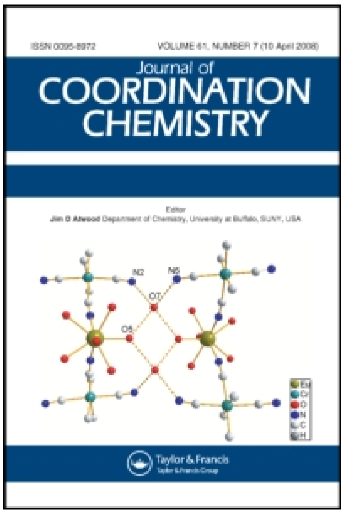

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Milan Strašák[a]; Ján Lučanský[a]; Pavol Novomeský[a]; Edita Dvořáková[a]
[a] Department of Analytical Chemistry, Faculty of Pharmacy, Comenius University, Bratislava, Czechoslovakia

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DIASTEREOSELECTIVITY IN METAL COMPLEXES OF SOME PHENYL-SUBSTITUTED ETHYLENE-DIAMINE-N,N,N′,N′-TETRAACETATE DERIVATIVES

MILAN STRAŠÁK*, JÁN LUČANSKÝ, PAVOL NOVOMESKÝ
and EDITA DVOŘÁKOVÁ

*Department of Analytical Chemistry, Faculty of Pharmacy, Comenius University,
832 32 Bratislava, Czechoslovakia.*

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Meso-1,2-diphenylethylenediamine-N,N,N′,N′-tetraacetic acid (*meso*-H_4DPHEDTA) and *rac*-1-phenylethylenediamine-N,N,N′,N′-tetraacetic acid (H_4PHEDTA) have been synthesized by the condensation of *meso*-1,2-diphenylethylenediamine or *R,S*-phenylethylenediamine, respectively, with bromoacetic acid and their cobalt(III) complexes prepared. The stereochemistry of both complexes was assigned on the basis of electronic, infrared, ^{1}H and ^{13}C NMR spectral data and elemental analyses. The stability constants of the chelating agents represented by monophenyl and both *meso*- and *rac*-diphenylderivatives of EDTA have been determined potentiometrically and polarographically for selected metal ions. It was found that these hexadentate ligands exhibit high diastereoselectivity in metal complexes. The factors determining stereochemistry and stabilities of these complexes are mainly intramolecular hydrophobic stacking interactions which cause different conformation of the central ethylenediamine E ring.

Keywords: Cobalt(III), hexadentates, chirality, stereoselectivity, stability constants

INTRODUCTION

The most thoroughly investigated multidentate ligands are certainly EDTA and its analogues. In general, these branched hexadentate ligands react in a very selective way. The earliest known compounds were derivatives of propylenediamine and diaminocyclohexane. Dwyer and Garvan demonstrated stereospecific coordination of both by forming cobalt(III) complexes.[1] This was due to the fact that the methyl group in the PDTA complex prefers an equatorial position and the cyclohexane diamine ring in the CyDTA complex prefers one particular conformation. Similarly, 2,3-diaminobutane-N,N,N′,N′-tetraacetate (DABTA) exhibits high diastereoselectivity in octahedral complexes and it was found that complexes of the racemic form generally exhibit higher stability than complexes of the *meso* form.[2–6] On the basis of a molecular mechanics treatment it has been postulated that the destabilizing factors in the *meso* form are primarily repulsive nonbonding interactions between the axial methyl group and hydrogen atoms of the out-of-plane R ring[7] and, consequently, the large steric strain in the *meso*-DABTA complexes can lead to opening of one chelate ring.[8] However, Kalina *et al.*,[9] recently reported the crystal and molecular structure of the K[Co(*meso*-DABTA)].2.5H_2O and showed that *meso*-DABTA acts as a hexadentate ligand; two main sources of strain in this complex arise from fused five-membered chelate rings and repulsion between axial methyl and in-plane G ring methylene hydrogen atoms.

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* Author for correspondence

In general, the introduction of an alkyl group in the 1- or 1,2-positions of EDTA results in an increase in stability constants. A similar effect may also be expected in the case of the phenyl substitution in EDTA. For 1,2-substitution, two diastereoisomers exist, *i.e.*, *rac* and *meso* forms. If one considers the steric effect of the phenyl group on the stability constants, it may be of interest to compare the stability constants of *rac*- and *meso*-DPHEDTA particularly in which phenyl groups appear to be the cause of unusual behaviour.

