO_2)]^{2+}$ and $[Co(etolen\mathit{H})_2]^{3+}$, but no such intermediates have yet been isolated. It has been found that the hydrogen of etolenH becomes more acidic on coordination. Thus, 0.001 *M* solutions of etolen*H* complexes are more acidic than those of etolenH complexes: $[Pt(etolen\mathit{H})Cl]Cl$, pH 4.2; $[Pd(etolen\mathit{H})Cl]Cl$, pH 4.6; $[Co(etolen)(etolen\mathit{H})]I_2$, pH 4.9. These compare with pH 5.9–6.5 for etolenH complexes. It may be argued that the conversion of bidentate etolenH in $[Co(etolenH)_2(NO_2)_2]^+$ into tridentate etolen*H* or etolen requires vacating a coordination site occupied by NO_2^-, a process which is assisted by high temperature, the presence of active carbon as a catalyst, ultraviolet excitation, and the presence of OH^-, roughly in the order of increasing efficiency. It has further been observed that removal of NO_2^- by N_3^- from $[Co(etolenH)_2(NO_2)_2]^+$ in dilute solution is faster than that from the comparable $[Co(en)_2(NO_2)_2]^+$.

Infrared Spectra. The infrared spectra of the compounds were recorded in Nujol mulls and in KBr disks by a Perkin-Elmer Model 21 spectrometer. It was found that all complexes containing a

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[7] W. E. Hanford and J. C. Sauer, *Org. Reactions*, 3, 132 (1946); J. W. Williams and C. D. Hurd, *J. Org. Chem.*, 5, 122 (1940).

[8] A. Werner and A. Miolati, *Z. Physik. Chem.*, 12, 35 (1893); 14, 506 (1896); 21, 225 (1896).

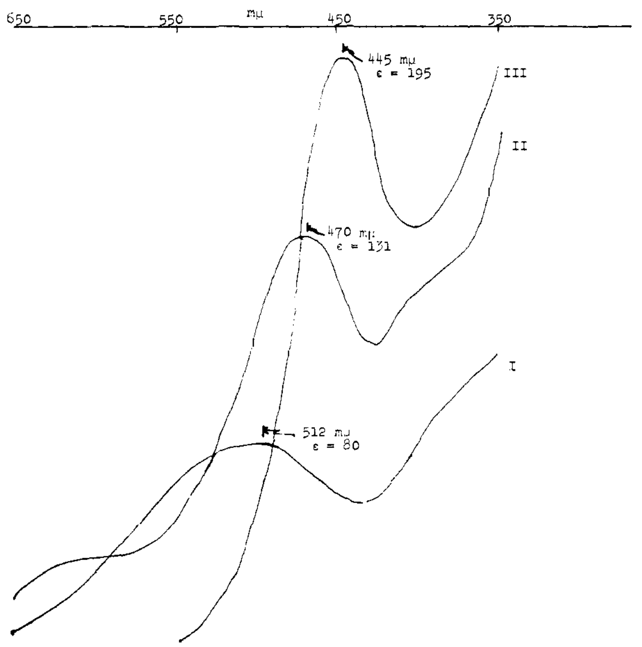

Figure 1. (I) [Co(etolen)$_2$]I; (II) [Co(etolen)(etolen*H*)]I$_2$; (III) [Co(etolenH)$_2$(NO$_2$)$_2$]I (0.002 *M* solution in water).

