Identification and characterization of the *trans*(O_5) and *trans*(O_5O_6) isomers of hexadentate rhodium(III) complex of 1,3-propanediamine-*N,N'*-diacetic-*N,N'*-di-3-propionic acid

Dušan J. Radanović and Miloš I. Djuran
Department of Chemistry, Faculty of Science, University of Kragujevac, 34000 Kragujevac (Yugoslavia)

Tomislav S. Kostić
Department of Chemistry, Faculty of Science, University of Priština, 38000 Priština (Yugoslavia)

Bodie E. Douglas*
Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260 (USA)

(Received December 24, 1992; revised March 1, 1993)

Abstract

Rhodium(III) complexes with the hexadentate ligand, 1,3-propanediamine-*N,N'*-diacetate-*N,N'*-di-3-propionate ion (1,3-pddadp) have been prepared, chromatographically separated and isolated into two geometrical isomers with respect to the N–O chelate ring size (*trans*(O_5) and *trans*(O_5O_6)). The ^1H and ^{13}C NMR and electronic absorption spectra were used to characterize the Rh(III) complexes. The ^{13}C NMR spectra for two isomers of the corresponding $[Co(1,3\text{-pddadp})]^-$ complex of known geometry (*trans*(O_5O_6) and *trans*(O_6)) are also reported. The related edta-type complexes of known structure were used as references for assignment of complexes studied.

Introduction

Structural studies have been reported for transition metal complexes containing the ethylenediaminetetraacetate ion (edta) [1] and their molecular structures have been discussed in terms of the size and d-electron configuration of the central metal ion M [2]. Bonding angles exhibited by edta complexes are strained as shown by significant deviations from ideal values. The two glycinate rings in an equatorial plane (G rings) are more strained than the two glycinate rings coordinated axially (R rings) for $[Co(edta)]^-$ [3, 4].

Ligands, structurally similar to edta, having longer carboxylate or diamine backbone chains are likely to function as a hexadentate ligand with larger metal ions by forming less-strained isomers [5–14]. The edta-like ligands (diamine-*N,N'*-diacetate-*N,N'*-di-3-propionate ions (eddadp or 1,3-pddadp)) might form three geometrical isomers for hexadentatc coordination: *trans*(O_5), *trans*(O_5O_6) and *trans*(O_6) (Fig. 1), where O_5 and O_6 refer to the five- and six-membered carboxylate rings. The ligand eddadp forms a five-membered diamine ring and 1,3-pddadp forms a six-membered diamine backbone ring. Two isomers (*trans*(O_5) and *trans*(O_5O_6)) have been characterized for $[M(eddadp)]^-$ complexes (M = Co(III) [8–10] or Rh(III) [11, 12]). For the $[Cr(eddadp)]^-$ complex, however, only the *trans*(O_5) isomer has been isolated and identified [13, 14]. The five-membered glycinate ring is strained as a G ring in $[M(edta)]^-$, and the strain is relieved when the ring is expanded. The six-membered 3-alaninate rings serve better for the formation of less-strained G rings favoring the *trans*(O_5) isomers of $[M(eddadp)]^-$ complexes [8–14].

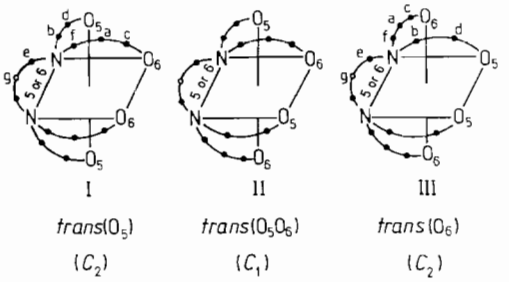


Fig. 1. Possible geometrical isomers of $[M(eddadp)]^-$ and $[M(1,3\text{-pddadp})]^-$ complexes.

The substitution of 1,3-propanediamine for ethylenediamine in eddadp to give 1,3-propanediamine-*N,N'*-

*Author to whom correspondence should be addressed.

