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Manganese Schiff Base Complexes. III. Circular Dichroism of Tetradentate Chelates of Manganese(III)

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Received June 4, 1973 AIC304138

The syntheses of several new optically active complexes, [Mn(SB)X], where $X^- = Cl^-$ or NO_2^- and SB is the optically active tetradentate Schiff base derived from salicylaldehyde or *o*-hydroxyacetophenone and (–)-1,2-propylenediamine, have been carried out. The electronic absorption spectra and circular dichroism spectra of the Mn(III) complexes have been measured in chloroform, methanol, and pyridine. Band assignments for the expected electronic transitions have been proposed. The CD spectra are consistent with a preferred conformation of the central chelate ring of δ (axial methyl) and with the absolute configuration of the flattened tetrahedral array of the Schiff base donor atoms of Λ.

During the course of the synthesis and characterization of a number of high-spin, five-coordinate Mn(III) complexes of tetradentate Schiff bases[1] we have had occasion to measure their electronic absorption properties. The spectra generally show broad bands with numerous shoulders of varying prominence, especially in the ligand field region. Thus it is difficult accurately to locate the maxima and consequently to analyze the spectra and make band assignments. Further, the interpretation of the electronic spectra of low-symmetry Mn(III) complexes in terms of ligand field, charge-transfer, and ligand transitions continues to be equivocal.[2] The usefulness of circular dichroism spectra in sorting out the spectra of tetradentate Schiff base complexes of divalent metal ions has been demonstrated by Urbach and his coworkers.[3] We have therefore synthesized and studied four new complexes of Mn(III) with optically active Schiff bases derived from (–)-1,2-propylenediamine, (–)pn, and salicylaldehyde or *o*-hydroxyacetophenone. The materials studied are shown in Figure 1.

Experimental Section

Synthesis. Optically active (–)-1,2-propylenediamine dihydrochloride was purchased from Strem Chemical Co.

[Mn(Salpn)X]. The optically active ligand was prepared *in situ* by combining 0.56 g (14×10^{-3} mol) of sodium hydroxide, 1.00 g (6.8×10^{-3} mol) of (–)-1,2-propylenediamine dihydrochloride, and 1.43 ml (13.8×10^{-3} mol) of salicylaldehyde in 30 ml of 95% ethanol. The resulting solution was refluxed for a few minutes and a solution of 13 g (67×10^{-3} mol) of $MnCl_2 \cdot 4H_2O$ in 40 ml of 95% ethanol was added. The final mixture was refluxed in air for 2.5 hr. The brown solution was filtered and the filtrate evaporated to dryness in an air stream. The residue was extracted with 100 ml of acetone and the acetone flooded with 1 l. of diethyl ether. A brown solid, 2.0 g, was isolated on a filter and air-dried. The yield of crude material was 79%, based on the ligand.

A portion of the solid, 0.25 g, was dissolved in 20 ml of distilled H_2O and the filtered solution treated with 1.1 g of potassium chloride (to give 1 *M* solution). After standing overnight at 2°, brown-red crystals separated. The crystals were isolated on a filter, washed with a little cold water, and air-dried. Final drying was accomplished by heating to 110° *in vacuo* over P_2O_5 for 12 hr; yield 0.085 g (34%). *Anal.* Calcd for [Mn(Salpn)Cl], $C_{17}H_{16}N_2O_2MnCl$: C, 55.07; H, 4.32; N, 7.56. Found: C, 54.57; H, 4.08; N, 7.71.[4] $\mu = 5.02$ BM.

A solution of 0.25 g of the original material in 20 ml of H_2O was treated with 1.3 g of sodium nitrite. A brown precipitate formed and was isolated on a filter, washed with a little water, and air-dried; yield 0.20 g (80%). *Anal.* Calcd for $[Mn(Salpn)NO_2]$, $C_{17}H_{16}N_3O_4Mn$: C, 53.56; H, 4.20; N, 11.03. Found: C, 53.31; H, 4.25; N, 10.62. $\mu = 4.94$ BM.

