

CONFORMATIONAL ANALYSIS OF METAL CHELATES.
A MOLECULAR MECHANICAL STUDY OF THE RELATIVE STABILITY
OF COBALT(III) 2,3-DIAMINO BUTANE-N,N,N',N'-TETRAACETATE
COMPLEXES

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The stereochemistry and relative energy of diastereoisomers of Λ -[Co(DBTA)]⁻ were studied in dependence on the absolute configuration of the ligand using molecular mechanical calculations. The calculated thermodynamic stabilities of the complexes decrease in the order (S,S)-DBTA > (R,S)-DBTA > (R,R)-DBTA. The destabilization factors are primarily repulsion non-bonding interactions between the axial methyl group and atoms of the acetate ring. (S,S)- and (R,R)-DBTA exhibit high diastereoselectivity in octahedral complexes. The large steric strain in the *meso*-DBTA complex can lead to opening of one chelate ring.

Molecular mechanical calculations have found broad application in the study of the stereochemistry and molecular properties (deformation energies, heats of formation, vibrational spectra) of organic and coordination compounds¹⁻⁴. The possible application of methods for studying the complexes of multidentate amino acid derivatives has recently been discussed^{5,6}.

A number of works by one of the authors deal with the study of the stability constants of the 2,3-diaminobutane-N,N,N',N'-tetraacetic acid (H₄DBTA) complexes⁷⁻¹¹ and it was found that complexes of the racemic form generally exhibit higher stability than complexes of the *meso* form. However, problems connected with the stereochemistry and a rational explanation of this phenomenon are practically untouched in these works⁷⁻¹¹. Consequently, this work will deal with the importance of steric effects for the stability of the complexes and the diastereoselectivity of optically active DBTA. The absolute configurations of the diastereoisomers of [Co((S,S)-DBTA)]⁻ are depicted in Fig. 1.

CALCULATIONS AND RESULTS

The energy and geometry of the [Co(DBTA)]⁻ complexes were calculated in a molecular mechanical approximation; the details of the method used have already been described^{5,6}. The total energy of the molecule consists of the bond length deformation energy (E^R) from the equilibrium values, the torsion energy (E^D), the energy of deformation of the planarity of the

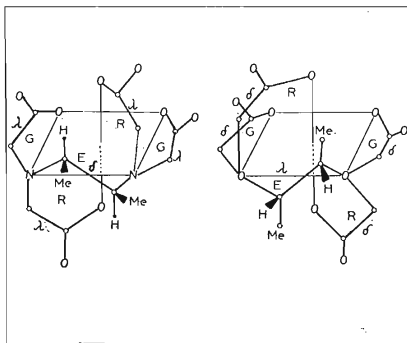


FIG. 1

Schematic depiction of the two isomers of $[\text{Co}((S,S)\text{-DBTA})]^-$ with designated conformation of the chelate rings. *a*) Absolute configuration of the complex²⁰ (OC-6-21-C) or $\lambda\lambda\lambda$ (ref.²¹) (abbreviated to the symbol λ). *b*) Absolute configuration of the complex²⁰ (OC-6-21-A) or $\Delta\Delta\Delta$ (ref.²¹) (abbreviated to the symbol Δ)

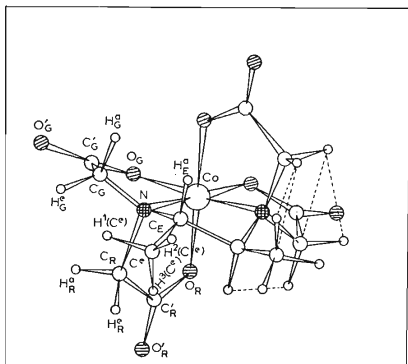


FIG. 2

Perspective projection of the minimized structure of the λ -[Co((S,S)-DBTA)]⁻ anion. ——— nonbonding interactions with energy greater than 1.20 kJ mol⁻¹

