by the amide oxygens in the inner coordination sphere of the complex. We are aware of only one other structurally characterized lanthanide complex with bonds to amide oyxgen atoms, namely the erbium complex[10] **3** (Figure 3). In complex **3** the bond lengths d(Er–O) for the two amide oxygens are 2.326 (6) and 2.267 (8) Å, both substantially shorter than the d(Er–O) of 2.412 Å predicted by ionic radii.[9]

This trend of short metal–oxygen bonds and long metal–nitrogen bonds is seen in a variety of polyaminopolycarboxylate complexes (Table IV).[11-19] With the lanthanide–EDTA structures used as a basis for comparison (entries 1–8), it is seen that the average Ln–O bond is 0.0321 (14) Å shorter than that calculated from ionic radii[9] while the average Ln–N bond is 0.087 (12) Å longer than calculated. In an examination of other lanthanide polyaminopolycarboxylate complexes (entries 9–13), only complex 2 (entry 13) and the Nd(DTPA)(H_2O) complex (entry 10) have Ln–N interactions significantly longer than expected (using a 3σ criterion) and only complex **2** and the Tb(TETA) complex (entry 12) have Ln–O interactions significantly shorter than expected. Although the complexes listed in Table IV are similar, the range of bond variation seen in complex **2** is greater than in any of the comparisons.

Chromatographic and solution equilibria behavior of aqueous Gd(DTPA-BEA) is consistent with a neutral, discrete complex. The T_1 proton relaxivity of the complex (4.8 mM^{-1} s^{-1}) is in the range indicative of Gd^{3+} ions with one coordinated water molecule.[1] The ligand comprises the remaining eight coordination sites (three amines, three carboxylates, and two carboxamides). This participation of amide or ester groups in the coordination of DTPA derivatives in aqueous solution has also been predicted from nuclear magnetic resonance dispersion studies.[20] The nine-coordinate geometry of Gd(III), which includes one water molecule, seems likely to be a key part of the promising contrast agent properties of this complex. The present work demonstrates the utility of amides as coordinating ligands for lanthanide complexes. This is particularly noteworthy in that amides are neutral chelating groups at physiological pH. Thus, a Gd(DTPA-bis(amide)) complex such as **2** possesses no net charge. As described in the Introduction, this leads to a 3-fold reduction in osmolality relative to salts of Gd DTPA dianions. This has profound implications for the physiological acceptance of the resulting complexes as contrast agents for MRI.[21]

Acknowledgment. We thank Dr. F. Ekkehardt Hahn for providing crystals of **2**. We thank Dr. Fred Hollander for help with the X-ray crystal structure. That portion of the research performed at UCB was supported by a grant from Salutar, Inc.

Supplementary Material Available: Tables of positional parameters (Table S-V), anisotropic thermal parameters (Table S-VI), rms amplitudes of thermal vibration (Table S-VII), and bond lengths and angles for **2** (Table S-IX) and an ORTEP diagram of **2** with the lattice water molecules (Figure S-4) (9 pages); a table of observed and calculated structure factors for **2** (Table S-VIII) (22 pages). Ordering information is given on any current masthead page.

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(11) Hoard, J. L.; Lee, B.; Lind, M. D. *J. Am. Chem. Soc.* **1965**, *87*, 1612–1613.
(12) Templeton, L. K.; Templeton, D. H.; Zalkin, A.; Ruben, H. W. *Acta Crystallogr., Sect. B* **1982**, *38*, 2155.
(13) Templeton, L. K.; Templeton, D. H.; Zalkin, A. *Acta Crystallogr., Sect. C* **1985**, *41*, 355–358.
(14) Polynova, T. N.; Filippova, T. V.; Porai-Koshits, M. A. *Koord. Khim.* **1986**, *12*, 409–414.
(15) Nassimbeni, L. R.; Wright, M. R. W.; VanNiekerk, J. C.; McCallum, P. A. *Acta Crystallogr., Sect. B* **1979**, *35*, 1341–1345.
(16) Gries, H.; Miklantz, H. *Physiol. Chem. Phys. Med. NMR* **1984**, *16*, 105.
(17) Stezowski, J. J.; Hoard, J. L. *Isr. J. Chem.* **1984**, *24*, 323–334.
(18) Spirlet, M.-R.; Rebizant, J.; Desreux, J. F.; Loncin, M.-F. *Inorg. Chem.* **1984**, *23*, 359–363.
(19) Spirlet, M.-R.; Rebizant, J.; Loncin, M.-F.; Desreux, J. F. *Inorg. Chem.* **1984**, *23*, 4278–4283.
(20) Geraldes, C. F. G.; Sherry, A. D.; Cacheris, W. P.; Kuan, K.-T.; Brown, R. D., III; Koenig, S. H.; Spiller, M. *Magn. Reson. Med.* **1988**, *8*, 191–199.
(21) O'Toole, M.; VanWagoner, M.; Broschart, J. L.; Prasad, R.; Leese, P. T.; Quay, S. C. *Program and Abstracts, SMRI 1989*; *Seventh Annual Meeting of the Society for Magnetic Resonance Imaging*; Society for Magnetic Resonance Imaging: Oak Brook, IL, 1989. Carvlin, M. J.; Muraki, A. S.; Francisco, J.; Rocklage, S. M.; Quay, S. *Scientific Program, 1988 Annual Meeting of the Radiological Society of North America*; Radiological Society of North America: Oak Brook, IL, 1988; Abstract No. 477.