[Mn(Acetpn)X]·H_2O. The optically active ligand was prepared *in situ* by combining 0.56 g (14×10^{-3} mol) of sodium hydroxide, 1.00 g (6.8×10^{-3} mol) of (–)-1,2-propylenediamine hydrochloride, and 1.67 ml (13.8×10^{-3} mol) of *o*-hydroxyacetophenone in 50 ml of absolute ethanol. The mixture was heated for 15 min on a steam bath and transferred by filtration into a 50-ml ethanol solution of 6.5 g (33.4×10^{-3} mol) of $MnCl_2 \cdot 4H_2O$. The resulting dark brown solution was aerated for 18 hr at room temperature, by which time the solvent had evaporated. The residue was extracted with 150 ml of acetone, and the filtered solution treated with 700 ml of diethyl ether. The brown solid that formed was isolated on a filter and air-dried. The yield of crude material was 0.75 g, 27% based on ligand.

A portion, 0.40 g, of the crude material was dissolved in 30 ml of H_2O and 1.3 g of sodium chloride was added. The resulting solution was set aside at 4° for 12 hr. The red-brown precipitate was isolated on a filter washed with a little cold water and air-dried. Final drying of the pure product was accomplished by heating at 110° *in vacuo* over P_2O_5 for 12 hr; yield 0.20 g (50%). *Anal.* Calcd for $[Mn(Acetpn)Cl] \cdot H_2O$, $C_{19}H_{20}N_2O_2MnCl \cdot H_2O$: C, 54.74; H, 5.33; N, 6.73. Found: C, 55.39; H. 4.90; N, 6.77. $\mu = 4.82$ BM.

A second portion, 0.30 g, of crude material was dissolved in 20 ml of distilled water and 3.6 g of sodium nitrite was added. The resulting solution was set aside at 4° for 12 hr. The red-brown precipitate was collected on a filter, washed with a little cold water, and air-dried. Final drying of the pure product was accomplished by heating at 110° *in vacuo* over P_2O_5 for 12 hr; yield 0.031 g (10%). *Anal.* Calcd $[Mn(Acetpn)NO_2] \cdot H_2O$, $C_{19}H_{20}N_3O_4Mn \cdot H_2O$: C, 53.40; H, 5.17; N, 9.83. Found: C, 53.88; H, 4.69; N, 9.91. $\mu = 4.85$ BM.

Spectral Measurements. Absorption spectra were recorded on a Cary Model 14 spectrophotometer while CD curves were recorded on a Durham-Jasco ORD/uv/CD/5 instrument. All measurements were made at room temperature. Methanol solution (0.004 g/ml) magnetic moments were determined by the nmr method at 34°,[5] with a 60-MHz spectrometer. The complexes are not sufficiently soluble in chloroform to measure magnetic moments accurately *via* this method.

Results and Discussion

Synthesis and Characterization. The optically active Schiff base was prepared *in situ* by the condensation of the optically active (–)-1,2-propylenediamine and salicylaldehyde or *o*-hydroxyacetophenone. Although less convenient than the method outlined here, the Schiff bases can be isolated and then used to form the metal complexes. The initial rapid reaction of the Schiff base and Mn(II) ion to form the metal chelate is followed by a slower air oxidation to form the Mn(III) chelate. The crude product of the oxidation, which has not been characterized, is converted into the [Mn(SB)X] by crystallization from aqueous solution in the presence of a large excess of the coordinating anion. Ir spectra of the isolated materials show the normal Schiff base

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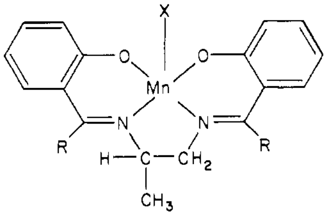

	R	X
Salpn	H	Cl
	H	NO$_2$
Acetpn	CH$_3$	Cl
	CH$_3$	NO$_2$

Figure 1. Structural representation of optically active Schiff base complexes of Mn(III).

ligand absorptions[6] and in the case of the nitro complexes a NO_2^- asymmetric stretching band is seen at 1380 cm^{-1}.

