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.

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Registry No. $[Mn(Acet((-)pn))ClH_2O]$, 50859-29-5; $[Mn(Acet((-)pn))(NO_2)H_2O]$, 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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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 $>NCH_2CH_2OH$ 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 $>NCH_2CH_2OH$ 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 $[Co(etolen)_2][Cr(NH_3)_2(NCS)_4]\cdot 2H_2O$.[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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[1] (a) Southern Connecticut State College; (b) University of Illinois.

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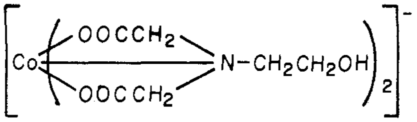
However, no solid products containing tetradentate heida were isolated.

Vieles and Seguin[11] isolated the copper and lead salts, $[Cu(heida)]\cdot 2H_2O$ and $[Pb(heida)]$, but evidently did not study either their structures or reactivity.

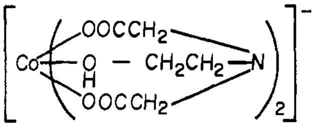
In this paper, we report a definitive examination of the coordination and reactivity of heida in cobalt(III) complexes. It was found that, as with the etolenH complexes, the hydroxyethyl group can take part in coordination or it can remain unattached. However, unlike etolenH complexes and in contrast to previous reports, the hydroxyethyl group was *not* found to be unreactive.

Results and Discussion

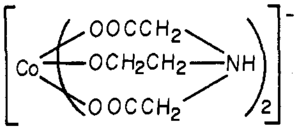
In the cobalt(III) complexes containing heida as the only ligand, the ligand tends to fill the six coordination positions by acting as a tridentate ligand, leaving one potential donor atom of each heida group unattached. Conceivably, this could be accomplished by three different arrangements,[5] I-III. There is also the possibility that the nitrogen and the hydroxy oxygen atoms are coordinated to the cobalt and that one carboxyl group remains free. This was not studied experimentally in this work, for it has been well established that the carboxyl group is a much stronger ligand than is the hydroxyl group.



I



II



III

Structures II and III are rejected, and structure I confirmed, by the results of an ir study of the deuterated and nondeuterated forms of $K[Co(heida)_2]$. The deuterated form was prepared by crystallizing $K[Co(heida)_2]$ several times from D_2O.

It was found that the free ligand (H_2heida) shows -OH stretching frequencies located at 3125 and 3245 cm^{-1} (broad) and -OD stretching frequencies at 2320 and 2395 cm^{-1}. The hydroxyl group as well as the acidic protons of the carboxyl groups exchanged protons during recrystallization from D_2O. Upon deuteration, the C=O stretching frequency at 1690 cm^{-1} shown by the free heida shifted to 1675 cm^{-1} (broad sh), but the one at 1725 cm^{-1} remained unchanged.

The same behavior was shown for $K[Co(heida)_2]$. The OH stretching frequencies located at 3310 and 3400 cm^{-1} were unequivocally identified by comparing the ir spectrum of the hydrated complex to that of a partially dehydrated sample. These bands are shifted to 2450 and 2510 cm^{-1} upon deuteration, indicating that the hydroxyl groups are protonated in the solid state and, due to the high energy vibrations they exhibit, it is unlikely that the oxygens of the hydroxyl groups are coordinated to cobalt. If they were coordinated, the protons would be more acidic and would exhibit lower energy -OH stretching frequencies. The positions of the C=O stretching frequencies (1640 and 1660 cm^{-1}) are indicative of coordination of the carboxyl groups. They are unaffected by deuteration of $K[Co(heida)_2]$.

Chemical confirmation of these results, which show the hydroxyethyl group to be uncoordinated, arises from the fact that the hydroxyl groups are readily acetylated in acetic acid and acetic anhydride (see the Experimental Section). This result is in direct contrast to those of previous investigators.[6,8]

The nmr spectrum of $K[Co(heida)_2]$ in D_2O at 5° is compatible with the proposed structure, giving an AB quartet centered at 4.1 ppm downfield from TMS, superimposed on an A_2B_2 set of triplets centered at 3.9 ppm.

If the complex $K[Co(heida)_2]$ is passed through an acidified cation exchange resin, the neutral Co(III) complex $[Co(Hheida)(heida)(H_2O)]\cdot H_2O$ is obtained. By analogy with $[Co(hedta)H_2O]^0$, it is thought that one acetate arm is protonated and replaced in the coordination sphere by water. Neutralization of this complex causes the $[Co(heida)_2]^-$ ion to form again. Titration of $K[Co(heida)_2]$ in aqueous solution does not reveal a pH break which can be attributed to the alcoholic protons. However, a gradual, reversible color change from blue-violet to purple is observed at about pH 12.