EXPERIMENTAL

Preparations

R,S-Phenylethylenediamine, (I)

The diamine dihydrochloride was synthesized from isoamyl alcohol *via* isoamyl nitrite, isonitrosoacetophenone, and phenylglyoxime successively.[10] The dihydrochloride was recrystallized from 60% (v/v) ethanol to give white needles which decompose above 265°C. *Anal.*; Calc. for $C_8H_{14}N_2Cl_2$: C, 45.95; H, 6.75; N, 13.40%. Found: C, 45.75; H, 6.69; N, 13.05%.

rac-*H_4PHEDTA.H_2O*

This ligand was synthesized by the alkaline condensation of bromoacetic acid with I by modification of a method used previously.[11] The crude product was purified by repeated crystallizations from hot water. The pure ligand is a white powder which decomposes at 132°C (monohydrate). Yield: 3.1 g (79%). *Anal.*; Calc. for $C_{16}H_{20}N_2O_8.H_2O$: C, 49.74; H, 5.74; N, 7.20%. Found: C, 49.41; H, 5.85; N, 7.22%.

Potassium(rac-*1-Phenylethylenediamine*-N,N,N'N'-*tetraacetato)cobaltate(III) sesquihydrate, K[Co(*rac-*PHEDTA)].1.5H_2O.*

To solution of potassium acetate (2.45 g, 25 mmol) in 33 ml of water were added *rac*-H_4PHEDTA.H_2O (1.93 g, 5 mmol), $Co(OAc)_2.4H_2O$ (1.24 g, 5 mmol), 0.1 g of activated charcoal and 1 cm^3 of 30% H_2O_2 diluted to 5 cm^3. The reaction mixture was air-oxidized for 24 h, then the activated carbon was filtered off. The wine-red solution was concentrated (about 10 cm^3) on a rotary evaporator and potassium acetate was removed by addition of absolute ethanol. After standing in a refrigerator overnight, the solution deposited acicular purple crystals of the complex (1.02 g, 45%), *Anal.*; Calc. for $KCoC_{16}H_{19}N_2O_{9.5}$: C, 39.27; H, 3.91; N, 5.72%. Found: C, 38.88; H, 3.98; N, 5.61%.

The partial resolution of the complex has been achieved by gel permeation chromatography on the molecular sieve Sephadex G-10 which has been used recently[12,13] for other cobalt(III) complexes.

meso-*1,2-Diphenylenediamine, (II)*

The synthesis of crude *meso*-diamine has been realized from benzaldehyde *via* *N*-benzoyl-*N'*-benzylidene-*meso*-1,2-diphenylenediamine after the procedure of Irvin and Parkins.[14] Of the two methods of purification, either extraction with ether with the extract dried over solid KOH and recrystallization from petroleum ether[14] or direct recrystallization from hot water, the second method gave the more satisfactory results. The yield was 76%, mp 120°C (reported[14] mp 120°C). *Anal.*; Calc. for $C_{14}H_{16}N_2$: C, 79.25; H, 7.60; N, 13.29%. Found: C, 79.34; H, 7.71; N, 13.20%.

meso-*$H_4DPHEDTA.H_2O$*

Bromoacetic acid (20.8 g, 0.15 mol) was dissolved in 20 cm^3 of water and neutralized to phenolphthalein with a solution of NaOH (12.0 g, 0.30 mol in 30 cm^3 of H_2O) under vigorous stirring while keeping the temperature about 0°C. After neutralization, another 2 cm^3 of NaOH were added. Into this solution **II** (5.3 g, 25 mmol) was added and the temperature of the mixture raised to 70°C. The pH of the reaction mixture was maintained at 9–10 by adding NaOH solution intermittently. The reaction slowed after 4 h when a white powder began to precipitate. 50 cm^3 of ethanol together with 2 cm^3 of NaOH solution were added and the temperature of the reaction mixture raised to 90°C (gentle reflux) for 10 h. Then the reaction mixture was cooled in an ice bath and acidified with 6M HCl to pH 1.5–2.0 when white microcrystals began to precipitate. After the mixture had been kept in an ice box during 1–3 days, precipitation was complete. The substance was purified by repeated conversion to the sodium salt and precipitation with HCl. The product was washed with cool water and with ethanol and dried under vacuum at 50°C. Mp 199°C (monohydrate). The yield was 2.67 g (24%). *Anal.*; Calc. for $C_{22}H_{24}N_2O_8.H_2O$: C, 57.13; H, 5.67; N, 6.05%. Found: C, 57.06; H, 5.57; N, 5.96%.