The spectral characteristics, elemental analyses, and other properties of the optically active complexes reported here indicate they are completely analogous to the previously studied *N,N'*-bis(salicylidene)ethylenediaminomanganese(III) complexes.[1,7] The methanol solution magnetic moments are in the range 4.8–5.0 BM. This is consistent with their formulation as high-spin manganese(III) complexes. The [Mn(Salpn)X] stoichiometry is consistent with six-coordinate dimers in the solid state which dissociate in chloroform solution.[1] A likely geometry of five-coordinate complexes is that of a square pyramid[8] with axial anion and Schiff base donor atoms roughly occupying the basal positions. In most cases of this kind the metal atom is above the plane of the basal ligands toward the axial ligand.[8] The presence of difficult to remove water molecules in the crystals of [Mn(Acetpn)XH$_2$O] is consistent with six-coordination and it is reasonable to assume by analogy with other metal complexes of this kind[8] that the water molecule would occupy a coordination position trans to the axial anion. The qualitative discussion of the electronic structure of these materials would be the same for five- or six-coordinate structures since the additional water ligand can be considered as a perturbation on the basic square-pyramidal structure.

Assignment of Spectra. The absorption and circular diochroism spectra of [Mn(Acetpn)XH$_2$O] were determined with chloroform, pyridine, and methanol solutions. Typical spectra are shown in Figures 2 and 3 and the frequency of the spectral maxima are given in Tables I and II. The chloroform solution CD spectra of the Cl$^-$ and NO_2^- complexes show negative bands at 16.7 and 16.4 kK with a shoulder at ~20 kK. The absorption spectrum shows shoulders in the region of the CD bands. Absorptions in the 14–20-kK region have been assigned to the allowed d-d transition.[2] Making the simplifying assumption that the basal donor atoms of the Schiff base contribute an average ligand field, the complexes can be considered as having pseudo-C_{4v} symmetry for five- or six-coordinate structures. The relevant ligand field transitions for the high-spin d^4 ion are $d_{z^2} \rightarrow d_{x^2-y^2}$ (I), $d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$ (II), $d_{xy} \rightarrow d_{x^2-y^2}$ (III) (from lower to higher energy).[9] In view of their similar rotatory strengths (and other considerations discussed below), it is reasonable tentatively to assign the bands at 16.7 and ~20 kK to transitions II and III, respectively. Transition I would then appear at lower energy which was inaccessible to this study. The near-constancy of the energy of the 16.7-kK band in going from the chloride complex to that of the stronger ligand field nitrite ion is consistent with transition

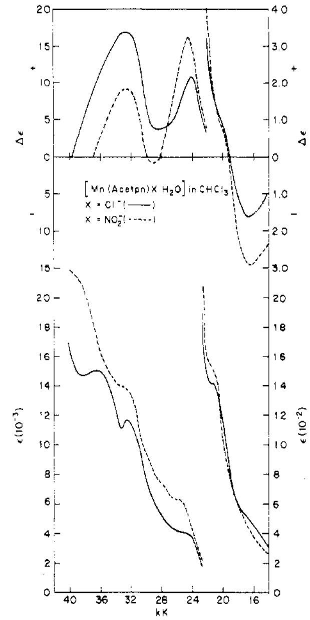

Figure 2. The circular dichroism (top) and absorption spectra (bottom) of [Mn(Acetpn)XH$_2$O] in chloroform.

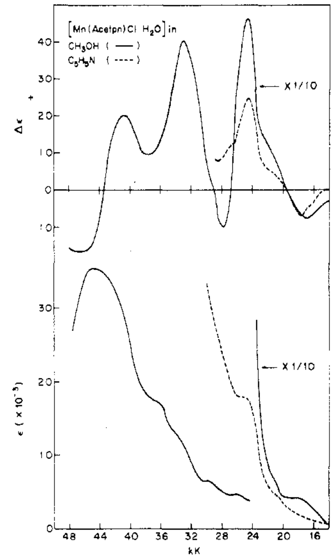

Figure 3. The circular dichroism (top) and absorption spectra (bottom) of [Mn(Acetpn)ClH$_2$O] in methanol and pyridine.

