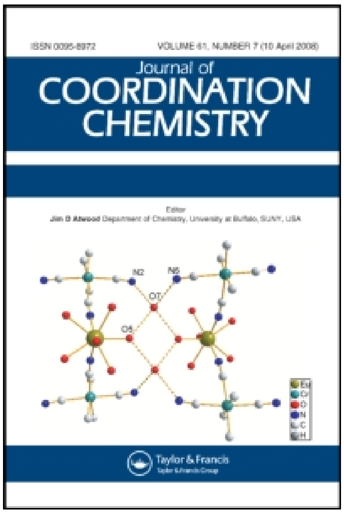

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CIRCULAR DICHROISM OF 1,3-PROPANEDIAMINETETRAACETATORHODATE(III) ION

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Electronic absorption and CD spectra are reported for the sexidentate $[Rh(1,3\text{-pdta})]^-$ complex (1,3-pdta = 1,3-propanediaminetetraacetate ion). The $(-)_D$ isomer of the $[Rh(1,3\text{-pdta})]^-$ complex is assigned the Λ configuration by comparison of its CD spectrum to that of *trans*(O_5)-$[Rh(S,S\text{-edds})]^-$ known to have the Λ configuration from the stereospecificity of the S,S-edds ligand (S,S-edds = (S,S)-ethylenediamine-*N*,*N*′-disuccinate ion).

INTRODUCTION

The $[Co(edta)]^-$ complex is somewhat strained as indicated by the X-ray structure determination of the complex ion.[1] The two glycinate rings of this complex, which lie in the plane of the diamine ring (G rings), are considerably more strained than the other two glycinate rings (R rings). Since the strain presumably is greater for the edta complexes of the larger Cr(III) and Rh(III) ions, usually these complexes are only quinquedentate with one water molecule occupying the sixth coordination site.[2–5] However, there is evidence for a sexidentate $[Cr(edta)]^-$ complex,[6] as well as a suggestion from NMR solution studies[7] of the existence of $[Rh(edta)]^-$.

Van Saun and Douglas[8] and Ogino *et al.*[9] prepared and resolved cobalt(III) complexes of 1,3-propanediaminetetraacetate (1,3-pdta) and suggested that the ligand acts as a sexidentate with less strain than in the sexidentate $[Co(edta)]^-$. This has been confirmed crystallographically.[10] The corresponding 1,3-propanediaminetetraacetate complexes with Cr(III)[11] and Rh(III)[12] also have been prepared and characterized. In each case the formation of the sexidentate M(III) complexes (M = Co(III), Cr(III) and Rh(III)) was attributed to the relief of strain due to the longer chain of the diamine backbone.

Ligands structurally similar to edta, but with longer carboxylate chains, S,S-edds[13,14] and eddda[15,16] (eddda = ethylenediamine-*N*,*N*′-diacetate-*N*,*N*′-di-3-propionate ion), have been prepared and their Co(III),[14,16,17] Cr(III)[18] and Rh(III)[19] complexes have been discussed. It has been demonstrated[14,16–19] that these ligands preferentially form isomers having six-membered rings in the G plane which should minimize the strain on the chelate system. Such complexes are of interest in the study of the influence of chelate ring size of edta-type ligands on the arrangement of rings about a central metal ion, and the relative effects of this and other factors contributing to optical activity of the resolved complexes.

The CD spectra of the sexidentate Rh(III) complexes containing the S,S-edds and eddda ligands have been discussed recently.[19] The sexidentate $[Rh(1,3\text{-pdta})]^-$ complex also has been characterized by ^{13}C and ^1H NMR and IR spectra.[12] In this paper the preparation and optical resolution of the $[Rh(1,3\text{-pdta})]$ complex ion and its electronic absorption and CD spectra will be described.

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EXPERIMENTAL

The 1,3-pdta ligand was prepared using the procedure of Weyh and Hamm.[11] Other reagent-grade chemicals were obtained commercially and used without purification.

