certainly happen on Ru metal particles.

## Conclusion

The first step of the reaction between $Ru_3(CO)_{12}$ and partially or fully hydroxylated magnesia is the formation of the hydrido anionic cluster $[HRu_3(CO)_{11}]^-$. In solution, this anionic cluster has been obtained by reaction of $Ru_3(CO)_{12}$ with a methanolic solution of KOH.[31] On the surfaces of magnesia and zinc and lanthanum oxides, $[HRu_3(CO)_{11}]^-$ probably results from the nucleophilic attack at coordinated CO by the basic OH groups of the surface; concomitant $CO_2$ evolution could not be observed due to adsorption of $CO_2$ as carbonates onto magnesia.

This behavior compares with the one observed in the case of $Fe_3(CO)_{12}$ on the surface of alumina or magnesia, for which the formation of $[HFe_3(CO)_{11}]^-$ had been evidenced.[17] Nevertheless, some differences deserve to be noticed. On alumina, $[HFe_3(CO)_{11}]^-$ is in strong interaction with the surface Lewis acid sites $Al^{3+}$, through a kind of tight ion pairing, as evidenced by the large shift of the bridging $\nu$(CO) band to lower frequency. In the case of $[HRu_3(CO)_{11}]^-$ on magnesia, such an interaction does not seem to occur: the $\nu$(CO) frequency in the bridging region is close to the values observed in solution with $[PPN]^+$ as counterion (Table I), where no tight ion pairing is existing, and far from the values reported for $[HRu_3(CO)_{11}]^-Li^+$ ($\nu$(CO) 1653 $cm^{-1}$).[40] The reason that such a type of interaction is not observed is not yet clear. However, the surface $Mg^{2+}$ sites of magnesia are weaker Lewis acids[32] than the $Al^{3+}$ of alumina.

The anionic cluster $[HRu_3(CO)_{11}]^-$ is stable under vacuum on the surface of magnesia up to temperatures of ca. 100 °C. Above this temperature, the trinuclear anion is mainly transformed into small metal particles and to a smaller extent into oxidized ruthenium (Ru(II)).

A kind of equilibrium seems to exist between ruthenium(0) and ruthenium(II) due to a redox process involving surface protons and gaseous hydrogen (eq 4 above). Under vacuum this equilibrium is shifted to the right whereas in static experiments this equilibrium is in favor of zerovalent ruthenium.

Various kinds of reactions are observed with the carbon monoxide issued from the carbonyl ligands of the cluster:

(i) A water gas shift reaction that is probably catalyzed by the cluster itself is observed although we have no proof in favor of such a conclusion. The fact that $[1]^-$ and $Ru(CO)_2(OMg<)_2$, as well as ruthenium metal, coexist at not too different temperatures on the surface makes a clear conclusion difficult.

(ii) A CO methanation reaction is observed on the three types of magnesia. It should be noticed that on magnesia-200 a very high percentage of the carbonyls of the cluster (ca. 6 among 12) are transformed into methane. The hydrogen is obviously coming from the water of the support (and therefore from the water gas shift reaction) since on magnesia-500 almost no methane is formed.

(iii) A CO disproportionation to gaseous $CO_2$ and surface C is also evidenced clearly from mass balance studies, especially on magnesia-500. It is very likely that a methanation reaction as well as CO disproportionation is occurring on the small metal particles of ruthenium that have been detected by electron microscopy.

All these observations indicate that great care must be taken before any conclusion is made regarding catalytic properties of supported molecular clusters. We have shown that at least three types of different species can coexist at the surface of magnesia after and/or during thermal decomposition of $[HRu_3(CO)_{11}]^-(Mg^{2+})_{1/2}$: the anion $[1]^-$ itself, mononuclear $Ru^{II}(CO)_2(OMg<)_2$, and ruthenium metal particles.

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**Registry No.** $Ru_3(CO)_{12}$, 15243-33-1; $HRu_3(CO)_{11}^-$, 60496-59-5; MgO, 1309-48-4; ZnO, 1314-13-2; $La_2O_3$, 1312-81-8.

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# Synthesis and Characterization of Hexadentate Cobalt(III) Complexes with Novel edta-Type Ligands. 1. Circular Dichroism of a Cobalt(III) Complex of Ethylenediamine-*N*-acetic-*N*,*N'*,*N'*-tri-3-propionic Acid

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The trans($O_5O_6$) geometrical isomer of the cobalt(III) complex of ethylenediamine-*N*-acetic-*N*,*N'*,*N'*-tri-3-propionic acid ($H_4$eda3p) has been prepared and resolved. More complete resolution of the previously reported $[Co(edtp)]^-$ complex (edtp = ethylenediaminetetra-3-propionate) has been achieved. The $^1H$ NMR, electronic absorption, and circular dichroism (CD) spectra were used to characterize the Co(III) complexes. The $(+)_{546}$-*trans*($O_5O_6$)-$[Co(eda3p)]^-$ complex with a positive CD peak at lowest energy in the first spin-allowed d–d absorption band region is tentatively assigned the Λ absolute configuration.