Potassium (meso-*1,2-diphenylethylenediamine*-N,N,N',N'-*tetraacetato)cobaltate(III) monohydrate, K[Co(*meso-*DPHEDTA)].H_2O*

The preparation and isolation of this complex was identical to that of the corresponding Co(III) complex with *rac*-PHEDTA except that 2.22 g (5 mmol) of *meso*-$H_4DPHEDTA.H_2O$ was used. The product was recrystallized from water and acicular violet crystals were obtained (1.60 g, 68.5%). *Anal.*; Calc. for $KCoC_{22}H_{22}N_2O_9$: C, 47.47; H, 3.74; N, 5.03%. Found: C, 47.49; H, 3.76; N, 4.92%.

Spectral Measurements

The visible absorption spectra were measured on a Specord UV VIS spectrophotometer using 1 and 3 cm cells. The concentrations of aqueous solutions were of the order of 10^{-3}M. CD spectra were recorded on a Jobin-Yvon Dichrographe III. Spectra were measured in 5 mm quartz cells in aqueous solution and concentrations were determined from absorption spectra. ^1H NMR spectra were obtained on a Bruker AM-300 spectrometer at 300.13 MHz, in D_2O, using TSP as internal reference. ^{13}C NMR spectra were recorded on a Jeol FX-100 spectrometer at 25.05 MHz. Samples were dissolved in D_2O and KOD was used for adjusting pH. A drop of *p*-dioxane was added as the internal reference ($\delta = 67.4$ ppm). Infrared spectra were measured on a Perkin Elmer 337 spectrometer. Spectra were obtained over the range 4000–400 cm^{-1} in KBr disks.

All spectral measurements were made at room temperature (*ca* 23°C).

Determination of Acid Dissociation Constants and Stability Constants

Acidobasic and chelate forming properties were studied potentiometrically and polarographically under standard conditions ($I = 0.10$ with KNO_3, $T = 293$ K). The values for the dissociation constants of the ligands from potentiometric neutralization titration curves (10^{-3}M) were evaluated on a Hewlett-Packard HP-97 calculator with an in-house programme. A PHM-4 fy Radiometer pH-meter with glass and SCE electrodes was used.

For determination of chelate stability constants for alkaline earth ions, the direct pH titration method was employed; the corresponding metal ions in equimolar and tenfold concentrations relative to the ligand concentration were used. In the case of the transition metal ions, the chelate stability constants were determined by a competitive reaction with tren as the auxiliary ligand.

The stability constants for Hg(II) were determined by polarographic evaluation of $E_{\frac{1}{2}} = f(pH)$; PA-2, a polarograph analyzer (Laboratorni přistroje Prague) was used.

RESULTS AND DISCUSSION

All chelate stability constants together with dissociation constants are summarized in Table I. As is shown herein, the acid dissociations of the first two steps are quite different from those of the last two steps. Thus, aryl–EDTA analogues are expected to exist as zwitter ions in an aqueous solution as in the case of EDTA alone, where the acid dissociation of the first two and the last two steps correspond to the dissociation of carboxylic protons and imino protons, respectively.

TABLE I
Chelate stability constants for aryl–EDTA derivatives for selected metal ions.