carboxyl groups (E^{δ}) and the non-bonding energy (E^{NB}). The molecular geometry was optimized by the Newton-Raphson procedure. The vibration frequencies were calculated using the multi-dimensional potential surface, resulting from minimization. The vibrational frequencies and the geometry of the molecules were used for calculation of the vibrational and rotational contributions to the enthalpy ($H_{v,r}$), the vibrational energy at 0K (ZPE) and the vibrational-rotational-translational contribution to the entropy ($S_{v,r,T}$). (The MOLBLD program¹², used in the calculations, is a modification of the Boyd's program¹³.) The potential function parameters were taken from Buckingham¹⁴ (set I in ref.⁶). The calculations were carried out for three diastereoisomers: Λ -[Co((S,S)-DBTA)]⁻, Λ -[Co((R,S)-DBTA)]⁻ and Λ -[Co((R,R)-DBTA)]⁻. Models were derived from the structural data for [Co(EDTA)]⁻ (ref.¹⁵). The coordinates of the atoms of the methyl groups and of the hydrogen atoms were calculated using the HELPR program¹⁶. The minimized geometry in internal coordinates and deformation energy values are given in Tables I—III. In Figs 2—4 are depicted the calculated structures of the complexes with indication of important non-bonding interactions. The individual atoms are designated according to the type of atom and type of chelate ring in which they participate. Symbols a , e designate

TABLE I

The minimized geometry and deformation energy of Λ -[Co((S,S)-DBTA)]⁻

Bond lengths					
Bond	R, nm	E_R , kJ mol ⁻¹	Bond	R, nm	E^R , kJ mol ⁻¹
Co-N	0.1941	0.25	C _G -C' _G	0.1530	0.17
Co-O _G	0.1892	0.04	C' _G -O _G	0.1294	0.04
Co-O _R	0.1894	0.00	N-C _R	0.1492	0.92
N-C _E	0.1487	0.54	C _R -C' _R	0.1516	0.00
C _E -C _E	0.1545	0.33	C' _R -O _R	0.1284	0.08
N-C _G	0.1481	0.21			
Bond angles					
Angle	θ , deg	E^{θ} , kJ mol ⁻¹	Angle	θ , deg	E^{θ} , kJ mol ⁻¹
N-Co-N	91.1	0.08	Co-N-C _G	103.0	1.51
N-Co-O _G	86.2	0.92	N-C _G -C' _G	105.7	1.05
N-Co-O _R	87.3	0.46	C _G -C' _G -O _G	118.3	0.29
N-Co-O _R ^s	95.5	1.88	Co-O _G -C' _G	109.6	3.98
O _G -Co-O _R ^s	85.9	1.05	Co-N-C _R	108.9	0.00
O _G -Co-O _R	91.4	0.13	N-C _R -C' _R	109.8	0.00
O _G -Co-O _G	97.3	3.35	C _R -C' _R -O _R	118.3	0.29
Co-N-C _E	103.9	1.17	Co-O _R -C' _R	114.2	1.26
N-C _E -C _E	106.5	0.80	C _E -N-C _G	115.4	3.22
N-C _E -C _E ^e	113.9	1.76	C _E -N-C _R	114.2	2.05
C _E -C _E -C _E ^e	112.8	1.00	C _G -N-C _R	110.4	0.08

TABLE I
(Continued)

Torsion angles					
Angle	ϕ , deg	E^Φ , kJ mol ⁻¹	Angle	ϕ , deg	E^Φ , kJ mol ⁻¹
Co-N-C _E -C _E	- 42.7	1.19	C _E -N-C _G -C' _G	152.2	1.76
C _G -N-C _E -C _E	- 154.7	1.19	C _R -N-C _G -C' _G	- 76.5	1.76
C _R -N-C _E -C _E	75.8	1.19	N-C _G -C' _G -O _G	- 25.1	1.98
Co-N-C _E -C ^e	- 167.6	1.19	Co-O _G -C' _G -C _G	- 4.6	0.16
C _G -N-C _E -C ^e	80.4	1.19	Co-N-C _R -C' _R	12.5	5.72
C _R -N-C _E -C ^e	- 34.1	1.19	C _E -N-C _R -C' _R	- 103.1	5.72
N-C _E -C _E -N	58.8	0.25	C _G -N-C _R -C' _R	124.9	5.72
N-C _E -C _E -C ^e	- 175.5	0.25	N-C _R -C' _R -O _R	- 8.0	0.43
C ^e -C _E -C _E -C ^e	- 49.9	0.25	Co-O _R -C' _R -C _R	- 1.1	0.01
Co-N-C _G -C' _G	39.7	1.76			