Table I. Absorption and Circular Dichroism Maxima (kK) of [Mn(Acet((–)pn))XH$_2$O] in CHCl$_3$

X$^-$ = Cl$^-$				X$^-$ = NO$_2^-$			
$\bar{\nu}$	log ϵ_{max}	$\bar{\nu}$	$\Delta\epsilon$	$\bar{\nu}$	log ϵ_{max}	$\bar{\nu}$	$\Delta\epsilon$
~16.5	2.6	16.7	−1.62	~16	2.5	16.4	−2.90
~21	3.1	~20	~+0.6	~21	3.1	~20	~+0.8
25.3	3.60	24.3	+10.9	26.0	3.80	24.6	+16.2
~28	3.7			~28	3.9	29.0	−0.8
32.5	4.07	32.8	+17	~33	4.1	32.8	+9
36.5	4.18			~37	4.3		

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Table II. Absorption and Circular Dichroism Maxima (kK) for $[Mn(Acet((-)pn))ClH_2O]$ in Two Solvents

Methanol				Pyridine			
$\bar{\nu}$	log ϵ_{max}	$\bar{\nu}$	$\Delta\epsilon$	$\bar{\nu}$	log ϵ_{max}	$\bar{\nu}$	$\Delta\nu$
18.2	2.60	17.7	−0.70	~17	2.2	17.0	−0.77
~21	2.6	~22	~+0.5	~21	2.2	~22	~−0.5
25.9	3.80	24.8	+4.60	25.3	3.25	24.5	+2.47
~30	3.7	27.8	−0.9				
~34	4.1	33.0	+40				
~36	4.2	40.8	+20				
44.4	4.55	46.5	−16				

II. If the d_{z^2} orbital was involved in the electronic absorption, a substantial shift of the band would be expected. The band at ~20 kK remains unchanged with anion reflecting the nonbonding nature of the d_{xy} orbital in these complexes.

The prominent positive CD band at 24.3 and 24.5 kK for Cl^- and NO_2^- can be assigned to a metal to ligand charge transfer $d_{xz}, d_{yz} \rightarrow \pi^*$ (azomethine).[10] The rotatory strengths of the other charge transfer-bands $d_{z^2} \rightarrow \pi^*$ and $d_{xy} \rightarrow \pi^*$ must be low[10] since no other prominent bands are seen. The fact that the CD band and absorption maxima do not exactly correspond here may be a consequence of the severe overlap of bands in the absorption spectrum and thus this band only appears as a shoulder on a higher energy band. The uv spectrum shows a positive CD band at 32.5 kK which closely corresponds to an absorption maximum. Previous work has led to the assignment of this band to a $\pi \rightarrow \pi^*$ transition of the azomethine linkage.[1,10] The band at 36.5 kK in the absorption spectrum has been assigned to a phenolate to d charge transfer.[10] The CD spectrum only shows an ill-defined shoulder at this frequency.

The spectral data for $[Mn(Acetpn)XH_2O]$ in methanol are identical for $X^- = Cl^-$ or NO_2^-. In the coordinating solvents previous results support the notion that the anion is ionized and the complexes exist as disolvated six-coordinate tetragonal complexes in solution.[11] In methanol solution the CD spectra show two visible features at 17.7 and ~22 kK. In pyridine the bands appear at 17.0 and ~22 kK. According to the scheme presented here the bands can be assigned to transitions II and III, respectively. Increase in coordination interaction along the *z* axis in going from chloroform solution, with Cl^-, to methanol donors should destabilize the d_{z^2} to a small extent. In addition, in a six-coordinate tetragonal structure the metal should be in the plane of the Schiff base donor atoms. The increase in σ interaction should destabilize the $d_{x^2-y^2}$ orbital substantially. Transition III does show the expected change from ~20 to ~22 kK while transition II changes from 16.7 to 17.7 kK. For methanol solutions the positive band at 24.8 kK can be assigned to $d_{xz}, d_{yz} \rightarrow \pi^*$. A positive band at 33.0 kK is assigned to $\pi \rightarrow \pi^*$ of the azomethine linkage. Finally the broad $\pi \rightarrow \pi^*$ absorption band of the phenolate chromophore[10] gives rise to two CD bands of opposite sign at 40.8 and 46.5 kK.