Optical isomers are identified by the sign of the optical rotation at a wavelength, $\lambda[(+)_\lambda$ or $(-)_\lambda]$. The Δ or Λ is the chirality assigned according to IUPAC rules.[20]

Preparation and Resolution of Sodium 1,3-Propanediaminetetraacetatorhodate(III) Trihydrate, Na[Rh(1,3-pdta)]·3H_2O

Rhodium(III) chloride trihydrate (1.32 g, 5 mmol) was dissolved in 3 ml of water in a Pyrex tube. To this mixture, a solution obtained by dissolving 1.54 g (5 mmol) of 1.3-pdta in 5 ml of 4 M NaOH (20 mmol) was added, the tube sealed and the mixture heated at 145°C in an oil-bath for 7 hr. After removal from the tube, the reaction mixture (pH ~ 4–5) was diluted, then heated and filtered to remove a small amount of Rh metal. The yellow filtrate (about 25 ml) was allowed to stand at room temperature overnight during which crystallization of highly-charged species† occurred. The precipitate was removed, the filtrate was evaporated to 15 ml and allowed to stand in a refrigerator overnight. The yellow crystals of sexidentate Na[Rh(1,3-pdta)]·3H_2O were separated by filtration, washed with ethanol, ether, and then air-dried. Yield: 0.9 g (37.8%). The pure complex was obtained by recrystallization from a small amount of water and cooling. *Anal.* Calcd for Na[Rh(1,3-pdta)]·3H_2O = $NaRhC_{11}H_{20}N_2O_{11}$ (FW = 482.31): C, 27.39; H, 4.17; N, 5.83. Found: C, 27.86; H, 4.05; N, 6.18.

Resolution of Complex

This complex (0.482 g, 1 mmol) was dissolved in a small amount of water and converted from the Na^+ to the Ag^+ form by passing the solution through a cation-exchange column (2 cm × 40 cm, Merck I Analytical Grade cation-exchange resin in the Ag^+ form). To the eluate, heated to 55–60°C, an equivalent amount of $(-)_D$-[Co(en)$_2$(ox)]Br·H_2O (0.365 g, 1 mmol) was added. The AgBr was removed, the filtrate was evaporated on a steam-bath to a volume of 4 ml, and the solution was left overnight in a refrigerator. During that time, the less soluble diastereoisomer, $(-)_D$-[Co(en)$_2$(ox)]-$(+)_D$-[Rh(1,3-pdta)]·xH_2O crystallized. The solid was removed by filtration, washed with ethanol, ether, and then air-dried (0.35 g). The remaining filtrate was then evaporated to a volume of 2 ml. After addition of ethanol and cooling in the refrigerator the more soluble diastereoisomer, $(-)_D$-[Co(en)$_2$(ox)]-$(-)_D$-(Rh(1,3-pdta)]·xH_2O, crystallized (0.28 g). Both diastereoisomers were crystallized from water (or a water–ethanol mixture) to constant values of optical rotation. Aqueous solutions (0.1%) gave $[\alpha]_D = -305°$; $[\alpha]_{436} = +830°$ and $[\alpha]_D = -468°$; $[\alpha]_{436} = +380°$ for the less and more soluble diastereoisomers, respectively.

The enantiomers of the [Rh(1,3-pdta)]$^-$ complex ion in the form of sodium salts were obtained using the ion-exchange column technique. The eluates were evaporated to a small volume at room temperature and the enantiomers were crystallized after cooling in the refrigerator overnight. $[\alpha]_D = \pm 130°$ and $[\alpha]_{436} = \pm 455°$ in 0.1% aqueous solution. *Anal.* Calcd for $(-)_D$-Na[Rh(1,3-pdta)]·3H_2O = $NaRhC_{11}H_{20}N_2O_{11}$ (FW = 482.31): C, 27.39; H, 4.17; N, 5.83. Found: C, 27.84; H, 3.93; N, 6.11.