## Introduction

The spectral data and structural parameters of the $[Co(edta)]^-$ complex (edta = ethylenediaminetetraacetate) are available.[2,3] This system, having a five-membered diamine backbone ring (E ring) and two different pairs of glycinate rings (G rings in equatorial positions and R rings in axial positions), was found to be strained.[3] This strain is manifested more in the girdle plane (the plane of two G rings) than in the glycinate rings lying outside of this plane (R rings). Similar structural data should be expected in the directly related $[Co(S\text{-pdta})]^-$ and $[Co(S,S\text{-cydta})]^-$ complexes[4,5] containing only five-membered rings (*S*-pdta = (*S*)-1,2-propanediaminetetraacetate; *S*,*S*-cydta = (1*S*,2*S*)-1,2-*trans*-cyclohexanediaminetetraacetate). Model complexes that are less strained than $[Co(edta)]^-$ contain ligands that are structurally similar to edta but have longer diamine backbone or carboxylate chains. Complexes such as $[Co(1,3\text{-pdta})]^{-}$[6,7] and

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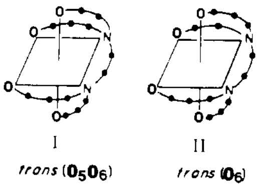

**Figure 1.** Two possible geometrical isomers of Λ-$[Co(eda3p)]^-$.

$[Co(S,S\text{-ptnta})]^{-}$[8] (1,3-pdta = 1,3-propanediaminetetraacetate; *S,S*-ptnta = (2*S*,4*S*)-2,4-pentanediaminetetraacetate) represent hexadentates with a six-membered diamine backbone ring. In these systems, with respect to $[Co(edta)]^-$,[3] the strain in the girdle plane is eased as shown in the crystal structure[7] of $[Co(1,3\text{-pdta})]^-$.

Complexes structurally related to $[Co(edta)]^-$ are of interest in the study of factors contributing to their optical activity. Because of that interest, ligands that are similar to edta but have various structural changes in the carboxylate arms have been studied and the CD spectra of their Co(III) complexes discussed.[6,9-13] Such ligands are as follows: ethylenediamine-*N*,*N'*-diacetate-*N*,*N'*-di-3-propionate, eddadp;[9,10] (2*S*,2'*S*)-ethylenediamine-*N*,*N'*-disuccinate, *S*,*S*-edds;[11] (2'*S*)-ethylenediamine-*N*,*N*-diacetate-*N'*-succinate, *S*-eddams;[12] ethylenediaminetetra-3-propionate, edtp.[6] For these ligands, having mixed (five- and six-membered) carboxylate arms (the eddadp, *S*,*S*-edds, and *S*-eddams ligands), geometrical isomers that differ in the number (0, 1, or 2) of six-membered rings lying in the girdle plane are possible. It was found that the eddadp, *S*,*S*-edds, and *S*-eddams ligands preferentially form isomers having six-membered rings in the G plane[9-13] to minimize strain.

Since the contribution to optical activity due to the asymmetric nitrogen or carbon atoms in these systems is small,[13] the chiral contribution of the chelate rings for $[Co(edta\text{-}type)]^-$ complexes strongly depends on both their relative size[12] and their disposition about an octahedron. The relative contributions of the carboxylate chelate rings could be clarified if the CD spectra of a complete series of related complexes, going from $[Co(edta)]^-$ to $[Co(edtp)]^-$, could be measured. This question requires the preparation of novel hexadentate edta-type ligands and the corresponding Co(III) complexes.

This paper deals with the preparation of ethylenediamine-*N*-acetic-*N*,*N'*,*N'*-tri-3-propionic acid ($H_4eda3p$) and the corresponding Co(III) complex. This unsymmetrical edta-type ligand, on hexadentate coordination, forms two five-membered and three six-membered chelate rings and two geometrical isomers, differing in the number (2 or 1) of six-membered rings in the girdle plane: trans($O_5O_6$) (I) and trans($O_6$) (II) (Figure 1). Only one, the trans($O_5O_6$) geometrical isomer, has been prepared and resolved. Additionally, the earlier reported $[Co(edtp)]^-$ complex[6] has also been prepared and its more complete resolution achieved for direct comparison. The $^1H$ NMR, electronic absorption, and CD spectra were used to characterize the complexes.

## Experimental Section

Ethylenediamine-*N*-acetic acid dihydrochloride dihydrate (Hedma·2HCl·$2H_2O$) was prepared by using a previously described procedure.[14] Other commercially obtained reagent-grade chemicals were used without further purification.

Optical isomers are identified by (+) or (−), corresponding to the sign of the lowest energy CD band, or by the sign of the optical rotation at a wavelength λ ($(+)_\lambda$ or $(-)_\lambda$). The chirality is designated as Δ or Λ according to IUPAC rules.[15]