0020-1693/93/$6.00

diacetate-*N*,*N*'-di-3-propionate (1,3-pddadp) might make it possible to form all geometrical isomers (Fig. 1). Three isomers of the $[Cr(1,3\text{-pddadp})]^-$ complex have been reported [15]. For the corresponding $[Co(1,3\text{-pddadp})]^-$ complex, however, only two isomers (*trans*(O_5O_6) and *trans*(O_6), isomers **II** and **III**, Fig. 1) have been isolated and characterized [7]. In both cases the dominant isomer of the $[M(1,3\text{-pddadp})]^-$ complex was found to be *trans*(O_6) with 3-propionate rings in axial positions, as verified by X-ray analysis [15, 16].

This paper deals with the preparation, chromatographic separation and isolation of two geometrical isomers of the $[Rh(1,3\text{-pddadp})]^-$ complex (*trans*(O_5) and *trans*(O_5O_6)). The isomers were characterized by use of ^1H and ^{13}C NMR, and electronic absorption spectra. ^{13}C NMR spectra for two isomers of the corresponding $[Co(1,3\text{-pddadp})]^-$ complex of known geometry (*trans*(O_5O_6) and *trans*(O_6)) [7] are also reported here. The spectral data of complexes are compared to those obtained for other edta-type complexes of known structures.

Experimental

The ligand 1,3-propanediamine-*N*,*N*'-diacetic-*N*,*N*'-di-3-propionic acid ($H_4$1,3-pddadp) was prepared using a previously described procedure [7]. Other commercially obtained reagent grade chemicals were used without further purification.

In reaction of rhodium(III) chloride with an aqueous solution of neutralized $H_4$1,3-pddadp using the sealed-tube technique (the mixture was heated at 145 °C in an oil-bath for 7 h) a number of complex anions with different charges were isolated via anion exchange chromatography and gel filtration (QAE-Sephadex, A-25 in Cl^- form and Sephadex G-10 were used for this purpose). The two complexes with 1− charge were assigned as geometrical isomers of the $[Rh(1,3\text{-pddadp})]^-$ complex (*trans*(O_5), eluate (1) and *trans*(O_5O_6), eluate (2), Fig. 1, isomers **I** and **II**)*.

The elemental analyses of the complexes are consistent with the following formulations: *trans*-(O_5)-$Na[Rh(1,3\text{-pddadp})]\cdot 2H_2O$ and *trans*(O_5O_6)-$Na[Rh(1,3\text{-pddadp})]\cdot 2H_2O$. *Anal.* Calc. for $Na[Rh(1,3\text{-pddadp})]\cdot 2H_2O = NaRhC_{13}H_{22}N_2O_{10}$ ($M_r = 492.22$): C, 31.72; H, 4.51; N, 5.69. Found for *trans*(O_5)-$Na[Rh(1,3\text{-pddadp})]\cdot 2H_2O$: C, 31.22; H, 5.32; N, 5.95%. Found for *trans*(O_5O_6)-$Na[Rh(1,3\text{-pddadp})]\cdot 2H_2O$: C, 31.30; H, 4.83; N, 5.90%.

Two complexes with higher (2−) charge (we believe hydroxo species) were also separated from the reaction mixture. Since some thermal decomposition of the ligand is expected [17], the formation of these complexes involves decarboxylation of 1,3-pddadp. For the complete assignment of each of these complexes, X-ray structure determination is required.

Physical measurements

Proton NMR spectra were measured on a Varian Gemini-200 NMR spectrometer (200 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.

High quality ^{13}C NMR spectra were obtained using a Varian Gemini-200 spectrometer operated at *c.* 50 MHz in the noise decoupling mode. All spectra were measured relative to external TMS dissolved in benzene.

Elemental 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 *trans*(O_5) isomer of the $[M(eddadp)]^-$ complex (M = Co(III) [8–10], Rh(III) [11, 12] and Cr(III) [13, 14]) were found to be dominant [8–14], as verified crystallographically [10, 12, 14]. In the complexes of $[M(1,3\text{-pddadp})]^-$ (M = Cr(III) [15] or Co(III) [7, 16]) the favored isomer was found to be *trans*(O_6), as verified by X-ray analysis [15, 16].