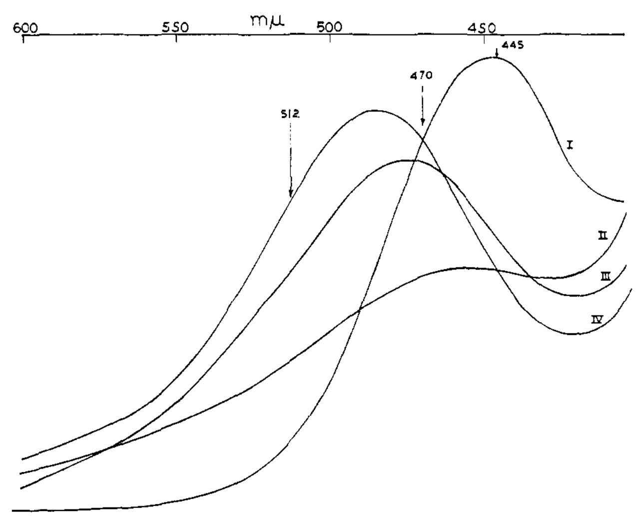

Figure 2. (I) [Co(etolenH)$_2$(NO$_2$)$_2$]NO$_3$, 0.002 *M* solution in 0.004 *M* HNO$_3$. (II) Above, without HNO$_3$ in diffused sunlight. (III) [Co(etolenH)$_2$(NO$_2$)$_2$]NO$_3$, 0.002 *M* solution in 0.002 *M* NaOH (in dark). (IV) [Co(etolenH)$_2$(NO$_2$)$_2$]NO$_3$, 0.002 *M* solution in 0.01 *M* NaOH (in dark). All spectra were taken 48 hr after mixing, at room temperature (about 28°).

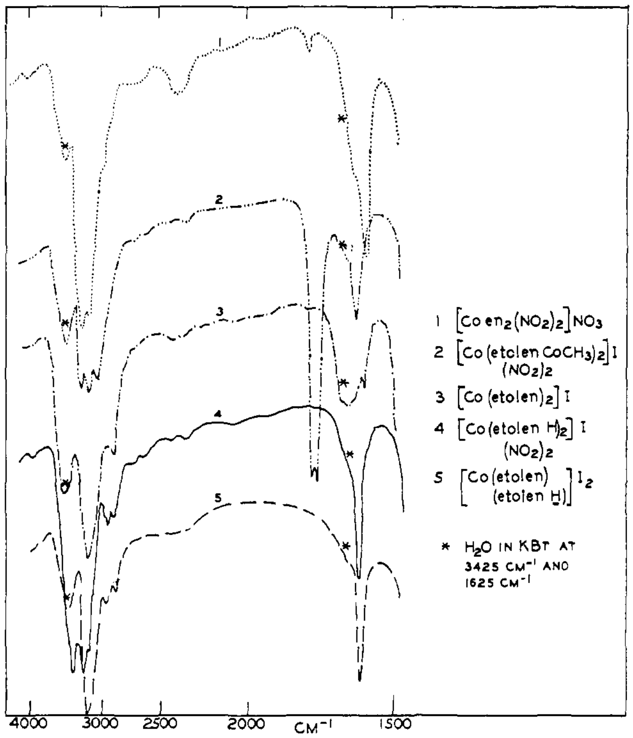

Figure 3. Infrared spectra in KBr disk.

noncoordinated hydroxyethyl group showed a strong sharp OH stretching frequency in their spectra, [Co(trien)(etolenH)]$^{3+}$ and [Co(etolenH)$_2$(NO$_2$)$_2$]$^+$ at 3370 cm^{-1}; [Ni(etolenH)$_2$]$^{2+}$ and [Pd-(etolenH)$_2$]$^{2+}$ at 3380 cm^{-1}. Broomhead[9] has recently reported the OH frequency in Pt(etolenH)$_2$$^{2+}$ at 3370 cm^{-1}. The OH frequency in the free ligand may be expected at a much lower frequency because of hydrogen bonding. It was found to be 3290 cm^{-1} for the liquid film. No corresponding OH frequency was recorded in the spectra of any etolen or etolen*H* complex prepared by us. The OH frequency of the Co(III), Pt(II), and Pd(II) complexes containing tridentate etolen*H* must have shifted to a lower frequency owing to the metal-oxygen bond into the region 3175–3225 cm^{-1}, overlapping the NH frequencies.

The spectra of the Co(III)–etolenH complexes are recorded in Figure 3 together with that of the acetylated complex. It can be clearly seen that in the spectrum of the acetylated complex the OH frequency at 3370 cm^{-1} has disappeared and the two very strong and sharp peaks of the C=O (str) frequency have appeared at 1720 and 1740 cm^{-1}. The double peaks indicate the nonequivalence of the ester groups in the complex, which can be due to the presence of any of the several possible isomers.