Non-bonding interactions greater than 0.8 kJ mol ⁻¹			
Atoms	E^{NB} , kJ mol ⁻¹	Atoms	E^{NB} , kJ mol ⁻¹
C _E ...H _R ^e	0.92	H _G ^a ...O _R ^s	0.92
C _G ...O _R ^s	0.96	H _G ^a ...H _E ^u	1.21
C _G ...H _R ^a	2.34	H _G ^c ...H _R ^a	1.17
C _R ...H _G ^c	0.84	H _R ^c ...C ^e	1.76
C _R ...C ^e	0.92	H _R ^c ...H ³ (C ^e)	3.52

predominant axial or equatorial character of the substituent. Symbol *s* in the tables indicates the symmetrically related atom. The calculations were carried out on a Siemens 4004/150 computer.

DISCUSSION

The conformations of the individual chelate rings can be described in all three cases by conformation type δ - $\lambda\lambda$ - $\lambda\lambda$ given by Lee¹⁷ or as *E*, *G*/*R* according to Porai-Koshits¹⁸.

In A -[Co((*S,S*)-DBTA)]⁻, both methyl groups are equatorial (Fig. 2) and the complex anion has a two-fold axis of symmetry. Consequently, the description is complete if data on one half of the molecule is given. The geometry of the chelate rings and the individual deformation energies are close to the analogous values found for the [Co(EDTA)]⁻ anion. The basic character of the strain is not changed in comparison with the EDTA complex, but certain differences result from large

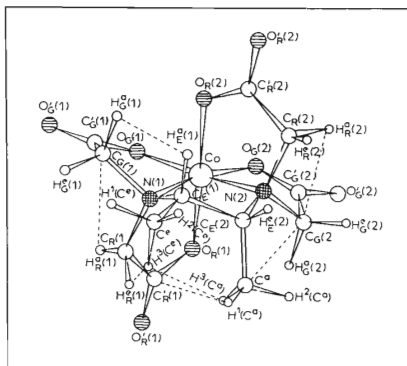


FIG. 3

Perspective projection of the minimized structure of the $A\text{-}[\text{Co}((R,S)\text{-DBTA})]^-$ anion. ----- nonbonding interactions with energy greater than 1.30 kJ mol^{-1}

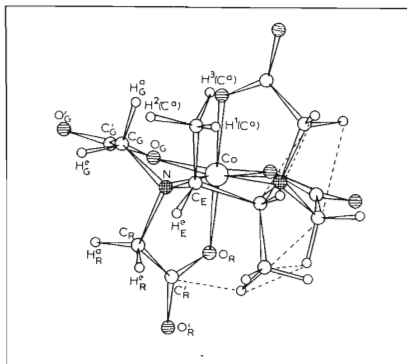


FIG. 4

Perspective projection of the minimized structure of the $A\text{-}[\text{Co}((R,R)\text{-DBTA})]^-$ anion. ----- nonbonding interactions with energy greater than 1.70 kJ mol^{-1}

TABLE II

The minimized geometry and deformation energy of $A\text{-[Co}((R,S)\text{-DBTA)]}^-$