The G ring strain in hexadentate edta-type complexes involves distortion of the ideal bonding geometry of the nitrogen atoms [6]. Sums of deviations of all angles are commonly compared because distortions do not correlate well with particular angles. For the same absolute configuration of the complex, changing from *trans*(O_5) to *trans*(O_6) for $[M(eddadp)]^-$ or $[M(1,3\text{-pddadp})]^-$ involves inversion at the chiral nitrogen centers. Both processes, nitrogen inversion or $\Delta \leftrightarrows \Lambda$ conversion, result in the exchange of in-plane substituents for out-of-plane substituents and the product of either process is a structure with neither group in its preferred, low energy position [18]. These changes can significantly affect the nature and extent of non-bonded interactions among the different chelate rings. Dreiding models show that there are significantly unfavorable non-bonding interactions between methylene hydrogen atoms of the R glycinate rings and those of the equatorial diamine ring for the *trans*(O_5)-$[M(1,3\text{-pddadp})]^-$ isomers. A glycinate arm as an R ring is required to be very nearly planar and does not allow for any flexibility

*The third substance with 1− charge, eluate (3) (mixture of at least two species), could not be purified and identified.

of movement by the methylene hydrogens to minimize repulsions.

The favored *trans*(O_5) geometrical isomer was found to dominate in complexes of [Rh(*SS*)-edds)]$^-$ ((*SS*)-edds = (*SS*)-ethylenediamine-*N*,*N*'-disuccinate ion) [11, 19], [Rh(eddadp)]$^-$ [11, 12], and also appeared in complexes of [Rh(1,3-pddadp)]$^-$ reported here. Based on the metal ion size (Co(III) < Cr(III) < Rh(III)) the formation of the *trans*(O_5) geometrical isomers might be expected to be even more strongly favored for Rh(III) than for Co(III) and Cr(III).

The ligand (*SS*)-edds was found to coordinate stereospecifically giving only one (*trans*(O_5)) geometrical isomer of known Λ configuration [11, 13, 19] (a *trans*(O_6) isomer is also possible in this case).

The *trans*(O_5) and *trans*(O_6) isomers (Fig. 1) have a tetragonal ligand field with actual C_2 molecular symmetry (neglecting any conformational differences). The *trans*(O_5O_6) isomer possesses a rhombic field with C_1 molecular symmetry. All isomers have pseudo-D_{4h} (holohedrized) symmetry with the quasi-C_4 axes being perpendicular to the planes containing the diamine ring. Absorption spectra can be interpreted in terms of D_{4h} symmetry, but NMR data require the actual molecular symmetry.

Distinguishing between the two geometrical isomers of Na[Rh(1,3-pddadp)]

^1H NMR spectra

The identification of AB patterns associated with the methylene protons of in-plane (G) glycinate rings and out-of-plane (R) glycinate rings in edta-type complexes has been very useful in determining coordination geometries [20]. A relationship between the chemical shift differences for glycinate proton geminates as well as the orientation of the coordinated glycinates are well established [20, 21]. These arguments were used to distinguish between isomers of hexadentate [Co(eddadp)]$^-$ [9], [Rh(eddadp)]$^-$ [22], [Co(eda3p)]$^-$ (eda3p = ethylenediamine-*N*-acetate-*N*,*N*',*N*'-tri-3-propionate ion) [23], [Co(ed3ap)]$^-$ (ed3ap = ethylenediamine-*N*,*N*,*N*'-triacetate-*N*'-3-propionate ion) [24] complexes and a series of pentadentates based on the general formula, [Co(ed3a)(X)] (ed3a = ethylenediamine-*N*,*N*,*N*'-triacetate ion; X = monodentate ligand) [25].