Nmr Spectra. Preliminary studies on the Varian A-60 nmr spectrometer indicate that all the protons in the ligand except those of the $-CH_2-O-$ group have about the same chemical shift with the center at 2.75 ppm in CDCl$_3$, 2.62 ppm in (CD$_3$)$_2$SO, and 2.66 ppm in D$_2$O. The $-CH_2-O-$ protons are at 3.60, 3.50, and 3.63 ppm in the respective solvents. The $-CH_2-O-$ protons are recorded in all of the etolenH complexes containing the $-CH_2-OH$ group at 3.62–3.77 ppm. All –NH– and –OH protons are removed in D$_2$O, but the $-CH_2-N-$ protons in the etolenH complexes have the same chemical shift as in the free ligand. No $-CH_2-O$ signal in the usual position in [Co(etolen)$_2$]I was observed. The $-CH_2-O$ proton resonance has also shifted upfield in [Co(etolen)(etolen*H*)]$^{2+}$. It may be that removal of the proton in the tridentate etolen has sufficiently reduced the electronegativity of oxygen to cause an upfield shift of $-CH_2-O^-$ in [Co(etolen)$_2$]I.

Results and Discussion

Formation of Tris(etolenH) Complexes. Contrary to the report of some previous investigators, no tris(etolenH) complex of Co(III) or of any other metal could be isolated. All complexes containing etolenH except [Co(trien)(etolenH)]Cl$_3$ and [Co(etolenH)$_2$(NO$_2$)$_2$]$^+$ were found to be extremely soluble in water, and these could never be crystallized from aqueous or aqueous-alcoholic solutions, except with very bulky anions like (C$_6$H$_5$)$_4$B$^-$. Addition of acetone to a concentrated water solution or addition of ether to a methanol solution resulted only in the formation of oils. These oils slowly deposited the bis(etolenH) complexes on treatment with cold absolute ethanol. Even though the three hydroxyethyl groups in a tris(etolenH) complex are rather bulky, and favorably placed for formation of a number of –N–H · · · O– hydrogen bonds, trials with Fisher–Hirschfelder–Taylor models indicate that the tris complex may be formed without much strain.

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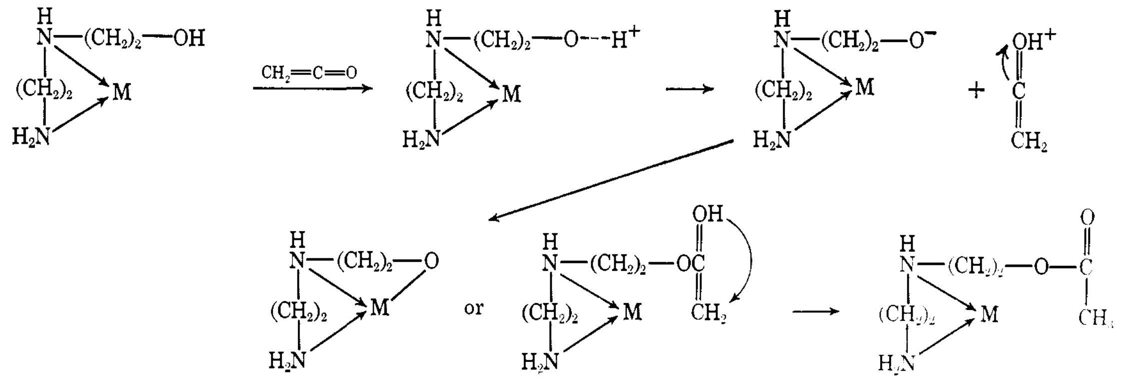
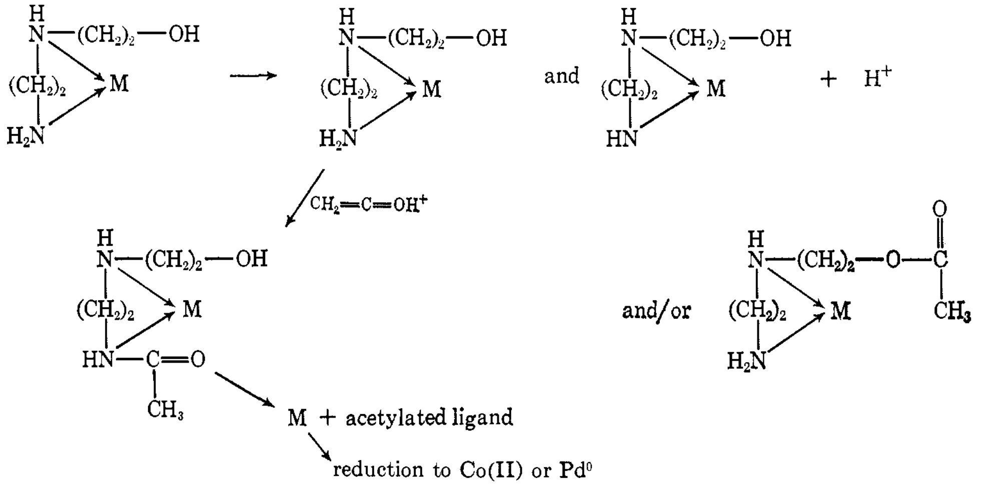
[9] J. A. Broomhead, *J. Am. Chem. Soc.*, 90, 4480 (1968).