Metal ion	log K			
	rac-PHEDTA	*meso*-DPHEDTA	*rac*-DPHEDTA[15]	EDTA[16]
Mg(II)	9.40 ± 0.02	4.66 ± 0.01	10.33 ± 0.03	8.69
Ca(II)	11.25 ± 0.03	5.67 ± 0.02	12.09 ± 0.02	10.69
Sr(II)	9.32 ± 0.02	4.05 ± 0.01	9.66 ± 0.02	8.63
Ba(II)	8.39 ± 0.02	3.20 ± 0.01	8.36 ± 0.02	7.76
Mn(II)	14.58 ± 0.12		15.10 ± 0.10	14.04
Zn(II)	17.05 ± 0.10	11.22 ± 0.06	17.36 ± 0.10	16.50
Co(II)	16.91 ± 0.10	11.70 ± 0.07	17.30 ± 0.11	16.31
Cd(II)	17.14 ± 0.03	12.93 ± 0.02	17.63 ± 0.03	16.46
Pb(II)	18.28 ± 0.12	12.57 ± 0.08		18.04
Cu(II)	19.30 ± 0.03	14.82 ± 0.03	19.81 ± 0.03	18.96
Hg(II)	22.06 ± 0.18	17.50 ± 0.10	23.04 ± 0.12	21.80
H^+ pK_1	2.10 ± 0.01	2.00 ± 0.06	2.44 ± 0.06	2.00
pK_2	3.23 ± 0.03	2.80 ± 0.01	3.76 ± 0.01	2.67
pK_3	5.42 ± 0.02	6.18 ± 0.02	5.44 ± 0.02	6.16
pK_4	9.95 ± 0.02	9.98 ± 0.02	9.97 ± 0.02	10.26

The order of the stability constants for these ligands for metal ions, which are shown in Table I, follows the Irving–Williams stability order, as is the case with other aminopolycarboxylate ligands. It is obvious that the introduction of the phenyl group in the 1- or 1,2-positions of EDTA results, in the case of *rac*-PHEDTA and *rac*-DPHEDTA, in an increase in stability constants. One of the most significant results with all investigated metal ions is the very large difference for stability constants between diastereoisomeric *rac*- and *meso*-DPHEDTA as well as *rac*-PHEDTA and *meso*-DPHEDTA. These vary from between 5 to 7 log K units.

From detailed examination of molecular models of the Co(III) complexes with the abovementioned ligands we conclude that ring conformational effects of the ethylenediamine backbone contribute mainly to the overall stability of these complexes. It was recognized recently that the chelate E rings of similar[9,17] as well as these[18] ligands could not adopt a planar structure. In the racemic ligands both phenyl groups (for PHEDTA one phenyl group) are placed in equatorial position A in Figure 1. In the *gauche* conformation of the E ring of the *meso*-complex one phenyl group necessarily adopts an axial position (B in Figure 1) while both phenyl groups are placed in an equatorial position only in the unstable envelope conformation with the phenyl groups in an eclipsed position (C in Figure 1). The assumption of an envelope conformation for the central diamine chelate ring of *meso*-DPHEDTA could explain the large stability difference in metal complexes, given in Table I for comparison, with respect to *rac*-DPHEDTA and PHEDTA. Whereas *rac*-DPHEDTA can react as a hexadentate ligand in a similar way to EDTA, *meso*-DPHEDTA would then be only pentadentate; one carboxylate group should point away from the coordination centre.

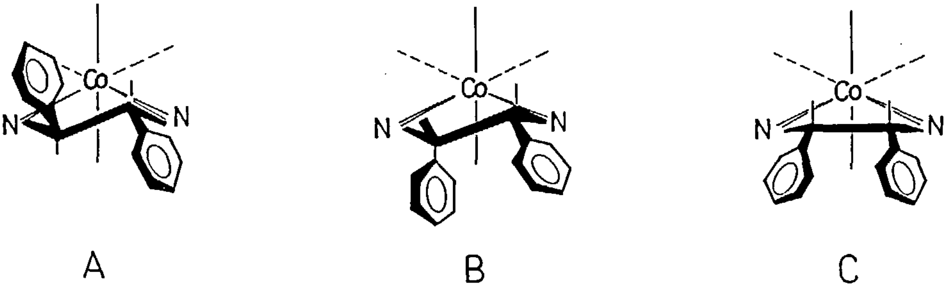

FIGURE 1 A schematic drawing of the three possible conformations of the central E ring in racemic and *meso*-DPHEDTA.