As expected, NMR spectra of the *trans*(O_6)-[Co(1,3-pddadp)]$^-$ [7] and *trans*(O_5)-[Rh(1,3-pddadp)]$^-$ complexes (Table 1) are simple with only one well resolved AB pattern evident in the glycinate region. The spectrum of the *trans*(O_5)-[Rh(1,3-pddadp)]$^-$ shows an AB quartet centered at 3.85 ppm with $\delta_A = 3.92$ ppm and $\delta_B = 3.78$ ppm, and $J_{AB} = 18.5$ Hz (Fig. 2(a), Table 1). These results are consistent with the expected C_2 symmetry of the *trans*(O_5) isomer having two equivalent glycinate R rings and two equivalent 3-alaninate rings in the equatorial positions.

Two AB patterns, $J_{AB} = 16.5$ Hz (centered at 3.83 ppm, with $\delta_A = 4.05$ ppm and $\delta_B = 3.60$ ppm) and $J_{AB} = 18.9$ Hz (centered at 3.90 ppm, with $\delta_A = 3.97$ ppm and $\delta_B = 3.84$ ppm), are found in the glycinate region of the spectrum of *trans*(O_5O_6)-[Rh(1,3-pddadp)]$^-$, as expected, corresponding to in-plane and out-of-plane glycinate rings (Table 1, Fig. 2(b)). This spectrum is shifted to lower field than that of *trans*(O_5O_6)-[Co(1,3-pddadp)]$^-$ [7] (Table 1) but otherwise, as expected, looks quite similar.

^{13}C NMR spectra

^{13}C NMR spectra of isomers of [M(eddadp)]$^-$ complexes (M = Co(III) or Rh(III)) were assigned [22]. The similarity between the spectra of these complexes is evident and assignments of resonances for these complexes are the same. Selective decoupling and deuterium exchange studies [26–30] allowed assignments of the isomers of [M(1,3-pddadp)]$^-$ complexes, as for the [M(eddadp)]$^-$ complexes [22]. The assignments of the peaks for the C_2 complexes (Fig. 1) are labeled as: a, the carbons α to the carboxyl group of the two 3-alaninate rings; b, the methylene carbons of the two glycinate rings; c, the two equivalent carboxyl carbons of the 3-alaninate rings; d, the two carboxyl carbons of the glycinate rings; f, the carbons β to the carboxyl group of the 3-alaninate rings (Fig. 3, Table 2).

The methylene resonance labeled e is assigned to the two carbons of the ethylenediamine backbone in accordance with assignments made for some [Co(edta-type)]$^-$ complexes [28, 29] which show that the ethylenediamine methylene resonances appear at higher field than those of the methylene carbons of the carboxylate arms [30]. The corresponding terminal carbons of the 1,3-propanediamine backbone (also labeled e) are not greatly shifted or split for *trans*(O_5O_6) isomers, as seen in Fig. 3.

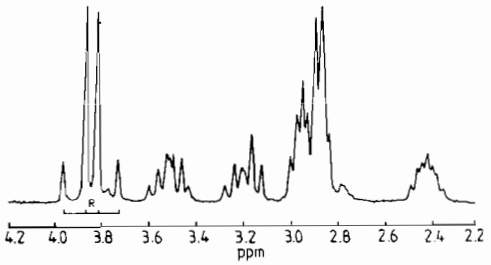
The highest field methylene resonances, g, for all isomers of [M(1,3-pddadp)]$^-$ are due to the middle carbon of the 1,3-propanediamine backbone since this carbon is in the greatest shielding environment. This peak is little changed for cases in Fig. 3. Resonances g are less intense for the *trans*(O_5) and *trans*(O_6) isomers having higher (C_2) symmetry.