**Preparation of Ethylenediamine-*N*-acetic-*N*,*N'*,*N'*-tri-3-propionic Acid, $H_4$eda3p.** Ethylenediamine-*N*-acetic acid dihydrochloride dihydrate (Hedma·2HCl·$2H_2O$; 45.41 g, 0.2000 mol) was dissolved in 60 mL of water, and NaOH (24.0 g, 0.600 mol in 50 mL of water) was added (solution I). 3-Chloropropionic acid (75.96 g, 0.7000 mol) was dissolved in 80 mL of water and cooled in an ice bath. A cooled solution of NaOH (28.0 g, 0.700 mol) in 70 mL of water was added dropwise, the rate of addition being adjusted so that the temperature remained below 20 °C (solution II). Solutions I and II were mixed, and the reaction mixture was refluxed at 55–60 °C with stirring for 6 h. During this process, an additional amount of NaOH (24.0 g, 0.600 mol in 60 mL of water) was added dropwise to keep the pH in the range 7–8. The volume of the resulting solution was reduced on a steam bath to 80 mL, and the deposited NaCl was separated by filtration. The mixture was neutralized with 100 mL of 12 M hydrochloric acid (pH ~1), cooled to room temperature, and allowed to stand in the refrigerator overnight. A white precipitate that formed was filtered, washed with a small amount of ethanol and then ether, and air-dried (55 g). The solution obtained by heating the white precipitate in 150 mL of water was neutralized slowly by adding aqueous NaOH until the pH was adjusted to 3.6. After the mixture stood in a refrigerator for several days, the white precipitate formed was collected by filtration, washed with ethanol and then ether, and air-dried (22 g). This product gave a negative test for $Cl^-$ and represents a mixture of two acids ($H_4$edtp and $H_4$eda3p, ca. 2.5:1). The mixture was fractionally crystallized from water to obtain a sample of pure $H_4$eda3p (ca. 0.6 g). Anal. Calcd for $H_4$eda3p, $C_{13}H_{22}N_2O_8$ ($M_r$ = 334.33): C, 46.70; H, 6.63; N, 8.37. Found: C, 47.02; H, 6.68; N, 8.64.

**Preparation and Separation of Complexes. Potassium (Ethylenediaminetetrapropionato)cobaltate(III) Octahydrate, K[Co(edtp)]·$8H_2O$, and the Trans($O_5O_6$) Geometrical Isomer of Potassium (Ethylenediamine-*N*-acetato-*N*,*N'*,*N'*-tri-3-propionato)cobaltate(III) Trihydrate, K[Co(eda3p)]·$3H_2O$.** Because of the difficulty in the separation of acids, the mixture of acids ($H_4$edtp + $H_4$eda3p) was used for the preparation of the complexes. $Co(OH)_3$,[16] freshly prepared from 5.82 g (0.0200 mol) of $Co(NO_3)_2·6H_2O$, was filtered, washed, and then added to the solution obtained by dissolving 6.70 g (~0.0200 mol) of the mixture of acids and 1.12 g (0.0200 mol) of KOH in 80 mL of water. The temperature of this solution was increased to 80 °C with stirring for 2 h. The volume of the solution was reduced to ca. 50 mL, which was then maintained by periodic addition of hot water. The resulting blue-violet solution was poured into a 5 × 60 cm column containing Dowex 1-X8 (200–400 mesh) anion-exchange resin in the $Cl^-$ form. The column was then washed with $H_2O$ and eluted with 0.1 M KCl (ca. 0.5 mL/min). Two blue-violet bands were obtained (ca. 3:1), in addition to a third (violet). The violet product formed in a very small amount was not characterized but probably represents the second isomer (trans($O_6$)) of the eda3p complex. The first and second eluates were evaporated to 10 mL and desalted by passage through a G-10 Sephadex column, with distilled water as the eluent. Each eluate was concentrated to a volume of 3 mL and stored in a desiccator over methanol for several days. The blue crystals were collected, washed with methanol and then ether, and air-dried; yield 5 g of K[Co(edtp)]·$8H_2O$[6] (the first band) and 2 g of *trans*($O_5O_6$)-K[Co(eda3p)]·$3H_2O$ (the second band). The substances for elemental microanalyses were dried in a desiccator over $ClCl_2$. The crystals of K[Co(edtp)]·$8H_2O$ lost five waters of crystallization. Anal. Calcd for K[Co(edtp)]·$3H_2O$, $KCoC_{14}H_{26}N_2O_{11}$ ($M_r$ = 496.40): C, 33.87, H, 5.28; N, 5.64. Found: C, 33.27; H, 5.22; N, 5.80. Calcd for *trans*($O_5O_6$)-K[Co(eda3p)]·$3H_2O$, $KCoC_{13}H_{24}N_2O_{11}$ ($M_r$ = 482.36): C, 32.37; H, 5.01; N, 5.80. Found: C, 32.78; H, 4.94; N, 6.29.

**Resolution of Potassium (Ethylenediaminetetrapropionato)cobaltate(III) Trihydrate, K[Co(edtp)]·$3H_2O$.** In the reported resolution[6] of $[Co(edtp)]^-$ the solid enantiomer was not isolated. A solution of the enantiomer was obtained by precipitation of the resolving agent. More complete resolution and isolation of Li[Co(edtp)]·$3H_2O$ was achieved by the following procedure.