Infrared Spectra

Infrared spectroscopy can be helpful for distinguishing between penta- and hexacoordination of aryl–EDTA analogues. The IR spectra of complexes containing pentadentate ligands exhibit two carbonyl stretching bands while only one carbonyl stretching band could appear in the IR spectrum of the hexadentate species.[19] Because only one νCOO^{-}_{as} band at 1650 cm^{-1} is observed for the [Co(*meso*-DPHEDTA)]$^-$ complex, it is evident that *meso*-DPHEDTA acts as a hexadentate ligand. In addition, according to Sawyer and Paulsen,[20] we may conclude that the Co–O bond is rather covalent such as the COO$^-$ stretching band lies between 1660 and 1630 cm^{-1}. The same is true for the Co–N bond since the NH stretch is completely absent in the IR spectrum of [Co(*meso*-DPHEDTA)]$^-$. Similarly, the corresponding COO$^-$ stretching vibration of [Co(*rac*-PHEDTA)]$^-$ at 1645 cm^{-1} confirms the hexadentate character of *rac*-PHEDTA.

Absorption and Circular Dichroism Spectra

Absorption and CD data of studied complexes are listed in Table II.

The spectra of $[Co(aryl\text{-}EDTA)]^-$ complexes are similar to those of the previously described $[Co(EDTA)]^-$ ion and related compounds. The absorption maxima are shifted toward the red and the intensities are less than for $[Co(EDTA)]^-$. Compounds of this type have been treated as CoN_2O_4 species, the chelate rings being ignored, and with approximate C_2 symmetry. Therefore, the spectrochemical parameter 10Dq, which measures the energy difference between the e_g and t_{2g} orbitals, and the interelectronic repulsion parameters B and C (Racah parameters) are for all complexes practically equal. The rather covalent character of both Co–N and Co–O bands in these complexes, is also supported by the values of the nephelauxetic ratio, $\beta = B_{complex}/B_{gas}$, which fall in the range 0.51–0.54. These values indicate that cloud expansion is large.

TABLE II
Absorption and circular dichroism data for $[Co(EDTA)]^-$ and related compounds.

	absorption		CD				
Compound[a]	$10^{-3}\tilde{\nu}$, cm^{-1}		$10^{-3}\tilde{\nu}$, cm^{-1}		10Dq[b]	B[b], cm^{-1}	ref.
Λ-K[Co(EDTA)]. $2H_2O$	18.60	347	17.30	+1.50	20.15	609	21
			19.83	−0.76			
	26.65	246	24.05	+0.29			
			27.90	+0.33			
Λ-K[Co(ss-DPHEDTA)]. $4H_2O$	18.42	295	16.81	+0.95	19.96	583	22
			18.80	−2.57			
	26.18	219	24.10	+0.43			
			27.78	+0.42			
Δ-K[Co(PHEDTA)]. $1.5H_2O$	18.17	219	16.95	−0.26	19.73	591	this work
			19.05	+0.68			
	26.00	181	25.64	+0.12			
			28.30	+0.14			
Λ-Isomer	18.17	219	16.95	+0.17	19.73	591	this work
			18.94	−0.23			
	26.00	181	23.81	+0.07			
			27.78	+0.06			
K[Co(*meso*-DPHEDTA)]. H_2O	18.33	289			19.86	574	this work
	26.00	216					

[a] The optical isomers are designated the Λ and Δ absolute configuration, according to the convention suggested by IUPAC.[23] [b] Calculated according to procedure in ref. 24.

Partial resolution of $[Co(\textit{rac}\text{-}PHEDTA)]^-$ has been achieved on Sephadex G-10 simultaneously with the desalting procedure.[12,13] The degree of resolution achievable on one passage through the column is exemplified by the data in Table II. Although no splitting can be detected in either absorption band of $[Co(\textit{rac}\text{-}PHEDTA]^-$, the CD curves clearly identify two components for the long wavelength ${}^1A_{1g} \rightarrow {}^1T_{1g}$ band. The positions of the CD maxima are remarkably constant for the phenyl substituted EDTA complexes and suggest that they derive from *cis*-$[CoN_2O_4]^-$ tetragonally distorted chromophores.

^{13}C *NMR Spectra*

The proton-decoupled ^{13}C NMR cofirmed the structures of *rac*-H_4PHEDTA, *meso*-H_4DPHEDTA and their Co(III) complexes. Table III gives chemical shift values. The ^{13}C spectra of [Co(EDTA)]$^-$, [Co(*rac*-PHEDTA)]$^-$ and [Co(*meso*-PHEDTA)]$^-$ are all simple thus indicating that the complexes are hexadentate. Spectra of the latter two exhibit four signals for carboxylate as well as neighbouring methylene carbons due to the formation of four nonequivalent glycinate rings. The four downfield carboxylate signals are assigned to the G and R rings according to the chemical shift order observed for those of [Co(EDTA)]$^-$. Only one signal for the two *ortho* carbons and another for the two *meta* carbons of each phenyl group of *meso*-DPHEDTA complex indicate rotation of these groups.