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Geometrical Isomerism of Mixed Tris(amino carboxylato)cobalt(III) Complexes Containing Glycinato and β-Alaninato Ligands. Crystal Structure of *trans*(O_5)-(β-Alaninato)bis(glycinato)cobalt(III) Trihydrate

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The geometry of six meridional isomers of tris(amino carboxylato)cobalt(III) complexes, containing glycinato and β-alaninato ligands, has been determined by considering the influence of the magnetic anisotropy of the cobalt(III) atom on the NMR chemical shifts of the methylene protons. A new synthesis, column chromatography, and electronic absorption spectra of these complexes are presented and discussed. The crystal structure analysis of *trans*(O_5)-(β-alaninato)bis(glycinato)cobalt(III) trihydrate confirmed the NMR deduction. The compound crystallizes in the monoclinic space group $P2_1/c$, with a = 8.958 (2) Å, b = 15.836 (4) Å, c = 10.234 (2) Å, β = 111.55 (3)°, and Z = 4. The structure consists of enantiomeric pairs of (β-alaninato)bis(glycinato)cobalt(III) complex molecules and molecules of water. In the complex molecule, the coordination around cobalt is distorted octahedral. The six-membered chelate ring adopts a twist-boat conformation, and the five-membered chelate rings adopt puckered conformations. The presence of relatively weak hydrogen bonds between the molecules of the complex and water is also established.

Introduction

A series of mixed tris(amino carboxylato)cobalt(III) complexes containing glycinato (Gly) and β-alaninato (β-Ala) ligands consists of eight complexes. They all belong to the CoN_3O_3 type of complexes and possess facial or meridional configuration. However, for the meridional configuration the chelate ligand positions are not equivalent and a redistribution of glycinato and β-alaninato chelate ligands generates three geometrical isomers (Chart I).

The synthesis of one of the tris(amino carboxylato)cobalt(III) complexes containing both α and β-amino carboxylato chelates

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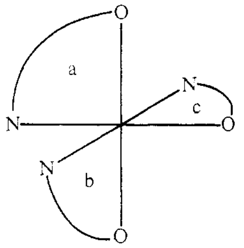
Table I. Order of Elution and Composition of the Investigated Mixed β-Alaninato/Glycinato Tris(amino carboxylato)cobalt(III) Complexes

order of elution[a] of complexes	eluted complexes	color and crystalline form	elemental anal.: % found (calcd)		
			C	H	N
III	*mer*-$[Co(\beta\text{-Ala})(Gly)_2]\cdot 2H_2O$	violet needles	26.62 (26.83)	4.68 (5.15)	13.60 (13.42)
IV	*mer*-$[Co(\beta\text{-Ala})(Gly)_2]$	violet prisms	28.92 (28.47)	4.51 (4.78)	14.16 (14.24)
V	*mer*-$[Co(\beta\text{-Ala})(Gly)_2]\cdot 3H_2O$	violet prisms	24.31 (24.06)	5.64 (5.77)	12.35 (12.04)
VI	*mer*-$[Co(\beta\text{-Ala})_2(Gly)]$	violet rods	30.88 (31.06)	4.87 (5.22)	13.50 (13.60)
VII	*fac*-$[Co(\beta\text{-Ala})(Gly)_2]\cdot {}^1/_2H_2O$	red prisms	27.52 (27.63)	4.66 (4.97)	13.49 (13.82)
VIII	*mer*-$[Co(\beta\text{-Ala})_2(Gly)]\cdot 2H_2O$	violet needles	27.63 (27.80)	6.09 (5.84)	12.11 (12.18)
IX	*mer*-$[Co(\beta\text{-Ala})_2(Gly)]\cdot 3.5H_2O$	violet needles	25.73 (25.81)	5.90 (6.23)	11.71 (11.29)
XI	fac-$[Co(\beta\text{-Ala})_2(Gly)]$	red prisms	31.31 (31.96)	5.69 (5.22)	13.71 (13.60)

[a] The complexes eluted as I, II, X, and XII are *mer*-$[Co(Gly)_3]$, *fac*-$[Co(Gly)_3]$, *mer*-$[Co(\beta\text{-Ala})_3]$, and *fac*-$[Co(\beta\text{-Ala})_3]$, respectively.

Chart I. Six Meridional Isomers Generated by Redistribution of Glycinato and β-Alaninato Ligands over Three Nonequivalent Chelate Ligand Positions (a, b, c)[a]



Position of the chelate ligands		Meridional isomer
Gly	β-Ala	
a,c	b	trans(N5,O5)
b,c	a	trans(N5)
a,b	c	trans(O5)
b	a,c	trans(N6,O6)
a	b,c	trans(N6)
c	a,b	trans(O6)

[a] The isomers are labeled by trans pairs of ligators from the ring of the same kind (the ligator index denotes the chelate ring size).

has been reported by Ĉelap and Paunović.[1] Kostić and Niketić[2] communicated the synthesis of all members of the series considered here. However, the geometrical isomerism of the meridional complexes has not been determined, although the electronic absorption[3] and carbon-13 NMR spectra[4] of their solutions have been discussed.