Scheme II



Scheme III



Besides the problem of high solubility, it has been found that etolenH tends to span three coordination positions as etolen*H*, or, if there is a base to accept the proton, as etolen. The presence of one tridentate etolen*H* or etolen would, of course, preclude the entry of more than one other chelated etolenH molecule unless the coordination number of the metal is expanded beyond six. Steric considerations and entropy and enthalpy factors will all normally favor tridentate bis(etolenH) complexes over the bidentate tris(etolenH) ones. The presence of excess etolenH, or liberation of any base, in the preparation of the complexes, as those from $[Co(NH_3)_6]^{3+}$, $[Co(CO_3)_3]^{3-}$, etc., results in the formation of etolen or mixed etolen–etolen*H* complexes. Hydroxyethylethylenediamine can thus be expected to behave as a bidentate diamine when (1) the pH is 7 or less and (2) the other coordination sites are occupied by ligands with bonds too strong for the $-CH_2OH$ group to substitute without prior activation or hydrolysis, or (3) the solvent medium is nonaqueous and thus reduces the acid dissociation of etolenH $\rightleftarrows$ etolen + H^+. No tris(etolenH) complex could, however, be isolated from the oils resulting from the reaction of $Na_3[Co(CO_3)_3]$, $Na_3[Co(NO_2)_6]$, or $[Co(NH_3)_6]Cl_3$ with three or more equivalents of etolenH in water, ethanol, acetone, or dimethylformamide.

Acetylation of the etolenH Complexes. One of the major interests on the study of complexes containing the noncoordinated N-hydroxyethyl group was the reported apparent inactivity of the hydroxyl group toward reagents that are reactive to primary alcohols. We have, however, found that the noncoordinated OH group of etolenH is readily and easily acetylated even under mild acetylating conditions. Broomhead has reported that another complex of Co(III) containing a noncoordinated hydroxyethyl group can be halogenated with thionyl chloride in dimethylformamide. It therefore remains to explain why such hydroxyl groups were assumed to be inactive.

It is most probable that in previous works no complex of etolenH containing the free hydroxyethyl group was actually employed for the acetylation reaction. We experienced more difficulty in isolating the pure acetylated product than in acetylating the etolenH complexes, especially under drastic conditions. The low rate of acetylation of the $M(etolenH)_n$ complexes is probably due chiefly to the difficulty of bringing the acetylating agent into contact with the OH group in the essentially heterogeneous suspension of the complexes. Acetylation proceeded fairly rapidly if the material was somewhat soluble in the solvent, as in the acetylation of $[Co(etolenH)_2(NO_2)_2]^+$ in acetone or in acetic acid–acetic anhydride. Reaction also proceeds quite rapidly if acetylation is carried out at an elevated temperature. The problem is that side reactions make the isolation of a pure acetylated product difficult when acetylation is carried out with strong acetylating agents or at higher temperatures. Some probable parallel reactions are discussed below. The mechanisms presented are purely tentative.

Acetylation reactions with ketene (or other acetylating agents) are catalyzed by acids which can transfer a proton to the carbonyl group of the acetylating agent and increase its electrophilicity, or by a base that can remove a proton from the addend and increase its nucleophilicity. Since the reaction involved here is between ketene and the hydroxy group of a bulky etolenH complex in the absence of external acids, the proton which activates the carbonyl group of ketene probably comes from the alcoholic OH group. The process must involve a weakening of the O–H bond prior to migration of the proton. As the OH bond is weakened, the oxygen becomes more negative and there is a competition for O^- between the metal ion and the electron-deficient carbon of the carbonyl group in the ketene, resulting in the formation of a mixture of the acetylated complex and the Co(etolen)$_n$ complexes. Tentatively, such a mechanism may be assumed to occur in the reaction of acetone suspensions of etolenH complexes with ketene, as pictured in Scheme II.