Silver acetate (0.417 g, 0.0025 mol) and $(-)_{589}$-$[Co(en)_2(ox)]Br·H_2O$ (0.91 g, 0.0025 mol) were stirred together at 60 °C for 20 min in 10 mL of water. AgBr was removed by filtration and washed with 2 mL of water. The combined filtrate and washing was added to the solution obtained by dissolving 2.48 g (0.005 00 mol) of K[Co(edtp)]·$3H_2O$ in 5 mL of water. About 10 mL of ethanol was added to the solution, the beaker containing the solution was scratched to induce crystallization, and the solution was left in the refrigerator overnight. The less soluble diastereoisomer, $(-)_{589}$-$[Co(en)_2(ox)]$-$(-)_{546}$-$[Co(edtp)]·xH_2O$, was filtered off, washed with ethanol and then ether, and air-dried (1.5 g). The

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diastereoisomer was crystallized from a water–ethanol (1:2) mixture to constant optical rotation. An aqueous solution (0.05%) gave $[\alpha]_{589}$ = +740° and $[\alpha]_{546}$ = −1120°. The corresponding enantiomer in the form of the lithium salt was obtained by dissolving the diastereoisomer in water and passing the solution through a cation-exchange column in the $Li^+$ form. The eluate was evaporated to a volume of 4 mL, and the enantiomer was crystallized after addition of ca. 8 mL of ethanol and cooling in a refrigerator overnight. The blue crystals were collected, washed with ethanol, and air-dried. The opposite enantiomer was obtained by the same procedure using $(+)_{589}$-$[Co(en)_2(ox)]I$ as the resolving agent. Aqueous solutions (0.05%) gave: $[\alpha]_{589} = \pm 1800°$; $[\alpha]_{546} = \mp 1150°$. Anal. Calcd for $(-)_{546}$-$Li[Co(edtp)]\cdot 3H_2O = LiCoC_{14}H_{26}N_2O_{11}$ ($M_r$ = 464.24): C, 36.22; H, 5.64; N, 6.03. Found: C, 36.04; H, 5.79; N, 6.30.

**Resolution of the Trans($O_5O_6$) Geometrical Isomer of Potassium (Ethylenediamine-*N*-acetato-*N*,*N'*,*N'*-tri-3-propionato)cobaltate(III) Trihydrate, *trans*($O_5O_6$)-K[Co(eda3p)]·3$H_2O$.** Silver acetate (0.167 g, 0.001 00 mol) and $(-)_{589}$-$[Co(en)_2(ox)]Br\cdot H_2O$ (0.37 g, 0.001 00 mol) were stirred together at 60 °C for 20 min in 10 mL of water. The AgBr was removed by filtration and washed with 2 mL of warm water. The wash was added to the filtrate, to which solid *trans*($O_5O_6$)-K[Co(eda3p)]·$3H_2O$ (0.482 g, 0.001 mol) was then added at room temperature with stirring. The resulting solution was evaporated to 10 mL, the same volume of ethanol was then added, and the mixture was left to stand at room temperature for 3 h. The less soluble diastereoisomer, $(-)_{589}$-$[Co(en)_2ox]$-$(+)_{546}$-$[Co(eda3p)]\cdot xH_2O$, was removed by filtration, washed with a small amount of ethanol and then ether, and air-dried (0.3 g). From the remaining filtrate, after it stood overnight in a refrigerator, the more soluble diastereoisomer, $(-)_{589}$-$[Co(en)_2(ox)]$-$(-)_{546}$-$[Co(eda3p)]\cdot xH_2O$, crystallized. The precipitate was collected and washed with ethanol and ether (yield 0.28 g). Both diastereoisomers were crystallized from a water–ethanol (1:1) mixture to constant values of optical rotation. Aqueous solutions (0.05%) gave $[\alpha]_{589}$ = −1750°, $[\alpha]_{546}$ = −220° and $[\alpha]_{589}$ = +650°, $[\alpha]_{546}$ = −740° for the less and more soluble diastereoisomers, respectively. The optical isomers in the form of the potassium salts were obtained by using the ion-exchange column technique. The eluates were evaporated to a small amount and then to dryness after standing in a desiccator over $CaCl_2$: $[\alpha]_{589} = \mp 1790°$, $[\alpha]_{546} = \pm 424°$ in 0.05% aqueous solution. Anal. Calcd for $(+)_{546}$-*trans*($O_5O_6$)-K[Co(eda3p)]·$3H_2O$, $KCoC_{13}H_{24}N_2O_{11}$ ($M_r$ = 482.36): C, 32.37; H, 5.01; N, 5.80. Found: C, 32.90; H, 5.47; N, 6.18.

**Physical Measurements.** The $[\alpha]_\lambda$ values were measured in a 1-dm tube at 20 °C on a Perkin-Elmer SP polarimeter.

The electronic absorption spectra were obtained with a Varian SuperScan 3 spectrophotometer. For these measurements aqueous solutions (ca. $2 \times 10^{-3}$ M) were used.

The circular dichroism spectra were recorded at room temperature on a JASCO Model J-500A spectropolarimeter using a xenon arc source.

Proton NMR spectra were measured on a Bruker/IBM AF-300 NMR spectrometer (300 MHz). $D_2O$, containing 0.1% sodium 4,4-dimethyl-4-sila-1-pentanesulfonate (DSS) as an internal reference, was used as a solvent, and ~1.5% $D_2O$ solutions of the substances were used.

**Analyses.** Elemental microanalyses for carbon, hydrogen, and nitrogen were performed by the Microanalytical Laboratory, Department of Chemistry, Faculty of Science, University of Belgrade.