Continuing this work, we undertook to determine geometrical isomerism of mixed tris(amino carboxylato)cobalt(III) complexes by applying proton NMR spectroscopy. The chemical shifts of the methylene protons of the amino carboxylato chelate ring are strongly influenced by cobalt(III) magnetic anisotropy.[5,6] This influence is different for each chelate ring position (a, b, or c, Chart I), and it should therefore allow assignment of geometrical isomerism of the meridional isomers. To confirm validity of such assignments, we have determined the crystal structure of one of the isomers. A new synthetic procedure affording substances used in this work has been developed.

Experimental Section

Synthesis. A 0.02-mol sample of freshly precipitated basic cobalt(III) carbonate (obtained by mixing dilute solutions of 4.76 g of $CoCl_2\cdot 6H_2O$ and 2.5 g of Na_2CO_3) was added to a 50-cm^3 solution of 4.5 g (0.05 mol) of β-alanine and 2.5 g (0.02 mol) of glycine, and the mixture was stirred intensively until complete dissolution of carbonate. During the next 10 min, 10 cm^3 of 30% H_2O_2 solution was added with stirring. The obtained dark solution was heated on a steam bath for 30 min; 1 cm^3 of concentrated HNO_3 was then added, and this solution was heated for 15 min and left to stand at room temperature for 2 h. A small amount of a violet unidentified solid precipitated and was filtered off by suction. The filtrate was transferred to an ion-exchange column (Dowex 50W, 1-X8, 200 mesh, o.d. = 4.6 cm, height = 12 cm) prepared in the hydrogen form. The elution was performed with water, and the first 1.5 dm^3 contained complexes I–V (see Table I). During this time a dark blue band (complex VI), followed by a red one (complex VII), was formed at the bottom of the column, and these were also eluted with water. The elution caused the appearance of new zones, producing four new eluates (complexes VIII–XI). The eluates containing complexes VI–XI were of different volumes (the eluate of slowly eluted complex XI amounted to 10 L). Each eluate was immediately concentrated (at 40–50 °C) under reduced pressure to 10 cm^3, to which 10 cm^3 of ethanol was added, and this solution was left in a refrigerator overnight. The precipitated crystals were filtered off, and the filtrate was concentrated (under reduced pressure) to half of its volume; up to 20 cm^3 of ethanol was then added, and again the solution was left in a refrigerator overnight. This procedure was repeated until practically the entire content of each fraction was precipitated in the crystalline form.

Table II. Crystallographic Data for *trans*(O_5)-(β-Alaninato)bis(glycinato)cobalt(III) Trihydrate

empirical formula	$C_7H_{20}N_3O_9Co$
fw	349
cryst syst	monoclinic
cryst size, mm	0.28 × 0.13 × 0.16
space group	$P2_1/c$
systematic absences	$h0l$, l odd; $0k0$, k odd
a, Å	8.958 (2)
b, Å	15.836 (4)
c, Å	10.234 (2)
β, deg	111.55 (3)
Z	4
V, Å^3	1350.3
d_{calcd}, g/cm^3	1.71
radiation (λ, Å)	Mo Kα, 0.71069
μ, cm^{-1}	13.12
scan method	$\theta/2\theta$
scan rate, deg min^{-1}	0.7–5.5
collection range, deg	$2 \le \theta \le 30$
no. of data collected	2830
total no. of unique data	1930
no. of params refined	239
R	0.027
R_w	0.036

This first eluate (of 1.5 dm^3) was concentrated under reduced pressure to 20 cm^3 and transferred to an ion-exchange column (Dowex 50W, 1-X8, 200 mesh, o.d. = 3.6 cm, height = 30 cm) prepared in the hydrogen form. The elution commenced with water. The first 150 cm^3 of blue eluate contained anionic species. The next 1 dm^3 of eluate contained *mer*- and *fac*-$[Co(Gly)_3]$. In the course of subsequent elution, three new bands appeared in the column (complexes III–V). They were also eluted with water, and the complexes were isolated by following the procedure described above.

The yields of the isolated complexes varied from 3 to 6%, and for each complex a satisfactory elemental analysis was obtained (Table I).

^{1}H NMR Spectra. The ^{1}H NMR spectra were recorded on a Varian FT-80A spectrometer at room temperature, using DSS as an internal standard. For each complex a D_2O solution (about 1 × 10^2 mol/dm^3) was used.

Electronic Absorption Spectra. The spectra were recorded on a Varian Super Scan spectrophotometer at room temperature. Aqueous solutions of the complexes (1 × 10^3 mol/dm^3) were used.

X-ray Crystal Structure Analysis of *trans*(O_5)-(β-Alaninato)bis(glycinato)cobalt(III) Trihydrate. All crystallographic measurements were made at room temperature (~23 °C), with a violet prismatic crystal elongated along the crystallographic axis *a*.