The absorption and circular dichroism of $[Mn(Salpn)Cl]$ and $[Mn(Salpn)NO_2]$ have been measured in chloroform and methanol. The chloroform solution CD spectra show markedly reduced optical activity in comparison to the corresponding $[Mn(Acetpn)XH_2O]$. Accordingly it is difficult to measure the CD spectra accurately for these strongly absorbing solutions and it is not possible to take even qualitative measurements above 28 kK. However, CD maxima can be seen at 15.5, 24.1 kK with $\Delta\epsilon = 0.56$, 4.0 for the NO_2^- complex and 15.4, 23.8 kK with $\Delta\epsilon = 0.36$, 3.0 for the Cl^- complex. Assignment of the two clearly observed bands can be made by analogy with those of $[Mn(Acetpn)XH_2O]$, *i.e.*, the band near 15 kK to transition II and the band near 24 kK to the $d_{xz}, d_{yz} \rightarrow \pi^*$ charge transfer. The red shift, ~1 kK, of the ligand field band for $[Mn(Salpn)X]$ as compared to the $[Mn(Acetpn)XH_2O]$ agrees with the weaker ligand field of the Salpn ligand[3] which results in a stabilization of the $d_{x^2-y^2}$ orbital. The charge-transfer transition shows a red shift of 0.5 kK in going from Acetpn to Salpn. This is a consequence of the expected stabilization of the π^* (azomethine) orbital with change of substituent on the azomethine linkage from CH_3 to H. The CD spectra in methanol show no measurable Cotton effects in the ligand field region. It is possible, however, to observe the $d_{xz}, d_{yz} \rightarrow \pi^*$ charge-transfer band at 24.4 kK with $\Delta\epsilon = 1.5$ in the methanol solution of $[Mn(Salpn)X]$. The absorption maxima for $[Mn(Salpn)X]$ in various solvents have been collected in Table III.

Configuration of Complexes. The complexes reported here are the first optically active Mn(III) complexes examined. Previous work with optically active Schiff base complexes of Ni(II),[10,12] Cu(II),[13] and VO^{2+} [3] has shown that the (−)-1,2-propylenediamine forms a chelate ring in the tetradentate ligand with a gauche conformation. The central chelate ring preferentially forms a δ conformation with the methyl substituent in a pseudoaxial position. The gauche conformation of the central chelate ring causes the Schiff base to adopt a configuration similar to a flattened tetrahedron;[14] *i.e.*, the terminal chelate rings have a skew relationship to one another. With (−)pn and axial methyl the configuration about the metal is Λ. Actually the two configurations $\lambda\Delta \rightleftarrows \delta\Lambda$ are in mobile equilibrium with a preponderance of $\delta\Lambda$ at equilibrium. The amount of the excess of one enantiomer over the other apparently depends on the complexes and the respective ligand substituents. The steric interactions of the (−)pn methyl group and the azomethine substituent, CH_3 *vs.* H, are greater in Acetpn than in Salpn. The steric interactions will favor the (−)pn methyl in an axial position and lead to an increased distortion of the donor atoms and the Schiff base from planarity.[15] The greater the steric interaction, the more one enantiomer is favored over another. This accounts for the fact that the $[Mn(Salpn)X]$ complexes show an appreciably reduced optical activity in comparison to $[Mn(Acetpn)XH_2O]$.

It is interesting to note that the $\pi \rightarrow \pi^*$ transition of the azomethine linkage for $[Mn(Acetpn)XH_2O]$ does not show any exciton splitting, much like that for the corresponding Ni(II) complexes.[10,12] The lack of exciton splitting may be a consequence of a more nearly coplanar distribution of the C=N groups or it may be due to a fortuitous cancelation of one component by other CD bands of opposite sign. The latter does not appear to be the case since the CD band is seen at the frequency of the absorption maxima. The sign of the azomethine CD maximum (positive) for $[Mn(Acetpn)XH_2O]$ is the same as for $[Ni(Acetpn)]$.[12] Since the latter

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Table III. Absorption Maxima (kK) for [Mn(Sal((−)pn))X] in $CHCl_3$ and CH_3OH