As expected, the similarity between the spectra of the *trans*(O_5O_6) isomers of corresponding Co(III) and Rh(III) is evident. The resonances associated with both *trans*(O_5O_6) isomers appear in the same regions as those of the *trans*(O_5) and *trans*(O_6) isomers. Since the *trans*(O_5O_6) complexes have four non-equivalent rings (two glycinate and two 3-alaninate), each carbon should be magnetically distinct. Thus, two resonances result in the *trans* (O_5O_6) spectra in regions where only one

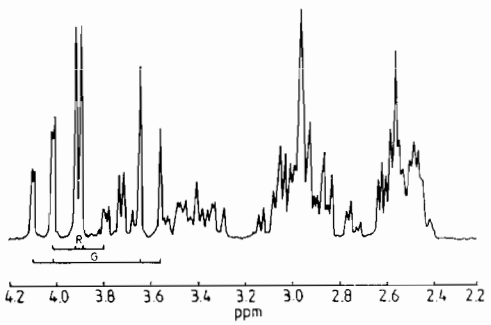
TABLE 1. Coupling constants and chemical shifts[a] for methylene protons of R and G glycinate rings of the [M(1,3-pddadp)]$^-$ complexes

Complex	δ_A (ppm)	δ_B (ppm)	$\delta_A - \delta_B$ (ppm)	J_{AB} (Hz)	R or G
trans(O_6)-[Co(1,3-pddadp)]$^-$[b]	4.11	3.33	0.78	16.6	G
trans(O_5O_6)-[Co(1,3-pddadp)]$^-$[b]	3.82	3.72	0.10	18.8	R
	3.89	3.24	0.65	16.7	G
trans(O_5)-[Rh(1,3-pddadp)]$^-$	3.92	3.78	0.14	18.5	R
trans(O_5O_6)-[Rh(1,3-pddadp)]$^-$	3.97	3.84	0.13	18.9	R
	4.05	3.60	0.45	16.5	G

[a]Values are in ppm downfield from DSS as internal standard. [b]Data taken from ref. 7.



(a)



(b)

Fig. 2. ^{1}H NMR spectra: (a) *trans*(O_5)-[Rh(1,3-pddadp)]$^-$; (b) *trans*(O_5O_6)-[Rh(1,3-pddadp)]$^-$.

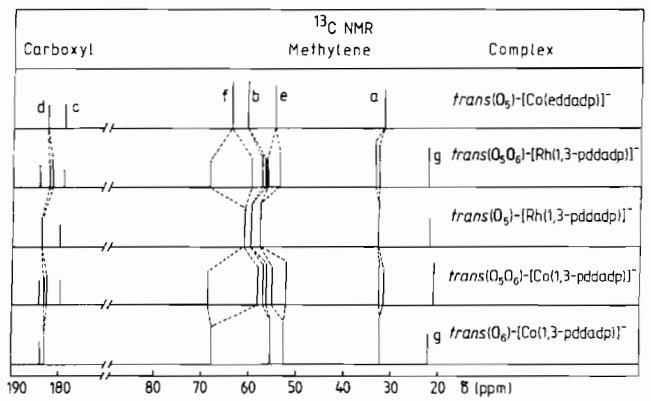


Fig. 3. ^{13}C NMR spectra of hexadentate [M(1,3-pddadp)]$^-$ complexes of Co(III) and Rh(III) in comparison to *trans*(O_5)-[Co(eddadp)]$^-$.

appears in the *trans*(O_5) and *trans*(O_6) spectra, except for g. ^{13}C NMR spectra of the *trans*(O_6)-[Co(1,3-pddadp)]$^-$ and *trans*(O_5)-[Rh(1,3-pddadp)]$^-$ complexes are simple. Because of the C_2 symmetry, the glycinate rings are equivalent and the 3-alaninate rings are equivalent. Each of these complexes shows the expected seven resonances.

The α carbons (a) of the 3-alaninate rings give only one intense resonance for the *trans*(O_5) and *trans*(O_6) isomers, but, as expected, two resonances appear for [M(1,3-pddadp)]$^-$ complexes of lower symmetry (at 32.84 and 33.50 ppm for the *trans*(O_5O_6)–Rh(III) complex and at 31.58 and 32.64 ppm for the *trans*(O_5O_6)–Co(III) complex). The corresponding peaks are little shifted for all complexes in Fig. 3. The α carbons of the 3-alaninate rings associated with *trans*(O_5O_6)-[M(eddadp)]$^-$ complexes are the least affected of the carbons and could not be resolved [22].