The slight acidity of the alcoholic proton of coordinated heida inferred by the above results was definitively shown by the preparation of $[Co(en)(heida)]^0$ (en = ethylenediamine). In this complex, heida serves as a trinegative, tetracoordinate ligand, with the hydroxyl group deprotonated and bound to cobalt. This proposed structure is supported by analysis of the ir spectrum of $[Co(en)(heida)]$, in which there were found to be no -OH stretching frequencies. The vibrational frequencies in the 3100 to 3500 cm^{-1} range are characteristic of N-H stretching of ethylenediamine, as shown by comparison with $K[Co(en)(CO_3)_2]$. The N-H stretching frequencies in $[Co(en)(heida)]$ at 3170, 3250, 3290, 3460, and 3500 cm^{-1} are nearly identical with those of $K[Co(en)(CO_3)_2]$ at 3170, 3250, 3280, 3460, and 3480 cm^{-1}. The carbonyl stretching frequencies at 1640 and 1660 cm^{-1} on $[Co(en)(heida)]$ and $K[Co(heida)_2]$ are the same.

The complex as prepared is a monohydrate, which loses its water of hydration upon desiccation at 110°. On reexposure to air, the complex regains the molecule of water. This process could conceivably involve the protonation of the hydroxyl group and the insertion of a hydroxide ion in the coordination sphere, or it could be simple association of water with the complex. Both ir and nmr techniques were incapable of distinguishing the possibilities.

Experimental Section

Infrared spectra were taken on a Perkin-Elmer Model 21 spectrometer (sodium chloride optics) and a Perkin-Elmer Model 237B spectrophotometer (grating optics) using Nujol mulls.

Elemental analyses were performed by Mr. Josef Nemeth and his staff in the Microanalytical Laboratory of the University of Illinois.

Nmr spectra were taken on two instruments: a Varian A60 and a Perkin-Elmer Hitachi R20A nmr spectrometer equipped with a variable temperature probe.

Preparation of $Na[Co(heida)_2]\cdot H_2O$. A slurry of 3.62 g (0.01 mol) of $Na_3[Co(CO_3)_3]\cdot 3H_2O$[12] in 100 ml of water was treated with 3.54 g (0.02 mol) of H_2heida. When effervescence ceased, 10 ml of 6 *N* HNO_3 was added, and the solution was warmed on a steam bath for 30 min. It was then concentrated to one-half of its volume by evaporation under vacuum and cooled in an ice bath. The purple crystals which formed were removed and a second crop was obtained by further evaporation. The two crops were combined, recrystallized

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from water, and dried at 100°. *Anal.* Calcd for $CoC_{12}H_{20}N_2O_{11}Na$: C, 32.00; H, 4.40; N, 6.22. Found: C, 31.63; H, 4.30; N, 6.30.

Preparation of $K[Co(heida)_2]\cdot H_2O$. Addition of $AgNO_3$ to an aqueous solution of $Na[Co(heida)_2]\cdot H_2O$ caused precepitation of the silver salt, $Ag[Co(heida)_2]$. The solid silver salt was collected, washed with H_2O and EtOH, and dried in air. Trituration of the silver salt with potassium iodide (KI) and extraction into water solution gave the potassium salt, which was obtained by volume reduction of the solution. *Anal.* Calcd for $CoC_{12}H_{20}N_2O_{11}K$: C, 30.90; H, 4.32. Found: C, 31.41; H, 4.21.

Preparation of $[Co(en)(heida)]\cdot H_2O$. The "blue form" of $K[Co(en)(CO_3)_2]\cdot H_2O$ was prepared from $K_3[Co(CO_3)_3]$ and $en\cdot H_2CO_3$ as described by Mori, *et al.*[13] To 100 ml of methanol was added 6 g of the "blue form" of $K[Co(en)(CO_3)_2]\cdot H_2O$ and 3.5 g of 1-hydroxyethyliminodiacetic acid (H_2heida), and the mixture was refluxed until the solids had dissolved (45 min). During the refluxing period, the color of the solution changed from blue to reddish purple. The solution was evaporated to 40 ml on a steam bath in a stream of air. A purple precipitate was filtered from the solution, washed with several portions of methanol, then with ether, and air dried; yield, 3 g, 50%. The compound is soluble in H_2O and in acidified methanol. The complex is unstable in hot H_2O, forming $[Co(en)_3]^{3+}$ and $[Co(heida)_2]^-$. *Anal.* Calcd for $CoC_8N_3H_{16}O_5\cdot H_2O$: Co, 18.94; C, 30.88; H, 5.83; N, 13.50; H_2O, 5.79. Found: Co, 18.86; C, 30.90; H, 5.61; N, 13.24; H_2O, 6.0. Water was determined by weight loss after drying for 12 hr at 110° *in vacuo*. *Anal.* Calcd for $CoC_8N_3H_{16}O_5$: C, 32.78; H, 5.50; N, 14.33. Found: C, 32.59; H, 5.69; N, 14.54.