$CHCl_3$				CH_3OH	
Cl^-		NO_2^-		Cl^-	
$\bar{\nu}$	log ϵ_{max}	$\bar{\nu}$	log ϵ_{max}	$\bar{\nu}$	log ϵ_{max}
~15	2.2	~15	2.4	~17	2.4
~20	2.5	~20	2.5	~21	2.9
24.6	3.62	24.0	3.64	25.2	3.71
~28	3.7	~28	3.7	~29	3.8
31.7	4.12	31.9	4.15	~33	4.1
~36	4.2	~36	4.2	35.6	4.24
				42.4	4.59

complex has been assigned to a Λ configuration,[12] it is reasonable to assign the same configuration to the Mn(III) complexes. This agrees nicely with the analysis concerning the δ conformation of (−)pn which imposes a Λ configuration on the metal. Finally it appears that the $\pi \rightarrow \pi^*$ phenolate) transition of the Schiff base which is broad and asymmetric in the methanol absorption spectrum gives rise to two CD bands of opposite sign and approximately equal rotatory power which flank the absorption frequency. This may be a consequence of exciton splitting of the type suggested by Bosnich.[10] In fact, the low-energy positive component and high-energy negative component are consistent with a Λ chirality.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No. [Mn(Acet((−)pn))ClH$_2$O], 50859-29-5; [Mn(Acet((−)pn))(NO$_2$)H$_2$O], 50859-30-8; [Mn(Acet((−)pn))(MeOH)$_2$]Cl, 50859-31-9; [Mn(Acet((−)pn))(Py)$_2$]Cl, 50859-32-0; [Mn(Sal((−)pn))Cl], 50859-37-5; [Mn(Sal((−)pn))(NO$_2$)], 50859-38-6.

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The Coordination Behavior of the *N*-Hydroxyethyliminodiacetate Ion

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Received July 11, 1973 AIC30523E

Several cobalt(III) complexes of the *N*-hydroxyethyliminodiacetate ion ("heida") have been prepared. Infrared and nmr studies, as well as exchange studies with D_2O, show that the ligand tends to be tridentate and that the alcoholic hydroxyl group does not coordinate. Moreover, the alcoholic group in the complex can be acetylated without destruction of the complex. However, in [Co(en)(heida)]^0, the alcoholic OH loses its proton, and the ligand becomes trinegative and tetradentate.

The behavior of the >NCH$_2$CH$_2$OH group in molecules in which the nitrogen atom is part of a strongly chelated group has been the subject of several studies. Two ligands containing the >NCH$_2$CH$_2$OH group have received particular attention, *N*-hydroxyethylethylenediamine (etolenH) and the hydroxyethyliminodiacetate ion (heida). Keller and Edwards[2a] reported that the alcoholic hydroxyl group in the [Co(etolenH)$_3$]$^{3+}$ ion does not react with thionyl chloride, sulfonyl chloride, phosphorus trichloride, or phosphorus pentachloride. Drinkard, Bauer, and Bailar[2b] confirmed this result and advanced the hypothesis that the lack of reactivity is due to the positive charge of the complex ion and to hydrogen bonding. Later work has shown that while etolenH can coordinate through just its two nitrogen atoms, it frequently acts as a tridentate ligand, attaching itself to the metal through the hydroxyl oxygen atom as well as through the two nitrogen atoms.[3] When the alcoholic hydroxyl group is coordinated, its acidity is greatly increased and the proton may be lost. This is illustrated by the preparation of [Co(etolen)$_2$]I[3] and [Co(etolen)$_2$][Cr(NH$_3$)$_2$(NCS)$_4$]·2H$_2$O.[4,5]

The present work is concerned with the coordination behavior of the ligand "heida." Krause and Goldby[6] studied the behavior of the Cr(III) complex of this ligand, which they formulated as [Cr(heida)$_2$]$^-$, in which heida acts as a dinegative tridentate ligand, leaving the hydroxyl group uncoordinated. This structure is supported by the work of Krause,[7] who found that the potassium salt of this complex shows asymmetric carboxyl stretching frequencies at 1650 and 1630 cm^{-1} and bands at 3380 and 3300 cm^{-1}, which are characteristic of the uncoordinated hydroxyl group. Krause and Goldby[6] found that this chromium complex is strongly resistant to acetylation by most agents that normally acetylate primary alcohols. Nicpon[8] prepared the corresponding cobalt(III) complex and found it to be quite unreactive toward acetylation. Thus, a similar lack of reactivity of the uncoordinated hydroxylethyl group is apparent in both etolenH and heida and in both cationic and anionic complexes.

Furthermore, titration studies[9,10] of heida complexes have indicated that this ligand, like etolenH, can lose its hydroxyl proton. It thus becomes a tetradentate ligand.

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