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(1) Ĉelap, M. B.; Paunović, D. S. *J. Coord. Chem.* **1977**, *7*, 85.
(2) Kostić, N. M.; Niketić, S. R. *J. Chem. Soc., Chem. Commun.* **1977**, 676.
(3) Niketić, S. R.; Urland, W. *Polyhedron* **1987**, *6*, 947.
(4) Kostić, N. M.; Niketić, S. R. Paper presented at the 21st Meeting of the Serbian Chemical Society, Belgrade, 1978.
(5) Yoneda, H.; Sakaguchi, U.; Nakashima, Y. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 209.
(6) Juranić, N.; Ĉelap, M. B.; Vučelić, D.; Malinar, M. J.; Radivojša, P. N. *Inorg. Chem.* **1980**, *19*, 802.

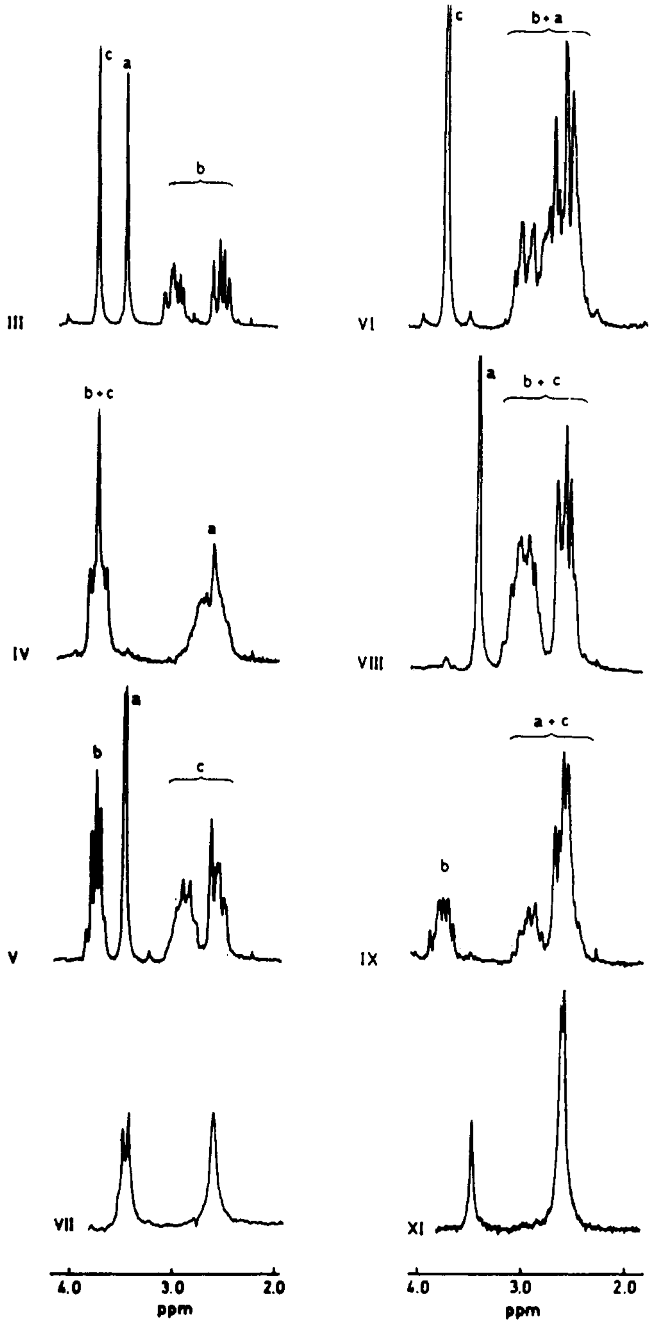

Figure 1. ^{1}H NMR spectra, in the methylene proton region, of the mixed β-alaninato/glycinato tris(amino carboxylato)cobalt(III) facial isomers VII [(β-alaninato)bis(glycinato)cobalt(III)], and XI [bis(β-alaninato)-(glycinato)cobalt(III)], and meridional isomers III [trans(N_5,O_5)], IV [trans(N_5)], V [trans(O_5)], VI [trans(O_6)], VIII [trans(N_6)], and IX [trans(N_6,O_6)].

The space group symmetry and the unit cell dimensions were obtained from oscillation and Weissenberg photographs taken with Cu Kα radiation. The cell dimensions were then adjusted by a least-squares treatment of 23 high-angle reflections measured on an Enraf-Nonius CAD4 diffractometer with Mo Kα radiation. Intensities of reflections were measured by continuous $\theta/2\theta$ scans. The intensities of three standard reflections, remeasured every 2 h, showed no significant variations during data collection. All measured intensities were corrected for background, Lorentz, and polarization effects, but no absorption correction was applied. Crystal data and some details of data collection and the refinement of the structure are shown in Table II.