Physical Measurements

The $[\alpha]_\lambda$ values were measured in a 1 dm tube at 20° on a Perkin-Elmer Model 241 Polarimeter.

The electronic absorption spectra were recorded on a Varian SuperScan 3 recording spectrophotometer. For these measurements a 5×10^{-3} M aqueous solution were used.

The circular dichroism curves were recorded at room temperature with a Jobin-Yvon Dichrographe Mark III using a xenon arc source.

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 six-membered chelate ring formed by the diamine backbone of the [M(1,3-pdta)]$^-$ complexes can have four possible conformers: chair, two twist (δ and λ), and boat forms. Molecular models show that the most stable sexidentate complex should have the twist form and, further, the δ twist should form a complex with the Λ

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†Ion exchange chromatography showed that the first precipitate contains species with higher charge which could not be isolated in pure form and which probably are hydroxo complexes.

configuration and that the λ twist should be associated with the Δ configuration, as has been found in the cobalt(III) complex.[9,10] Preliminary results of a crystallographic study[21] of the 1,3-propanediaminetetraacetate complexes with chromium(III)[11] and rhodium(III)[12] show that these are stable sexidentate complexes in which the conformation (δ and λ) of the diamine backbone ring determines the absolute configuration of the complex.

Electronic Absorption and CD Spectra

The electronic absorption and CD data for the [Rh(1,3-pdta)]$^-$ complex are shown in Table I and Figure 1. For comparison, the corresponding values of the recently investigated [Rh(S,S-edds)]$^-$ complex[19] are also given. Both ε and Δε values for the [Rh(1,3-pdta)]$^-$ complex are significantly lower than those for the other Rh(III) edta-type complexes containing S,S-edds and eddda ligands, although the reduction in ε is significant only for the major component. Lower ε and Δε values might be expected because of the less rigid 1,3-pdta framework. Low intensities were observed for some Co(III) complexes containing six-membered diamine backbone rings.[8,22,23]

The [Rh(1,3-pdta)]$^-$ complex has C_2 symmetry. The degeneracy of the T_{1g} and T_{2g} (O_h) energy levels is removed for C_2 symmetry, each giving three components. Here we see only two components (Figure 1) in the region of the lower energy $T_{1g}(O_h)$ transition in the absorption and CD spectra. No splitting is apparent for the higher energy (T_{2g}, O_h) absorption band. Complexes of edta which show only two components in the $T_{1g}(O_h)$ region usually have been treated as having holohedrized D_{4h} symmetry. Using Wentworth and Piper's treatment[24] the $^1E_g^a(D_{4h})$ component of $^1T_{1g}(O_h)$ parentage should be lower in energy than the $^1A_{2g}(^1T_{1g})$ component since the donor atoms in the equatorial plane have higher field strengths than the axial atoms. Also the $^1B_2(^1T_{2g})$ component should be lower in energy than the $^1E_g^b(T_{2g})$ component. The CD data and tentative band assignments in D_{4h} of $(-)_D$-[Rh(1,3-pdta)]$^-$, prepared from the more soluble diastereoisomer, are summarized in Table I.

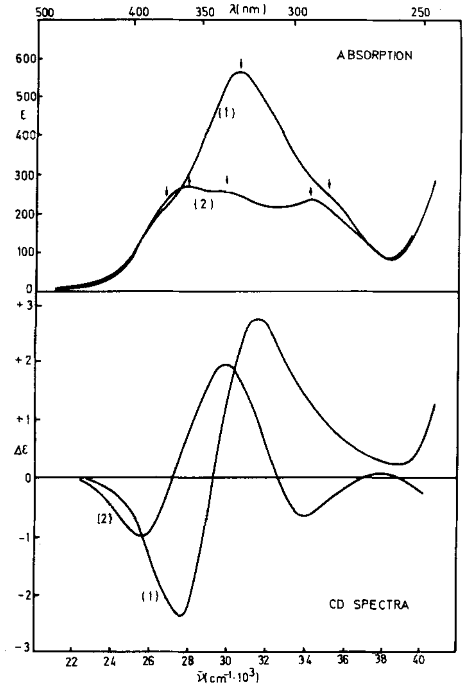

FIGURE 1 The electronic absorption and CD spectra of:
1) *trans*(O_5)-$(+)_D$-Na[Rh(S,S-edds)]·H_2O
2) $(-)_D$-Na[Rh(1,3-pdta)]·$3H_2O$