The reaction with ketene in dimethyl sulfoxide must operate by attack on the NH group of the etolenH complexes along with the OH, since similar reactions occur with ethylenediamine complexes as well. The mechanism in this case probably involves partial dissociation of a metal–nitrogen bond, or acid dissociation of an NH bond, liberating a proton to further activate the carbonyl group of ketene, or both. Both of the above processes will weaken the metal complex, leading to reduction of incompletely complexed metal. This second process will be favored in highly polar solvents like dimethyl sulfoxide, but may occur to a small extent in reactions in acetone suspension (see Scheme III).

All the etolenH complexes described in this paper are capable of existence in several stereoisomeric forms, but no attempt has been made to identify the structures or to isolate these.

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Contact Shift Studies of Some Octahedral Benzamide Complexes of Iron(II), Cobalt(II), and Nickel(II)

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Abstract: Isotropic shifts are reported for some paramagnetic, six-coordinate complexes of benzamide, with Ni(II), Fe(II), and Co(II). Although it is impossible to draw any conclusions about a π-bonding interaction between the metal "d" orbitals and the ligand π orbitals from the Ni(II) shifts alone, a very convincing case can be made for interaction of metal t_{2g} orbitals and ligand π orbitals by comparing the shifts in the Ni(II) and Fe(II) complexes. These results further support our earlier claim that one cannot necessarily assume similar delocalization mechanisms in octahedral iron(II), cobalt(II), and nickel(II) systems. These interpretations are supported, and a mechanism for spin delocalization in the Ni(II) and Fe(II) complexes is proposed from the results of EHT molecular orbital calculations. It is also shown that a σ-delocalization mechanism does not necessarily lead to attenuation of the shift as one proceeds away from the metal. Pronounced variation in the Co(II) shifts with change in solvent, change in anion, and change in concentration of the complex are attributed to a pseudocontact effect induced by ion pairing. Conditions for observing a pseudocontact contribution to the shift are elucidated for six-coordinate complexes undergoing rapid ligand exchange.

Amides are known to be very good donors toward the first-row transition metal ions, and many coordination compounds involving amides as ligands have been synthesized.[2] In this laboratory we first became interested in coordination compounds of amides such as N,N-dimethylacetamide (DMA) and N,N-dimethylformamide (DMF)[2a] in studies of nonaqueous solvents.[3] Recently, because of our interest in understanding the nmr spectra of paramagnetic transition metal complexes, we investigated the contact shifts of the octahedral nickel(II) complexes of N,N-dimethylacetamide and N,N-dimethylformamide[4] and proposed possible mechanisms for the delocalization of unpaired electron spin density in these complexes. It was not clear, however, whether spin was being transferred *via* a σ or π mechanism or *via* a combination of both. The six-coordinate iron(II)-, cobalt(II)-, and nickel(II)-benzamide complexes, recently reported by Ragsdale, *et al.*,[5] were prepared in this study in order to determine how spin is delocalized in amide complexes of O_h symmetry. Benzamide (BA) and *p*-toluamide (PTA) were chosen as ligands because they contain phenyl groups which possess several nonequivalent protons whose proton contact shifts can be very useful in recognizing σ or π delocalization of unpaired electrons. Furthermore, two solvents (acetone and propylene carbonate) and two anions (ClO_4^- and BF_4^-) were utilized in order to study

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(1) Abstracted in part from the Ph.D. Thesis of M. Wicholas, University of Illinois, Urbana, Ill., 1967.

(2) See, for example, (a) R. S. Drago, D. W. Meek, M. D. Joesten, and L. LaRoche, *Inorg. Chem.*, **2**, 124 (1963); (b) W. E. Bull, S. K. Madan, and J. E. Willis, *ibid.*, **2**, 303 (1963); (c) S. K. Madan, *ibid.*, **6**, 421 (1967).

(3) R. S. Drago and K. F. Purcell, *Progr. Inorg. Chem.*, **6**, 271 (1964).

(4) B. B. Wayland, R. S. Drago, and H. F. Henneike, *J. Am. Chem. Soc.*, **88**, 2455 (1966).

(5) M. B. Welch, R. S. Stephens, and R. O. Ragsdale, *Inorg. Chim. Acta*, **2**, 367 (1968).