## Results and Discussion

The geometrical isomers of the $[Co(eda3p)]^-$ complex shown in Figure 1 differ in the position of the glycinate ring (trans($O_5O_6$) (I) with a glycinate ring in an axial position (R ring) and trans($O_6$) (II) with a glycinate ring in an equatorial position (G ring)). Both geometrical isomers have a rhombic ligand field and $C_1$ molecular symmetry. These isomers, however, have pseudo-$D_{4h}$ (holohedrized) symmetry with the quasi-$C_4$ axes being perpendicular to the plane containing the diamine ring. Because of the observed larger strain for the G glycinate rings[3,7] than for the corresponding R rings, it is reasonable to expect that the trans($O_5O_6$) isomer (Figure 1, isomer I) with the larger (six-membered) chelate rings in the G plane should form preferentially relative to the corresponding trans($O_6$) isomer. The favored *trans*($O_5O_6$)-$[Co(eda3p)]^-$ isomer was the one isolated. It was found to be stable in aqueous solution. Its geometry was assigned on the basis of the $^1H$ NMR spectrum, which indicated an R (out-of-plane) glycinate ring.

**$^1H$ NMR Spectra and Geometry of Complexes.** The $^1H$ NMR spectra of K[Co(edtp)]·$3H_2O$ and K[Co(eda3p)]·$3H_2O$ are shown in Figure 2 for comparison. The spectrum of $[Co(edtp)]^-$ (Figure 2a) can be reconciled to a molecular system with $C_2$ symmetry having five relatively isolated ethylenic fragments, all with high amounts of conformational purity. For example, 2D $^1H$ *J* NMR spectroscopy[17] was used to help determine that the doublet at δ 3.48 is due to the axial protons of the ethylendiamine backbone and these are coupled to the equatorial protons of the same backbone at δ 2.86 with *J* = 10.1 Hz.[18] The multiplets at 3.58, 3.21, 3.04, and 2.44 ppm are assigned to axial protons of the ethylenic fragments in the propionate arms. The other multiplets are all due to equatorial protons in the same arms. The very simple spectrum, integration results, and peak patterns suggest the existence of two equivalent coordinated 3-propionate arms as R rings and two equivalent coordinated 3-propionate arms as G rings, but it could not be determined unequivocally in this study which is which.

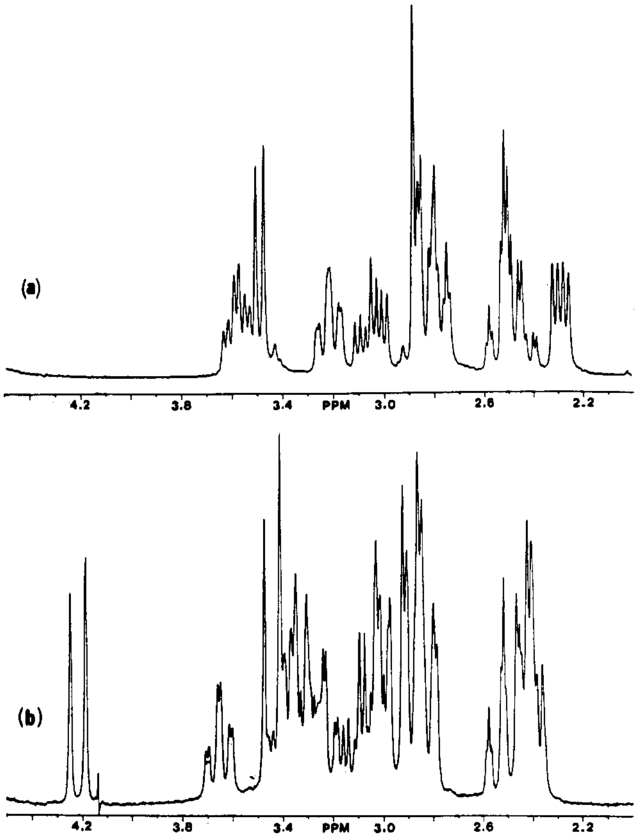

**Figure 2.** $^1H$ NMR spectra: (a) $[Co(edtp)]^-$; (b) *trans*($O_5O_6$)-$[Co(eda3p)]^-$.

The $^1H$ NMR spectrum of $[Co(eda3p)]^-$ is shown in Figure 2b. This spectrum shows an AB quartet centered at δ 3.85 with $\delta_A$ = 4.21 and $\delta_B$ = 3.44. The measured coupling constant $J_{AB}$ = 18.2 Hz is typical for the geminal hydrogens of a glycinate arm coordinated out of plane to a Co(III) ion.[19,20] In addition, it has been shown that the spread of the quartet pattern, $\delta_A - \delta_B$ = 0.77, also suggests an out-of-plane (R-ring) rather than in-plane (G-ring) coordination for the glycinate arm. $\Delta\delta_{AB}$ values for in-plane coordination are usually smaller and are on the order of ~0.6 ppm for other six-coordinate Co(III) edta-type complexes.[10] The $[Co(eda3p)]^-$ ion is a structural modification of $[Co(edtp)]^-$ in which one of the axially coordinated 3-propionate rings is replaced with a glycinate ring. The results along with integration studies and a consideration of overall peak patterns help to confirm the substance as the trans($O_5O_6$) isomer of $[Co(eda3p)]^-$ with no symmetry element higher than $C_1$.