The phase problem was solved by a three-dimensional Patterson function, which revealed the position of the metal atom. The positions of the remaining non-hydrogen atoms were obtained from successive difference electron density syntheses. The hydrogen atoms were included in the structural model in calculated positions, and their isotropic thermal parameters were refined. For the hydrogen atoms in the water molecules, positional parameters were also refined, while those in the [Co(β-Ala)(Gly)$_2$] molecules were allowed to ride on the carbon and nitrogen atoms to which they were bonded. All non-hydrogen atoms were allowed anisotropic thermal parameters. The refinement converged at $R = 0.027$ and $R_w = 0.036$, where $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum_w(|F_o| - |F_c|)^2/\sum_w|F_o|^2]^{1/2}$. A final difference Fourier map revealed no peaks higher than 0.3 e/Å^3. Neutral-atom scattering factors and anomalous dispersion corrections for cobalt were taken from ref 7.

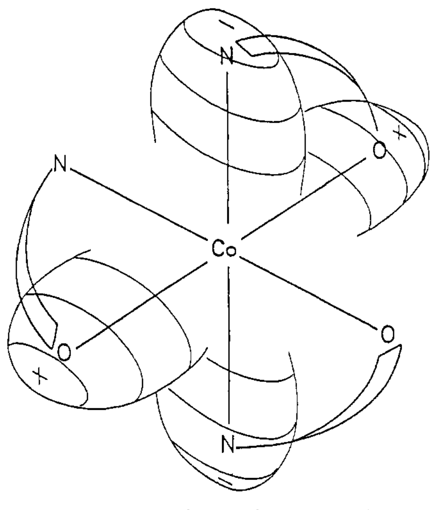

Figure 2. Shape of the angular factor of the magnetic anisotropy of the cobalt(III) shielding tensor in meridional tris(amino carboxylato)cobalt(III) complexes (the radial factor has R^{-3} dependence).

Results and Discussion

Preparation and Determination of the Facial and Meridional Configurations of the Investigated Complexes. A complete series of 12 complexes, which includes not only the mixed-ligand complexes but also the tris(glycinato) and tris(β-alaninato) complexes, was obtained by a new synthetic method which is simpler than that previously reported.[2] The method used for column separation of the complexes, based on application of a cation-exchange resin in the hydrogen form and elution with water, is essentially that of Kostić and Niketić.[2]

The red complexes (II, VII, XI, and XII) exhibit a symmetric first absorption band in the electronic spectra, and they were classified as facial isomers. The violet complexes (I, III–VI, and VIII–X), showing an asymmetric first absorption band, were classified as meridional isomers.[2]

Determination of the Geometrical Isomerism of the Meridional Complexes from Their ^{1}H NMR Spectra. The ^{1}H NMR spectra of the investigated complexes, in the region of methylene proton resonances, are presented in Figure 1. In the spectra of the facial isomers, the methylene protons of the glycinato ligand exhibit a single resonance with a chemical shift of 3.40 ppm, while those of β-alaninato ligand show a single resonance at 2.50 ppm. In the facial isomers, the magnetic anisotropy of cobalt(III) is close to zero and the chemical shifts of the methylene protons are determined by the local effects. A small difference in the chemical shifts of the two glycinato or β-alaninato chelates in the mixed-ligand facial isomers could well be accounted for by a weak cobalt(III) magnetic anisotopy, induced by slightly different ligand fields of glycinato and β-alaninato ligands. In this context, the surprising result is that a single resonance is obtained for the methylene protons of the β-alaninato chelate. This means that the α- and β-methylene groups are magnetically equivalent, which is not the case in the free ligand. Such a finding facilitates the analysis of the spectra of meridional isomers, in which magnetic anisotropy of cobalt(III) removes degeneracy of proton resonances, thus producing even more complex spectra.

The influence exerted by the magnetic anisotropy of cobalt(III) on the shielding of the methylene protons in amino carboxylato chelate complexes has been expressed in terms of chelate geometry and excitation energy anisotropy.[5,6] On this basis, deshielding

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(7) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 71–151.

Table III. Calculated Chemical Shifts (δ, ppm) of the Methylene Protons of Glycinato and β-Alaninato Chelates in the Three Possible Positions of Meridional Isomers

ligand position	chelate		
	glycinato	β-alaninato	
	H_α	H_α	H_β
a	3.4	2.3–2.5	2.4–2.6
b	3.7	2.5–2.6	2.9–3.1
c	3.7	2.6–2.7	2.8–3.0

along the N–N axis and shielding along the O–O axis were calculated in meridional tris(amino carboxylato)cobalt(III) complexes (see Figure 2). In view of the relatively rigid geometry of a glycinato chelate, the precise values of the chemical shifts for methylene protons were calculated for each of the three possible chelate ligand positions in meridional isomers.[5] The slight difference in the ligand fields of glycinato and β-alaninato carboxylate oxygen[3] affects these values by about 0.05 ppm through the series. The average values of the calculated chemical shifts for methylene protons in glycinato chelates in the different positions are given in Table III.

For a β-alaninato chelate the situation is more complex, since the chelate geometry is flexible. The crystal structures of *trans*(O_5)-(β-alaninato)bis(glycinato)cobalt(III) trihydrate and of the previously reported *mer*-tris(β-alaninato)cobalt(III)[8] show that the β-alaninato chelate rings invariably adopt a twist-boat conformation. However, the sense of twisting is not always the same. The magnetic anisotropy influence was therefore calculated for all the observed conformations. It turned out that the variation of the chelate geometry is not prohibitively large for prediction of the chemical shifts induced by the magnetic anisotropy of cobalt(III). As is evident from Table III, the chemical shifts for α- and β-methylene protons are well separated when the β-alaninato chelate occupies position b or c, the separation being larger for the position b. With the β-alaninato chelate in position a, an overlapping of all proton signals may be expected.