The N-bonded methylenes of the carboxylate arms are b (glycinate ring) and f (3-alaninate ring). The resonance for f is at lower field for all complexes in Fig. 3 because it is bonded to another methylene group. The b resonance is only slightly split for *trans*(O_5O_6) isomers, but the splitting for f is much greater. These results are understandable because the rigid glycinate ring can change little in conformation in an axial or equatorial position. The 3-alaninate ring is more flexible and greater conformational changes are expected.

Assuming correct assignment for carboxyl resonances for *trans*(O_5O_6)-[Rh(eddadp)]$^-$ [22], it would be expected that the glycinate carboxyl resonances (d and d') of the *trans*(O_5O_6)-[M(1,3-pddadp)]$^-$ complex would be only slightly separated and quite close to the corresponding resonance of the spectrum of *trans*(O_5)-[Co(eddadp)]$^-$ [22, 26]. It can be seen (Fig. 3, Table 2) that the two resonances (at 182.71 and 182.84 ppm, of *trans*(O_5O_6)-[Co(1,3-pddadp)]$^-$, separated by 0.13 ppm and at 181.64 and 182.07 ppm, of *trans*(O_5O_6)-[Rh(1,3-pddadp)]$^-$, separated by 0.43 ppm) are very close to the lowest field (glycinate carboxyl) resonance (d) in the *trans*(O_5)-[Co(eddadp)]$^-$ spectrum [22, 26].

TABLE 2. ^{13}C resonance positions[a,b]

Complex	Carboxyl	Methylene
trans(O_5)-[Co(eddadp)]$^-$	182.54, 178.88	63.80, 60.31, 54.54, 31.49
trans(O_5O_6)-[Co(1,3-pddadp)]$^-$	184.37, 182.84, 182.71, 179.60	68.85, 58.25, 57.18, 56.41, 55.10, 52.11, 32.64, 31.58, 21.05
trans(O_5O_6)-[Rh(1,3-pddadp)]$^-$	184.44, 182.07, 181.64, 178.96	68.29, 59.57, 57.12, 56.75 56.44, 53.74, 33.50, 32.84, 22.23
trans(O_5)-[Rh(1,3-pddadp)]$^-$	183.85, 179.96	61.06, 59.63, 57.76, 32.71, 21.98
trans(O_6)-[Co(1,3-pddadp)]$^-$	183.93, 183.08	67.89, 55.39, 52.17, 32.38, 22.12

[a]δ (ppm) relative to external TMS dissolved in benzene. [b]Data from this work except for *trans*(O_5)-[Co(eddadp)]$^-$, ref. 22.

TABLE 3. Electronic absorption data for hexadentate edta-type Rh(III) complexes forming six-membered diamine ring

Complex	Absorption		Assignment (D_{4h} state)	Reference
	ν (10^3 cm^{-1})	ϵ		
[Rh(1,3-pdta)]$^-$	≃27.94(sh)	284	$^1E_g^a$	31
	≃29.58(sh)	274	$^1A_{2g}$	
	34.13	243	$^1B_{2g}$, $^1E_g^b$	
trans(O_5)-[Rh(1,3-pddadp)]$^-$	≃25.64(sh)	224	$^1E_g^a$	this work
	27.93	300	$^1A_{2g}$	
	32.89	209	$^1B_{2g}$, $^1E_g^b$	
trans(O_5O_6)-[Rh(1,3-pddadp)]$^-$	≃26.11(sh)	167	$^1E_g^a$	this work
	28.57	207	$^1A_{2g}$	
	33.55	180	$^1B_{2g}$, $^1E_g^b$	