TABLE III
^{13}C NMR chemical shift data (ppm) for EDTA^{4-}, *rac*-PHEDTA^{4-}, *meso*-DPHEDTA^{4-} and their Co(III) complexes.

Compound	glycinate ring	$-COO$	$-CH_2-CO$	$-CH_2-N$	$-CH-N$	Phe
EDTA^{4-} [a]		180.3	59.7	52.6		
[Co(EDTA)]$^-$ [b]	R	183.6	66.6	64.6		
	G	183.0	66.4			
rac-PHEDTA^{4-} [a]		180.3	60.0 55.9	57.2	62.3	137.1, 130.5, 129.1, 128.6
rac-HPHEDTA^{3-} [c]		177.1 174.2	57.6 55.5	55.3	62.3	132.6, 130.6, 130.3, 129.8
[Co(*rac*-PHEDTA)]$^-$	R_1	182.9	65.8	58.6	74.2	131.7, 130.5, 129.8, 129.1
	R_2	183.4	66.8			
	G_1	182.5	66.5			
	G_2	182.3	66.2			
meso-DPHEDTA^{4-} [a]		179.5	56.2		65.6	136.7, 131.2, 128.8, 128.4
meso-HDPHEDTA^{3-} [c]		174.9	55.8		66.5	131.3, 130.9, 130.2
[Co(*meso*-DPHEDTA)]$^-$	R_1	183.6	73.1		86.9	131.6, 130.6,
	R_2	182.9	68.5		78.9	129.9, 129.3
	G_1	182.1	63.4			132.5, 131.8,
	G_2	181.9	61.5			131.1, 130.8

[a] Solution pH = 12.5. [b] Data taken from ref. 25. [c] Solution pH = 7.8.

In [Co(*rac*-PHEDTA)]$^-$, the R_1-ring methylene carbon resonance is upfield from that of the G-ring methylene carbons. This is an indication of a steric compression shift of the R_1-ring methylene carbon resonance since, upon complexation of *rac*-PHEDTA, the backbone phenyl group stereospecifically interacts with the R_1-ring methylene protons (see discussion in the next paragraph).

^1H *NMR Spectra*

^1H NMR spectra are suitable to distinguish geometrical isomers of Co(III) complexes. The methylene protons of the glycinate rings of both [Co(*rac*-PHEDTA)]$^-$ and [Co(*meso*-DPHEDTA)]$^-$ show four well-resolved AB patterns (Figure 2).