In view of data in Table III, the ^{1}H NMR spectra of meridional complexes allow the positions of glycinato and β-alaninato chelates to be unambiguously determined in all isomers (Figure 1). Applying Chart I, geometry of the meridional complexes is therefore as follows:

complex	geometry	complex	geometry
III	trans(N_5,O_5)	VI	trans(O_6)
IV	trans(N_5)	VIII	trans(N_6)
V	trans(O_5)	IX	trans(N_6,O_6)

Additional information, supporting this assignment, is obtained from the deuteration rate of the amino group of the glycinato chelate. It has been established[9,10] that this rate is mainly determined by the *trans* influence of ligands. Thus, in the present case, it should be a function of the chelate position in meridional isomers. As is obvious from the spectra shown in Figure 1, only the resonance of the methylene proton of the glycinato chelate in position b is split by the coupling with the amine protons. Consequently, for a chelate in that position the deuteration rate is the slowest. Investigation of the deuteration rate of the amine protons in *mer*-[Co(Gly)$_3$] has established that it is the fastest for the chelate in position a,[10] but it did not show in which of positions b and c it is the slowest. However, carbon-13 NMR investigation of glycinato chelates in cobalt(III) complexes[6] indicated that a variation of charge distribution on the ligand, so that deuteration in position c is expected to be faster than in position b.

Table IV. Final Fractional Atomic Coordinates and Equivalent Isotropic Temperature Factors for *trans*(O_5)-(β-Alaninato)-bis(glycinato)cobalt(III) Trihydrate, with Esd's in Parentheses[a]

	x/a	*y/b*	*z/c*	*U*, Å^2
Co	0.04225 (4)	0.30072 (2)	0.37846 (3)	0.0210 (2)
O(1)	0.0866 (2)	0.2061 (1)	0.5034 (2)	0.027 (1)
O(2)	0.1587 (3)	0.0766 (1)	0.5713 (2)	0.050 (1)
O(3)	−0.0981 (2)	0.2339 (1)	0.2302 (2)	0.028 (1)
O(4)	−0.3222 (3)	0.1592 (1)	0.1727 (2)	0.049 (1)
O(5)	0.1722 (2)	0.3680 (1)	0.5295 (2)	0.029 (1)
O(6)	0.2456 (3)	0.5001 (1)	0.5938 (2)	0.043 (1)
N(1)	0.2190 (3)	0.2782 (1)	0.3165 (2)	0.027 (1)
N(2)	−0.1411 (3)	0.3180 (1)	0.4341 (2)	0.026 (1)
N(3)	−0.0039 (3)	0.4027 (1)	0.2670 (2)	0.029 (1)
C(1)	0.1552 (3)	0.1364 (2)	0.4934 (2)	0.029 (1)
C(2)	0.2328 (4)	0.1296 (2)	0.3866 (3)	0.038 (1)
C(3)	0.3262 (4)	0.2074 (2)	0.3814 (3)	0.037 (1)
C(4)	−0.2288 (3)	0.2120 (2)	0.2460 (3)	0.030 (1)
C(5)	−0.2649 (4)	0.2544 (2)	0.3635 (3)	0.036 (1)
C(6)	0.1789 (3)	0.4471 (2)	0.5037 (3)	0.030 (1)
C(7)	0.0929 (4)	0.4735 (2)	0.3526 (3)	0.036 (1)
O(W1)	0.5968 (3)	0.0396 (2)	0.3588 (3)	0.053 (1)
O(W2)	0.4722 (3)	0.4051 (2)	0.4105 (3)	0.054 (1)
O(W3)	0.6428 (3)	0.4057 (1)	0.1342 (2)	0.049 (1)
H(C21)	0.1444	0.1210	0.2863	0.040 (8)
H(C22)	0.3085	0.0780	0.4068	0.040 (8)
H(C31)	0.4059	0.1905	0.3307	0.08 (1)
H(C32)	0.3971	0.2250	0.4741	0.037 (8)
H(C51)	−0.2599	0.2077	0.4283	0.036 (8)
H(C52)	−0.3714	0.2828	0.3167	0.046 (9)
H(C71)	0.1741	0.4927	0.3162	0.06 (1)
H(C72)	0.0090	0.5233	0.3455	0.051 (9)
H(N11)	0.2955	0.3255	0.3347	0.06 (1)
H(N12)	0.1711	0.2696	0.2242	0.033 (7)
H(N21)	−0.1069	0.3108	0.5251	0.031 (7)
H(N22)	−0.1866	0.3694	0.4130	0.051 (9)
H(N31)	−0.1207	0.4197	0.2413	0.056 (9)
H(N32)	0.0160	0.3936	0.1889	0.036 (8)
H(W11)	0.677 (5)	0.006 (2)	0.373 (4)	0.06 (1)
H(W12)	0.602 (5)	0.070 (3)	0.301 (4)	0.08 (1)
H(W21)	0.533 (5)	0.444 (3)	0.393 (4)	0.07 (1)
H(W22)	0.530 (5)	0.381 (3)	0.480 (5)	0.08 (1)
H(W31)	0.579 (6)	0.431 (3)	0.145 (5)	0.13 (2)
H(W32)	0.628 (4)	0.418 (2)	0.047 (4)	0.05 (1)

[a] For anisotropic atoms the equivalent isotropic temperature factors of the form $U_{eq} = {}^1/_3\sum\sum U_{ij}\mathbf{a}^*_i\mathbf{a}^*_j\mathbf{a}_i\mathbf{a}_j$ are given.