The outer two carboxyl resonances of *trans*(O_5O_6)-[M(1,3-pddadp)]$^-$ would then be assigned to the 3-alaninate carboxyl carbons. The resonance at 183.85 ppm for *trans*(O_5)-[Rh(1,3-pddadp)]$^-$ is much closer to the glycinate carboxyl carbon value (183.54 ppm) for *trans*(O_5)-[Rh(eddadp)]$^-$ [22] than the other carboxylate carbon (179.96 ppm). Thus the d glycinate carbon should be assigned to 183.85 ppm and the c 3-alaninate carbon as 179.96 ppm. For *trans*(O_6)-[Co(1,3-pddadp)]$^-$ the two carboxylate carbons are close together (Table 2 and Fig. 3). Here the higher field resonance at 183.08 ppm is closer to that of the glycinate carboxyl carbon of *trans*(O_5)-[Co(eddadp)]$^-$ (182.54 ppm) [22], and very close to the center of the corresponding slightly split resonances (182.84, 182.71) assigned as glycinate carbons of *trans*(O_5O_6)-[Co(1,3-pddadp)]$^-$. The resonances associated with the glycinate carboxyl carbons are connected by dashed lines in Fig. 3 and the 3-alaninate carboxyl carbon resonances remain unconnected.

Electronic absorption spectra

The electronic absorption data for the two isomers (*trans*(O_5) and *trans*(O_5O_6)) of the hexadentate [Rh(1,3-pddadp)]$^-$ complex are shown in Table 3. For comparison, the corresponding values of the [Rh(1,3-pdta)]$^-$ complex ion [22, 31] are given also.

All complexes given in Table 3 contain 1,3-propanediamine backbone rings and their ϵ values are significantly lower than those for Rh(III) edta-type complexes with a five-membered diamine ring [11, 32]. Lower ϵ values might be expected because of the less rigid 1,3-pddadp (and 1,3-pdta) framework as was observed for Co(III) complexes [33–35].

All of the [Rh(edta-type)]$^-$ complexes studied [11, 31, 32] and complexes treated here (Table 3) show two components in the region of the lower energy $T_{1g}(O_h)$ absorption band. No splitting is apparent for the higher energy $T_{2g}(O_h)$ absorption band. Splitting of the first absorption bands is in accordance with a D_{4h} model. The $^1E_g^a(D_{4h})$ component of $^1T_{1g}(O_h)$ parentage is expected to 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 [36].

In general, absorption spectra of the Rh(III) complexes [11, 31, 32] (including complexes studied) are more intense than those of the corresponding Co(III) [7–9, 19, 33] and Cr(III) [13, 37] complexes. The greater effects of spin–orbit coupling of Rh(III) could very well result in broadening of absorption bands.

Acknowledgements

This work was supported by the US–Yugoslav Joint Fund for Scientific and Technological Cooperation from the National Science Foundation under Grant No. 8818818. Financial support was also received from the Serbian Ministry for Science and Technology.