Preparation of $[Co(Hheida)(H_2O)]^0\cdot H_2O$. A solution of 1 g of $Na[Co(heida)_2]$ in 50 ml of water was passed through a column packed with 10 g of Dowex 50W-X8 cation exchange resin in the acid form, washed through the column, and concentrated to a volume of approximately 10 ml. The purple crystals which precipitated when the solution was cooled in ice were filtered and dried at 100°. *Anal.* Calcd for $CoC_{12}H_{23}N_2O_{12}$: C, 32.29; H, 5.16; N, 6.30; Co, 13.20. Found: C, 32.30; H, 5.31; N, 6.39; Co, 13.26.

Preparation of $K[Co(CH_3COOCH_2CH_2N(CH_2COO)_2)_2]$. The acetyl derivative of $K[Co(heida)_2]$ was prepared by refluxing 50 ml of glacial acetic acid, 75 ml of acetic anhydride, and 1 g of $K[Co(heida)_2]$ for 2.5 hr. The solution turned from purple to brown. This solution was filtered to remove excess starting material and evaporated to dryness. The brown product obtained was washed with methanol three times and dried in air. It was recrystallized from water and dried at room temperature under vacuum. *Anal.* Calcd for $CoC_{16}H_{22}N_2O_{12}K$: C, 36.09; H, 4.16. Found: C, 36.25, 36.36; H, 4.07, 4.10. The compound showed carbonyl bands at 1725 (acetyl carbonyl) and 1640 cm^{-1} (coordinated carbonyl) and no hydroxyl band.

Acknowledgment. The authors are greatly indebted to Dr. James R. Barrante, for running and interpreting the nmr spectra, and to the Mobil Research and Development Co. Inc., for financial aid.

Registry No. $Na[Co(heida)_2]$, 50601-02-0; $K[Co(heida)_2]$, 50601-03-1; [Co(en)(heida)], 50601-04-2; $[Co(Hheida)(heida)(H_2O)]$, 50790-63-1; $K[Co(CH_3COOCH_2CH_2N(CH_2COO)_2)_2]$, 50601-05-3.

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Characterization of Two Structural Isomers of a Cobalt(III) Complex with an Ethylenediamine-*N,N',N'*-triacetate-Type Ligand

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Two isomers of the complex $K[Co((R)\text{-}(-)\text{-PD3A})NO_2]$ (PD3A = 1,2-propanediaminetriacetate) have been isolated and characterized. The red isomer has the same visible absorption spectrum as the nitro complexes formed with several N-substituted ethylenediaminetriacetate ligands, and is designated *cis equatorial*. The purple isomer has been shown by infrared, visible absorption, circular dichroism (CD), and proton magnetic resonance spectra to have *trans equatorial* geometry. The change in the position of the acetate ring attached to the secondary nitrogen in the two isomers results in significant changes in the CD and pmr spectra. The CD spectra of these complexes support previous work which indicates that the asymmetric nitrogen donor atom is the major source of optical activity in complexes of this type.

Introduction

Several cobalt(III) complexes containing pentadentate N-substituted ethylenediamine-*N,N',N'*-triacetate ligands and a nitro group in the sixth position have been prepared and studied thoroughly using circular dichroism and proton magnetic resonance spectroscopy.[1-3] Three structural isomers (Figure 1) of these compounds are possible. These isomers have been designated[3] as *equatorial* if the NO_2 group lies in the plane formed by the metal and the two other coordinated nitrogen atoms or as *polar* if the NO_2 group does not lie in this plane. Two equatorial isomers can form. For one, the two acetate groups on the tertiary nitrogen are coordinated *cis* to one another and in the other, they are coordinated *trans* to one another. Because the *polar* isomer can form only when the acetates are coordinated in *cis* positions, the three possible isomers can be designated *cis equatorial, trans equatorial,* and *cis polar*.

The X-ray structural data[4] for $[Co(EDTA)]^-$ indicated the two acetate rings planar with the ethylenediamine ring, the G rings, are more strained than the out-of-plane acetate rings, the R rings. Thus the favored isomer with an ethylenediamine-*N,N',N'*-triacetate ligand has been assumed to be the

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