Table V. Selected Bond Lengths (Å) and Angles (deg) for *trans*(O_5)-(β-Alaninato)bis(glycinato)cobalt(III) Trihydrate, with Esd's in Parentheses

Co–O(1)	1.914 (2)	Co–O(3)	1.898 (2)
Co–O(5)	1.886 (2)	Co–N(1)	1.943 (3)
Co–N(2)	1.945 (3)	Co–N(3)	1.933 (3)
O(1)–C(1)	1.286 (3)	O(2)–C(1)	1.230 (3)
O(3)–C(4)	1.287 (4)	O(4)–C(4)	1.224 (4)
O(5)–C(6)	1.286 (3)	O(6)–C(6)	1.228 (4)
N(2)–C(5)	1.476 (4)	N(3)–C(7)	1.490 (4)
C(2)–C(3)	1.501 (4)	C(1)–C(2)	1.499 (4)
C(6)–C(7)	1.511 (4)	C(4)–C(5)	1.513 (4)
N(1)–C(3)	1.467 (4)		
O(1)–Co–O(3)	90.6 (1)	O(1)–Co–O(5)	88.9 (1)
O(1)–Co–N(1)	94.6 (1)	O(1)–Co–N(2)	84.5 (1)
O(1)–Co–N(3)	174.5 (1)	O(3)–Co–O(5)	176.8 (1)
O(3)–Co–N(1)	90.9 (1)	O(3)–Co–N(2)	86.0 (1)
O(3)–Co–N(3)	93.4 (1)	O(5)–Co–N(1)	92.3 (1)
O(5)–Co–N(2)	90.8 (1)	O(5)–Co–N(3)	86.9 (1)
N(1)–Co–N(2)	176.8 (1)	N(1)–Co–N(3)	89.1 (1)
N(2)–Co–N(3)	92.0 (1)	Co–O(1)–C(1)	127.4 (2)
Co–O(3)–C(4)	114.6 (2)	Co–O(5)–C(6)	116.3 (2)
Co–N(1)–C(3)	117.9 (2)	N(1)–C(3)–C(2)	111.3 (3)
Co–N(2)–C(5)	108.9 (2)	O(3)–C(4)–O(4)	123.8 (3)
Co–N(3)–C(7)	109.2 (2)	N(2)–C(5)–C(4)	110.5 (3)
O(1)–C(1)–O(2)	120.6 (3)	O(1)–C(1)–C(2)	118.8 (3)
O(2)–C(1)–C(2)	120.6 (3)	C(1)–C(2)–C(3)	112.4 (3)
O(3)–C(4)–C(5)	116.8 (3)	O(4)–C(4)–C(5)	119.5 (3)
O(5)–C(6)–O(6)	124.0 (3)	O(5)–C(6)–C(7)	115.8 (3)
O(6)–C(6)–C(7)	120.2 (3)	N(3)–C(7)–C(6)	111.2 (2)

Crystal Structure of *trans*(O_5)-(β-Alaninato)bis(glycinato)cobalt(III) Trihydrate. The crystal structure of V, characterized

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(8) Soling, H. *Acta Chem. Scand.* **1978**, *A32*, 361.
(9) Ama, T.; Kawaguchi, H.; Kanekiyo, M.; Yasui, T. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 956.
(10) Miyanaga, A.; Sakaguchi, U.; Morimoto, Y.; Kushi, Y.; Yoneda, H. *Inorg. Chem.* **1982**, *21*, 1387.

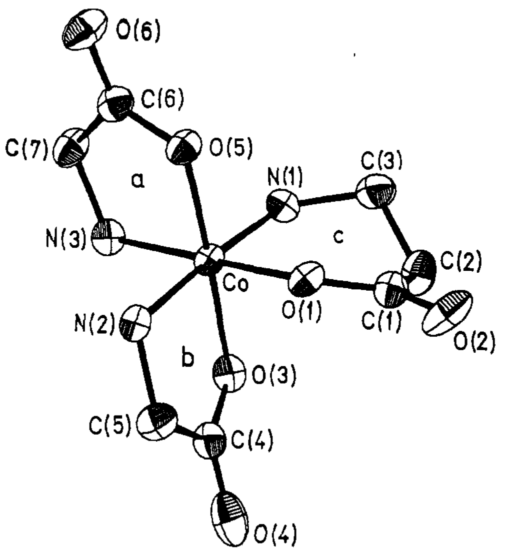

Figure 3. Crystal structure of the *trans*(O_5)-(β-alaninato)bis(glycinato)cobalt(III) molecule. The chelate positions are denoted by a, b, and c in accordance with Chart I.

by atomic parameters given in Table IV, comprises enantiomeric pairs of [Co(β-Ala)(Gly)$_2$] molecules and molecules of water. Selected bond lengths and angles are listed in Table V.