References

1 R.H. Nuttall and D.M. Stalker, *Talanta, 24* (1977) 355.
2 T. Yamamoto, K. Mikata, K. Miyoshi and H. Yoneda, *Inorg. Chim. Acta, 150* (1988) 237.
3 H.A. Weakliem and J.L. Hoard, *J. Am. Chem. Soc., 81* (1959) 549.
4 K. Okamoto, T. Tsukihara, J. Hidaka and Y. Shimura, *Bull. Chem. Soc. Jpn., 51* (1978) 3534.
5 D.J. Radanović, *Coord. Chem. Rev., 54* (1984) 159.
6 M. Parvez, C. Maricondi, D.J. Radanović, M.I. Djuran and B.E. Douglas, *Inorg. Chim. Acta, 182* (1991) 177.
7 D.J. Radanović, S.R. Trifunović, M.S. Cvijović, C. Maricondi and B.E. Douglas, *Inorg. Chim. Acta, 196* (1992) 161.
8 W. Byers and B.E. Douglas, *Inorg. Chem., 11* (1972) 1470.
9 D.J. Radanović and B.E. Douglas, *Inorg. Chem., 14* (1975) 6.
10 T. Mizuta, T. Yamamoto, N. Shibata and K. Miyoshi, *Inorg. Chim. Acta, 169* (1990) 257.
11 D.J. Radanović, K. Gailey, M.I. Djuran and B.E. Douglas, *J. Coord. Chem., 10* (1980) 115.
12 R. Herak, Lj. Manojlović-Muir, M.I. Djuran and D.J. Radanović, *J. Chem. Soc., Dalton Trans.,* (1985) 861.
13 D.J. Radanović and B.E. Douglas, *J. Coord. Chem., 4* (1975) 191.
14 F.T. Helm, W.H. Watson, D.J. Radanović and B.E. Douglas, *Inorg. Chem., 16* (1977) 2351.
15 S. Kaizaki, M. Byakuno, M. Hayashi, J.I. Legg, K. Umakoshi and S. Ooi, *Inorg. Chem., 26* (1987) 2395.
16 M. Parvez, C. Maricondi, D.J. Radanović, S.R. Trifunović and B.E. Douglas, unpublished results.
17 S. Kaizaki and M. Hayashi, *J. Chem. Soc., Chem. Commun.,* (1988) 613; N. Sakagami, M. Hayashi and S. Kaizaki, *J. Chem. Soc., Dalton Trans.,* (1992) 285; N. Sakagami and S. Kaizaki, *J. Chem. Soc., Dalton Trans.,* (1992) 291.
18 T. Frank and R.F. Evilia, *Inorg. Chim. Acta, 171* (1990) 107.
19 J.A. Neal and N.J. Rose, *Inorg. Chem., 7* (1968) 2405; *12* (1973) 1226; L.M. Woodward, *Thesis,* University of Washington, 1970.
20 J.L. Sudmeier, A.J. Senzel and G.L. Blackmer, *Inorg. Chem., 10* (1971) 90.
21 P.F. Coleman, J.I. Legg and J. Steele, *Inorg. Chem., 9* (1970) 937.
22 K.D. Gailey, D.J. Radanović, M.I. Djuran and B.E. Douglas, *J. Coord. Chem., 8* (1978) 161.
23 D.J. Radanović, M.I. Djuran, V.D. Miletić, C. Maricondi and B.E. Douglas, *Inorg. Chem., 27* (1988) 1265.
24 D.J. Radanović, M.I. Djuran, T.S. Kostić, C. Maricondi and B.E. Douglas, *Inorg. Chim. Acta, 207* (1993) 111.
25 C. Maricondi, S. Utsuno, D.J. Radanović, S.R. Trifunović, J.E. Abola and B.E. Douglas, *Inorg. Chim. Acta, 142* (1988) 135.
26 K.D. Gailey and B.E. Douglas, *J. Coord. Chem., 5* (1975) 23.
27 K.D. Gailey, K. Igi and B.E. Douglas, *Inorg. Chem., 14* (1975) 2956.
28 O.W. Howarth, P. Moore and N. Winterton, *Inorg. Nucl. Chem. Lett., 10* (1974) 553.
29 O.W. Howarth, P. Moore and N. Winterton, *J. Chem. Soc., Dalton Trans.,* (1975) 360.
30 G.L. Blackmer and T.M. Vickrey, *J. Coord. Chem., 3* (1974) 225.
31 D.J. Radanović, M.I. Djuran, K. Gailey and B.E. Douglas, *J. Coord. Chem., 11* (1982) 247.
32 D.J. Radanović, M.I. Djuran and B.E. Douglas, *Inorg. Chem., 24* (1985) 4239.
33 C.W. Van Saun and B.E. Douglas, *Inorg. Chem., 8* (1969) 1145.
34 K. Igi and B.E. Douglas, *Inorg. Chem., 13* (1974) 425.
35 K. Igi and B.E. Douglas, *Inorg. Chim. Acta, 10* (1974) 109.
36 R.A.D. Wentworth and T.S. Piper, *Inorg. Chem., 4* (1965) 709.
37 D.J. Radanović, M.I. Djuran, M.M. Djorović and B.E. Douglas, *Inorg. Chim. Acta, 146* (1988) 199.