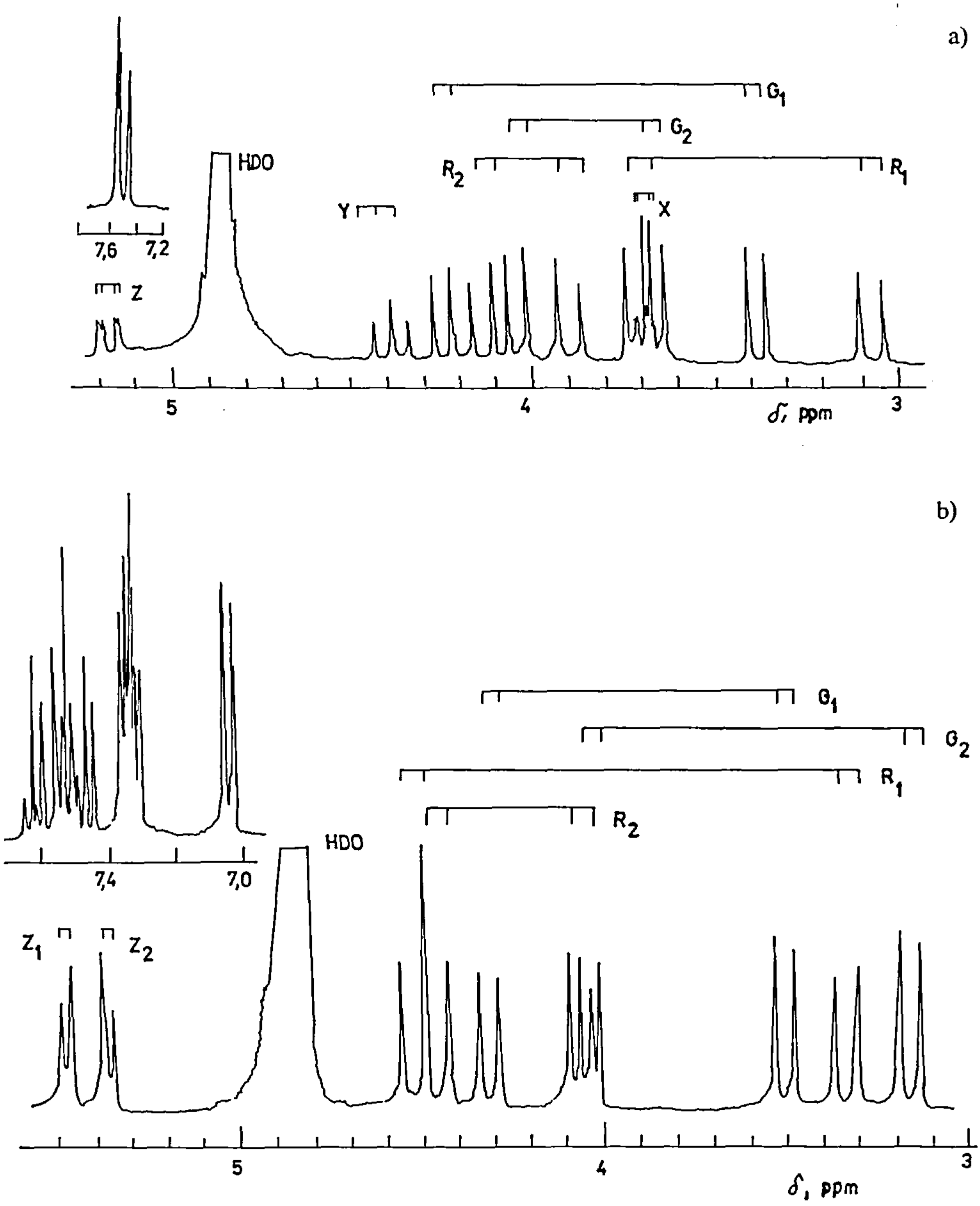

FIGURE 2 ^{1}H NMR spectra of a) [Co(*rac*-PHEDTA)]$^-$ and b) [Co(*meso*-DPHEDTA)]$^-$. R_1, R_2, G_1, and G_2 are signals from the methylene protons of the glycinate rings and X, Y, Z from the protons of the diamine E ring.

Differences in chemical shifts of the methylene protons of geometrically nonequivalent glycinate rings in Co(III)-aminopolycarboxylates have been explained by the influence of Co(III) anisotropy,[25,26] but in the studied complexes, ring currents (of the phenyl groups) can also influence chemical shifts. Geminal coupling constants for these protons fall into two categories, those in vicinity of 16 Hz for glycinate G rings and those in the vicinity of 18 Hz for glycinate R rings.[27] Magnitudes of the geminal coupling constant J_{AB} are influenced by distortion of valence angles in the glycinate rings. Geminal coupling constants of [Co(*rac*-PHEDTA)]$^-$ and [Co(*meso*-DPHEDTA)]$^-$ (Table IV) are consistent with the fact that G rings are more strained than R rings.

TABLE IV
^{1}H NMR data for the methylene protons of the glycinate rings of [Co(*rac*-PHEDTA)]$^-$ and [Co(*meso*-DPHEDTA)]$^-$·

Type of ring	[Co(*rac*-PHEDTA)]$^-$			[Co(*meso*-DPHEDTA)]$^-$		
	δ_A, ppm	δ_B, ppm	J_{AB}, Hz	δ_A, ppm	δ_B, ppm	J_{AB}, Hz
R_1	3.71	3.07	18.8	4.52	3.34	19.1
R_2	4.13	3.90	18.4	4.46	4.06	18.5
G_1	4.25	3.39	15.3	4.31	3.51	15.3
G_2	4.04	3.67	15.7	4.03	3.16	15.7

From the ^{13}C NMR spectra it is obvious that the phenyl groups can rotate partially. However, we observe in the ^{1}H NMR spectrum of [Co(*rac*-PHEDTA)]$^-$ that the R_1-ring methylene proton resonances are significantly upfield from those of the R_2-ring. Such an upfield shift is due to the magnetic anisotropy of the aromatic ring systems and indicates that the proton is oriented towards the face of an aromatic system. Thus, the doublet at 3.07 ppm is assigned to the axial H_B proton which is located within the shielding range of the benzene ring. Similar assignments are made for the G_1 ring AB pattern for the doublet centred at 3.39 ppm.