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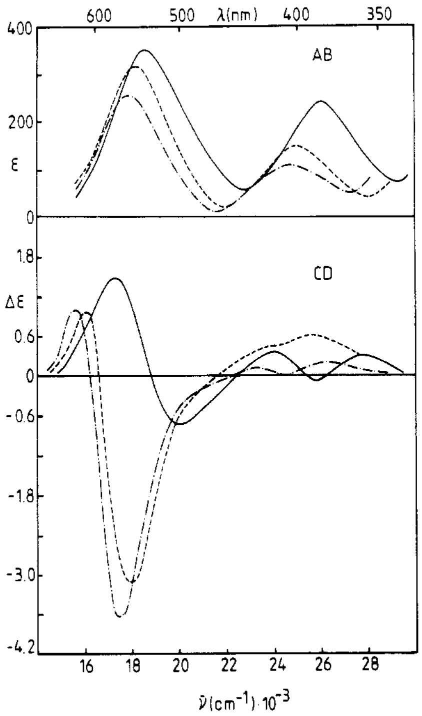

**Figure 3.** Electronic Absorption and CD spectra: (—) Λ-(+)-[Co(edta)]⁻; (---) Λ-(+)-*trans*($O_5O_6$)-[Co(eda3p)]⁻; (-·-) Λ-(+)-[Co(edtp)]⁻.

**Electronic Absorption and Circular Dichroism.** The electronic absorption and CD spectra of the *trans*($O_5O_6$)-[Co(eda3p)]⁻ complex compared to those of the Λ-[Co(edta)]$^{-}$ [2,3] and Λ-[Co(edtp)]$^{-}$ [6] complexes are shown in Figure 3. The corresponding numerical data of absorption and CD maxima for these and other related edta-type complexes are summarized in Table I. The absorption spectra of these complexes (Figure 3) are very similar in shape, with two bands corresponding to transitions to the $T_{1g}$ and $T_{2g}(O_h)$ states. The bands (I and II) are symmetrical and show no obvious splitting. Although splitting might be expected for *cis*-[Co(N)$_2$(O)$_4$] type complexes, it is usually not observed for [Co(edta-type)]⁻ complexes.

All [Co(edta-type)]⁻ complexes (Table I) have the same effective crystal field and general arrangement of chelate rings as [Co(edta)]⁻. The complexes contain the ethylenediamine "backbone" ring (E ring) but differ in the number of five-membered (glycinate) and six-membered (3-propionate) rings. In general, the absorption bands for this series of complexes shift to lower energy on going from [Co(edta)]⁻, having four glycinate rings, to [Co(edtp)]⁻, having four 3-propionate rings. The absorption energies of the *trans*($O_5O_6$)-[Co(eda3p)]⁻ complex, containing one glycinate and three 3-propionate rings (the bands at 18 250 cm$^{-1}$, $\epsilon_1 = 318$, and at 25 190 cm$^{-1}$, $\epsilon_2 = 147$), are closer to those of the [Co(edtp)]⁻ species than to those of the [Co(edta)]⁻ complex. As seen in Table I, the observed trend regarding the positions of absorption maxima for these complexes is in accordance with the decrease of the ligand field strengths on going from the edta to the edtp ligand (edtp < eda3p < eddadp < edta).

The absence of apparent splitting of the $T_{1g}$ and $T_{2g}$ absorption bands suggests pseudooctahedral symmetry, but the interpretation of the electronic absorption spectra for these complexes based on a tetragonal field is preferred.[11]

The two spin-allowed ligand field transitions in a low-spin d$^6$ system in an octahedral field are $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$. In a tetragonal field, the two transitions split into two components each, i.e., $^1T_{1g} = {}^1A_{2g} + {}^1E_g{}^a$ and $^1T_{2g} = {}^1B_{2g} + {}^1E_g{}^b$. All complexes given in Table I can be considered to have holohedrized $D_{4h}$ symmetry. With use of pseudo-$D_{4h}$ symmetry and Wentworth and Piper's treatment[21] the $^1E_g{}^a(D_{4h})$ state from the $^1T_{1g}(O_h)$ state should be lower in energy than $^1A_{2g}$ from the same $O_h$ state. Also, $^1B_{2g}$ should be lower in energy than the $^1E_g{}^b$ state (both derived from the same $^1T_{2g}(O_h)$ state).

**Table I.** Absorption (AB) and Circular Dichroism (CD) Data for [Co(eda3p)]⁻ and Related Hexadentate edta-Type Complexes