Many sexidentate complexes with edta-type ligands[8,16–18,25–27] have been treated in terms of C_2 symmetry. Mason has shown[28] that the signs of the Cotton effects of the components under the lowest energy (O_h) band for complexes with C_2 symmetry are related to signs of Cotton effects of the parent levels in complexes with D_3 symmetry having the same con-

TABLE I
Numerical data of absorption (AB) and circular dichroism (CD) spectra, $\tilde{\nu}$ in 10^3 cm^{-1} (ε) and ($\Delta\varepsilon$). Assignments are for D_{4h}.

Complex ion[a]	Absorption	Circular dichroism
[Rh(1,3-pdta)]$^-$	27.94sh (284) ^1E_g	25.51 (−1.03) E_g^a
	29.58sh (274) $^1A_{2g}$	30.03 (+2.05) A_{2g}
	34.13 (243) $^1B_{2g}$, $^1E_g^b$	34.01 (−0.65) B_{2g}
		38.02 (+0.09) E_g^b
trans(O_5)-[Rh(S,S-edds)]$^-$	26.66sh (215) ^1E_g	27.54 (−2.29) E_g^a
	30.48 (565) $^1A_{2g}$	31.54 (+2.74) A_{2g}
	35.08sh (245) $^1B_{2g}$, $^1E_g^b$	B_{2g}, E_g^b

[a]The numerical data for [Rh(S,S-edds)]$^-$ complex are taken from Ref. 19.

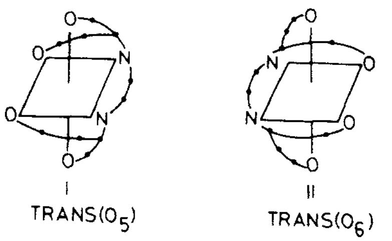

FIGURE 2 Possible isomers of [Rh(S,S-edds)]$^-$ complex.

figuration. 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 edta-type complexes of d^3 and low-spin d^6 metal ions, and the lowest energy CD components of these complexes (A(C_2) or E(D_{4h})) are positive for the Λ (ΛΔΛ) configuration.[8,16–18,25–27]

The optically active S,S-edds ligand, upon coordination, forms only the *trans*(O_5) isomer, which can have only the Λ configuration shown in Figure 2 ($(+)_D$ isomer I). The CD sign pattern for [Rh(S,S-edds)]$^-$ did not correspond to that predicted by empirical correlations for Co(III) complexes. The assignment of the absolute configuration of this and related complexes was made on the basis of the stereospecificity of S,S-edds. Since the CD spectrum of the $(-)_D$ isomer of [Rh(1,3-pdta)]$^-$ shows no more than two components in the first band region, one can use effective D_{4h} symmetry for its interpretation, as for [Rh(S,S-edds)]$^-$. Both complexes shown in Figure 1 have a negative CD peak in the lowest energy spin-allowed region which would suggest that the isomer of each complex has the Δ absolute configuration by analogy to Co(III) edta-type complexes if no reversal of order of the E and A_2 energies occurs. However, both are assigned the Λ configuration because of the stereospecificity of S,S-edda. Preliminary results of a crystallographic study of the $(-)_D$-[Rh(1,3-pdta)]$^-$ complex confirm its Λ absolute configuration. Apparently other factors, such as perhaps spin–orbit coupling, are important in determining the shape and sign of the CD spectra of these Rh(III) complexes.

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