The conformation of the diamine E ring of both complexes can be determined from vicinal ^{1}H–^{1}H coupling constants. Multiplets due to the diamine protons are denoted as X, Y, and Z (Figure 2a). Z is due to a methine proton and X and Y to nonequivalent methylene protons according to signals in the *R*-phenylethylenediamine complex.[28] Chemical shifts and coupling constants are as follows:

$$\delta_X = 3.69\,\text{ppm} \qquad \delta_Y = 4.39\,\text{ppm} \qquad \delta_Z = 5.17\,\text{ppm}$$

$$^2J_{XY} = 13.7\,\text{Hz} \qquad ^3J_{XZ} = 13.8\,\text{Hz} \qquad ^3J_{XZ} = 3.2\,\text{Hz}$$

Two conformers can exist for this E ring: λ- and δ-*gauche* with the pheynl group equatorial and axial, respectively (Figure 3). The λ-*gauche* form can provide two kinds of vicinal coupling: *trans* and *gauche*, whereas the δ-*gauche* gives only one kind (*gauche*). Vicinal coupling constants are strongly dependent on the dihedral angle so that $^3J_{YZ}$ corresponds to the *trans* and $^3J_{XZ}$ to the *gauche* ^{1}H–^{1}H coupling, respectively. These results indicate that the E ring of [Co(*rac*-PHEDTA)]$^-$ has the λ-*gauche* conformation.

From the multiplet for the methine diamine protons of [Co(*meso*-DPHEDTA)]$^-$, denoted as Z1 and Z2 (Figure 2b), the following parameters were calculated:

$$\delta_{Z1} = 5.36\,\text{ppm} \qquad \delta_{Z2} = 5.48\,\text{ppm} \qquad ^3J = 7.6\,\text{Hz}$$

Because vicinal coupling constants decrease with increasing electronegativity of the substituent(s) attached, one predicts $^3J < {}^3J_{XZ} = 3.2$ Hz for the *gauche* conformation of the [Co(*meso*-DPHEDTA)]$^-$ E ring. The value of ^3J indicates a dihedral angle with methine protons significantly smaller than 60°C. Hence, the central E ring has the distorted envelope conformation with partially rotated phenyl groups in an equilibrium between synperiplanar and synclinal positions ($\theta \approx 30°$). This conformation is supported by the values of chemical shifts in Table IV and is stabilized by intramolecular aromatic ring stacking.

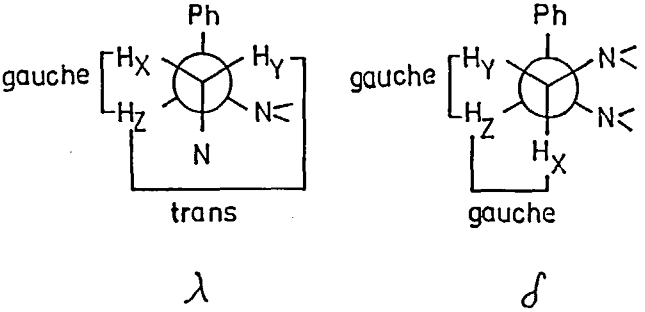

FIGURE 3 Two possible conformers of the [Co(*rac*-PHEDTA)]$^-$ diamine E ring and representation of ^1H-^1H vicinal coupling.

From steric considerations it is obvious that the most important factor in determining stereochemistry and therefore stability of these complexes is the conformation of the central E ring. Puckering is influenced by the strong tendency of the phenyl group to occupy an equatorial position. The energy difference between the more stable *gauche* conformation and the rather unstable envelope conformation may be the main reason for the difference between the formation constants of metal complexes with the racemic and *meso* aryl derivatives of EDTA. Just as with alkyl derivatives of EDTA, the aryl analogues also coordinate stereospecifically because the benzene rings prefer these equatorial positions.

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