| | AB | | CD | |
|---|---|---|---|---|
| complex[a] | ν, 10³ cm⁻¹ | ε | ν, 10³ cm⁻¹ | Δε |
| Λ-(+)-[Co(edta)]$^{-}$ [b] | 18.63 | 347 | 17.10 | +1.50 |
| | | | 19.80 | −0.69 |
| | 26.04 | 246 | 23.80 | +0.28 |
| | | | 25.60 | −0.09 |
| | | | 27.60 | +0.29 |
| Λ-(+)-*trans*($O_5O_6$)-Ag[Co(eddadp)]·H$_2$O[10] | 18.60 | 253 | 16.50 | +2.25 |
| | | | 18.40 | −3.12 |
| | 25.80 | 142 | 24.40 | +0.31 |
| | | | 26.60 | +0.56 |
| Λ-(+)-*trans*($O_5$)-Ag[Co(eddadp)]·2H$_2$O[9,10] | 18.50 | 342 | 16.20 | +0.40 |
| | | | 18.30 | −2.78 |
| | 25.70 | 186 | 24.20 | +0.29 |
| | | | 26.30 | +0.36 |
| Λ-(+)-*trans*($O_5O_6$)-K[Co(eda3p)]·3H$_2$O | 18.25 | 318 | 16.05 | +0.90 |
| | | | 18.08 | −3.18 |
| | 25.19 | 147 | 23.81 sh | +0.43 |
| | | | 26.04 | +0.58 |
| Λ-(+)-Li[Co(edtp)]·3H$_2$O[c] | 18.00 | 253 | 15.77 | +1.05 |
| | | | 17.57 | −3.68 |
| | 24.80 | 110 | 23.30 | +0.10 |
| | | | 26.30 | +0.20 |

[a] Data are given for isomers having a positive rotatory strength associated with the lowest energy CD bands. [b] Reference 2. Absorption data are for Na[Co(edta)]·4H$_2$O and CD data for K[Co(edta)]·2H$_2$O. [c] Reference 6 and this work.

The transition to the A($C_2$) state, derived from the $E_g{}^a(D_{4h})$ state, is thought to be responsible for the low-energy CD peak for hexadentate [Co(edta-type)]⁻ complexes with the lowest energy CD components of these complexes (A($C_2$) or E($D_{4h}$)) positive for the Λ (ΔΔΛ) configuration,[2,5,6,8-12,22-24] corresponding to the chirality[15] of the isomers shown in Figure 1. This assignment is consistent with the empirical observation[25] that the sign of the A → A($C_2$) component can be correlated with the absolute configuration. This assignment has been verified crystallographically in the case of Λ-[Co(edta)]⁻,[3] Λ-[Co(1,3-pdta)]⁻,[7] and Λ-[Co(*S*,*S*-edds)]$^{-}$ [26] complex ions.

The CD spectrum[2,6] of [Co(edta)]⁻ (Table I) shows two low-energy peaks of opposite sign, one on either side of the first absorption band. The $D_{4h}$ model is consistent with this CD pattern, the lower energy peak being $E_g(D_{4h})$ and the higher energy peak being $A_{2g}(D_{4h})$. The sign of $E_g(D_{4h})$ is retained by the A($C_2$) component of $E_g$ parentage.

The actual symmetry of the (+)-*trans*($O_5O_6$)-[Co(eda3p)]⁻ complex is $C_1$. However, its CD spectrum and the CD spectra of other related complexes ((+)-[Co(edtp)]⁻ and the two isomers of (+)-[Co(eddadp)]⁻) are also in accordance with the $D_{4h}$ model. The CD spectra of these complexes differ from that of (+)-[Co(edta)]⁻ and show two CD peaks in the low-energy region, occurring at lower energy than the absorption maximum, suggesting that they are components split from the $E_g(D_{4h})$ state because of lower symmetry. The third transiton, expected for the complexes of $C_2$ symmetry, should be on the higher energy side of the absorption maximum, but presumably it is obscured by the dominant neighboring peak.

The optically active *S*,*S*-edds ligand, upon coordination, apparently forms only one (trans($O_5$)) isomer of known (Λ) absolute configuration.[11,26] For this complex, three peaks of alternating sign were observed,[11] corresponding to the number of transitions

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expected for $C_2$ symmetry. The sharpness of these peaks argues strongly against this pattern resulting from the overlap of two peaks of opposite sign.

The $[Co(edta\text{-}type)]^-$ complexes with $C_2$ symmetry can be related to $[Co(en)(mal)_2]^-$, which can be correlated with *cis*-$[Co(en)_2X_2]^{n+}$ complexes.[25] The $A(C_2)$ component for these complexes was considered[25] to retain the sign of the $E_a(D_3)$ component for $[Co(en)_3]^{3+}$. The empirical correlation has weaknesses because the *cis*-$[Co(N)_2(O)_4]$-type complex has the weak- and strong-field ligands reversed compared to the case for *cis*-$[Co(N)_4(X)_2]$.

For the $[Co(edta\text{-}type)]^-$ complexes, the empirical correlations are consistent with the results from $D_{4h}$ symmetry when there are two CD peaks, one on each side of the absorption maximum, or from $C_2$ symmetry when there are three CD peaks or only two peaks, both on the low-energy side of the absorption maximum.

The geometry of the *trans*$(O_5O_6)$-$[Co(eda3p)]^-$ complex was assigned on the basis of its $^1H$ NMR spectrum, which indicated an R (out-of-plane) glycinate ring. The CD spectrum of (+)-$[Co(eda3p)]^-$ is compared with spectra of other related complexes (Table I) of known $\Lambda$ configuration. All complexes shown have positive lowest energy CD peaks ($A(C_2)$), indicating the same $\Lambda$ absolute configuration. The CD data obtained for the (+)-$[Co(eda3p)]^-$ complex (see Figure 3 and Table I) are more similar to those of the $\Lambda$-$[Co(edtp)]^-$ complex than to those of the $\Lambda$-$[Co(edta)]^-$ complex. The positive lowest energy CD peak of this complex is presumed to be the $A(C_2)$ component of $E_g(D_{4h})$ parentage, and the (+)-$[Co(eda3p)]^-$ isomer is also assigned the $\Lambda$ configuration.