The geometry of the [Co(β-Ala)(Gly)$_2$] molecule, shown in Figure 3, confirms that deduced from the PMR spectra. Thus the glycinato ligands occupy positions a and b (Chart I) and coordinate the metal center through the nitrogen and carboxylato oxygen atoms, the former lying cis and the latter trans to one another. The β-alaninato ligand is also bonded to the cobalt atom through the nitrogen and carboxylato oxygen atoms, thus completing an octahedral coordination geometry around the metal center. Substantial distortions of this geometry from that of an idealized octahedron, evident from the bond angles shown in Table V, reflect formation of the three chelate rings.

The six-membered chelate ring, involving the β-alaninato ligand, adopts a twist-boat conformation characterized by puckering parameters $\theta = 74.5°$, $\phi = 148.8°$, and $Q = 0.60$ Å.[11] The five-membered chelate rings of the glycinato ligands show puckered conformations, as is obvious from the displacements of the ring atoms from their least-squares planes (Table SV, supplementary material). The puckering is more pronounced in the ring in position b than in the ring in position a, and this may be caused by the steric requirements of the β-alaninato ligand.

The bond lengths and angles in V are comparable with the corresponding ones found in the literature.[8,10] Notably, the Co–O(5) bond of 1.886 (2) Å lies in the range of the shortest Co–O distances so far observed for coordinated glycine.

In the crystal structure of V the molecules of water (W) and of the cobalt complex are held by relatively weak hydrogen bonds of the type O_W–H···O, O_W–H···O_W, N–H···O, and N–H···O_W. They are characterized by the H···O distances of 1.89–2.32 Å (Table SIII, supplementary material).

Electronic Absorption Spectra. Electronic absorption spectra of the meridional complexes considered here are presented in Figure 4 and compared with those previously reported.[2,3] Generally, these spectra correspond to those previously reported.[2,3] An exception is the spectrum of the trans(N_6) isomer, and this could be a consequence of different conditions under which the spectra were recorded. Namely, the spectra reported by Kostić and Niketić[2] were obtained by using concentrated aqueous Ca(NO_3)$_2$ solutions.

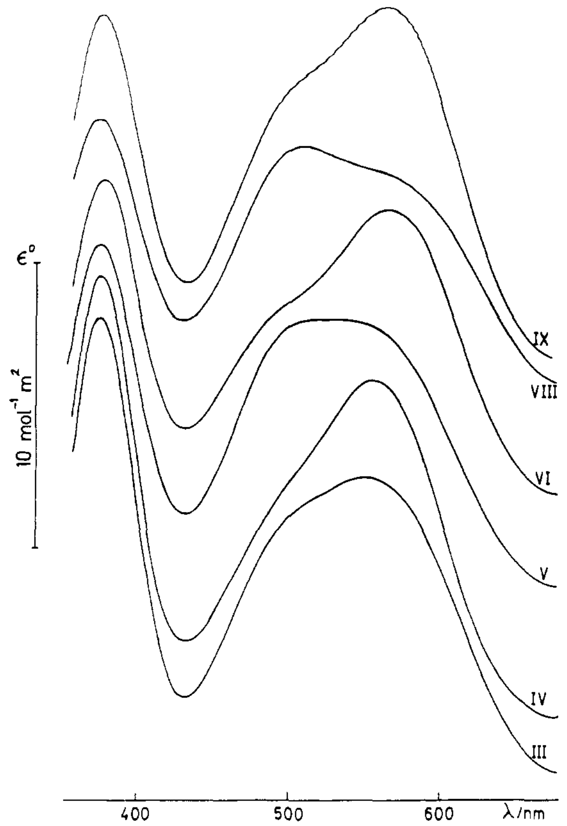

Figure 4. Electronic absorption spectra of the mixed β-alaninato/glycinato meridional isomers III [trans(N_5,O_5)], IV [trans(N_5)], V [trans(O_5)], VI [trans(O_6)], VIII [trans(N_6)], and IX [trans(N_6,O_6)].

Ligand field analysis of the spectra has been reported, and the band shapes have been simulated.[3] A comparison of these data with the present results shows that the simulation was successful for trans(O_5), trans(N_5,O_5), and trans(O_6) isomers.

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Supplementary Material Available: Tables of anisotropic thermal parameters for non-hydrogen atoms, bond lengths and angles (including hydrogen atoms), hydrogen-bond parameters, mean least-squares planes through the atoms of five-membered chelate rings, and values of electronic absorption maxima in the visible region and the corresponding molar absorption coefficients for the complete [Co(Gly)$_x$(β-Ala)$_{3-x}$] (x = 0–3) series of complexes and a diagram of the molecular packing in the crystal structure (6 pages); a listing of observed and calculated structure amplitudes (5 pages). Ordering information is given on any current masthead page.

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(11) Cremer, D.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 1354.