In the $\Lambda$-(+)-$[Co(eda3p)]^-$ complex there are possible contributions to the CD intensities from one asymmetric nitrogen atom, as well as from the configurational effect. The latter effect, however, is thought to dominate.[10–13] The contribution of the asymmetric nitrogen of $\Lambda$-$[Co(eda3p)]^-$ is *R* for the trans$(O_5O_6)$ isomer (Figure 1, isomer I). The similarity in shapes of the CD curves of the $\Lambda$-$[Co(edtp)]^-$ complex (in which case there is no contribution due to asymmetric nitrogens) and the $\Lambda$-$[Co(eda3p)]^-$ complex and the relative intensities of their lowest energy CD components (Figure 3 and Table I) support the idea that the contribution due to the asymmetric nitrogen is not great in hexadentate edta-type complexes. Thus, the difference in CD spectra of these complexes is mostly due to different configurational effects associated with the distribution of the five- and six-membered chelate rings. In the case of these two complexes only one chelate ring in an axial position (3-propionate for the $\Lambda$-$[Co(edtp)]^-$ complex and (*R*)-glycinate for the $\Lambda$-$[Co(eda3p)]^-$ complex) makes a difference in their CD spectra. For clarification of the relative contributions of chelate rings and the dependence on their size and position about an octahedron, more examples with known structure are needed.

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**Registry No.** $H_4$eda3p, 112988-86-0; $H_4$edma·2HCl, 25240-38-4; K[Co(edtp)], 113008-33-6; *trans*$(O_5O_3)$-K[Co(eda3p)], 113085-23-7; $(-)_{589}$-$[Colen)_2(ox)]Br$, 31126-57-5; $(-)_{589}$-$[Co(en)_2(ox)]$-$(-)_{546}$-[Co(edtp)], 113158-26-2; $(+)_{589}$-$[Co(en)_2(ox)]I$, 40028-98-6; $(-)_{546}$-Li[Co(edtp)], 113158-24-0; $(+)_{546}$-Li[Co(edtp)], 113083-09-3; $(-)_{589}$-$[Co(en)_2(ox)]$-$(+)_{546}$-[Co(eda3p)], 113008-32-5; $(-)_{589}$-$[Co(en)_2(ox)]$-$(-)_{546}$-[Co(eda3p)], 113084-39-2; $(+)_{546}$-*trans*$(O_5O_6)$-K[Co(eda3p)], 113008-30-3; $(-)_{546}$-*trans*$(O_5O_6)$-K[Co(eda3p)], 113084-40-5; 3-chloropropionic acid, 107-94-8.

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# Vanadium(V) Oxyanions: Interactions of Vanadate with 1,1,1-Tris(hydroxymethyl)ethane and with the Buffer Tris(hydroxymethyl)aminomethane

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$^{51}V$ NMR spectroscopy has been used to study the interactions of vanadate with 1,1,1-tris(hydroxymethyl)ethane (tris-eth) and with the buffer tris(hydroxymethyl)aminomethane. The reaction of vanadate with tris-eth was found to proceed readily at pH 7.5 to give a variety of products. From variation of vanadate and ligand concentration it was possible to obtain the ligand stoichiometry and formation constants for the various products. The products identified included the monoester of vanadate, the mono- and diesters of divanadate, and a binuclear product for which a bipyramidal coordination geometry about each vanadium nucleus was proposed. The reaction of Tris buffer with vanadate was similar to that of tris-eth. However, a variety of products, which could not be properly studied, were found to occur below pH 7.6. Studies at pH 7.6 and 9.0 showed the formation of vanadate esters of tetrahedral coordination, a bis(ligand) product, assigned an octahedral coordination, and, as well, two binuclear products, one with a single Tris ligand and the second with two ligands. The results were consistent with a bipyramidal/tetrahedral mixed anhydride in the first case and a symmetrical bipyramidal anhydride analogous to that formed with tris-eth in the second case. A rather surprising observation was that these two products exhibited a large chemical shift dependence on pH, presumably reflecting the protonation/deprotonation of the amino group of Tris. The $pK_a$ determined for this reaction was 7.33, which is considerably smaller than that normally associated with tetrahedral products such as the $8.64 \pm 0.02$ value determined here for the vanadate ester of tris-eth. Investigation of vanadate in the presence of *cis*- or *trans*-1,2-cyclohexanediol and with or without Tris buffer revealed a strong synergistic reaction of Tris with the products of the reaction of vanadate with either of the diols. This result suggests that Tris buffer should be used with extreme caution when vanadate/ligand interactions are studied. Preliminary studies indicated that HEPES buffer is much less reactive toward vanadate and vanadate derivatives.

## Introduction

Over the past few years the aqueous chemistry of vanadium has been a subject of developing interest not only because vanadium may be an essential element but also because vanadium has a significant effect on the function of a variety of enzymes.[1,2] Furthermore, it is possible that vanadium may prove to be useful as a therapeutic agent for the treatment of various diseases such as diabetes[3,4] and sickle cell anemia.[5] There may also be ap-

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