Bond lengths					
Bond	R, nm	E^R kJ mol ⁻¹	Bond	R, nm	E^R kJ mol ⁻¹
Co-N(1)	0.1936	0.13	C _E (1)-C _E (2)	0.1552	0.71
Co-N(2)	0.1945	0.33	C _E (1)-C ^e	0.1543	0.25
Co-O _G (1)	0.1892	0.04	C _E (2)-C ^a	0.1543	0.25
Co-O _R (2)	0.1892	0.00	C _G (1)-C' _G (1)	0.1529	0.13
Co-O _G (2)	0.1894	0.00	C' _G (1)-O _G (1)	0.1293	0.00
Co-O _R (1)	0.1893	0.04	C _R (2)-C' _R (2)	0.1516	0.04
N(1)-C _E (1)	0.1489	0.63	C' _R (2)-O _R (2)	0.1284	0.08
N(1)-C _G (1)	0.1483	0.29	C _G (2)-C' _G (2)	0.1531	0.17
N(1)-C _R (1)	0.1491	0.84	C' _G (2)-O _R (2)	0.1294	0.04
N(2)-C _E (2)	0.1494	1.00	C _R (1)-C' _R (1)	0.1517	0.00
N(2)-C _R (2)	0.1493	0.96	C' _R (1)-O _R (1)	0.1284	0.08
N(2)-C _G (2)	0.1483	0.29			

Bond angles					
Angle	θ , deg	E^0 kJ mol ⁻¹	Angle	θ , deg	E^0 kJ mol ⁻¹
N(1)-Co-N(2)	90.8	0.04	N(1)-C _G (1)-C' _G (1)	106.2	0.80
N(1)-Co-O _G (1)	87.0	0.54	C _G (1)-C' _G (1)-O _G (1)	118.2	0.33
N(1)-Co-O _R (2)	95.5	1.84	Co-O _G (1)-C' _G (1)	109.5	4.06
N(1)-Co-O _R (1)	87.2	0.46	Co-N(2)-C _G (2)	102.3	1.93
N(2)-Co-O _R (2)	87.1	0.50	N(2)-C _G (2)-C' _G (2)	105.3	1.30
N(2)-Co-O _G (2)	85.9	1.05	C _G (2)-C' _G (2)-O _G (2)	118.1	0.33
N(2)-Co-O _R (1)	97.3	3.35	Co-O _G (2)-C' _G (2)	109.4	4.14
O _G (1)-Co-O _R (2)	85.8	1.09	Co-N(1)-C _R (1)	109.6	0.00
O _G (1)-Co-O _G (2)	97.1	3.18	N(1)-C _R (1)-C' _R (1)	109.6	0.00
O _G (1)-Co-O _R (1)	89.8	0.00	C _R (1)-C' _R (1)-O _R (1)	118.3	0.29
O _R (2)-Co-O _G (2)	91.9	0.21	Co-O _R (1)-C' _R (1)	114.2	1.26
O _G (2)-Co-O _R (1)	85.7	1.13	Co-N(2)-C _R (2)	108.2	0.08
Co-N(1)-C _E (1)	104.2	1.00	N(2)-C _R (2)-C' _R (2)	109.6	0.00
N(1)-C _E (1)-C _E (2)	110.6	0.13	C _R (2)-C' _R (2)-O _R (2)	118.1	0.38
Co-N(2)-C _E (2)	107.9	0.08	Co-O _R (2)-C' _R (2)	114.0	1.34
N(2)-C _E (2)-C _E (1)	106.4	0.88	C _E (1)-N(1)-C _G (1)	114.4	2.26
N(1)-C _E (1)-C ^e	114.5	2.34	C _E (1)-N(1)-C _R (1)	115.0	2.76
C _E (2)-C _E (1)-C ^e	113.9	1.84	C _G (1)-N(1)-C _R (1)	110.0	0.00
N(2)-C _E (2)-C ^a	114.4	2.26	C _E (2)-N(2)-C _G (2)	118.3	7.08
C _E (1)-C _E (2)-C ^a	114.2	2.05	C _E (2)-N(2)-C _R (2)	110.4	0.08
Co-N(1)-C _G (1)	102.6	1.72	C _G (2)-N(2)-C _R (2)	109.1	0.00

TABLE II
(Continued)

Torsion angles					
Angle	ϕ , deg	E^Φ kJ mol ⁻¹	Angle	ϕ , deg	E^Φ kJ mol ⁻¹
Co-N(1)-C _E (1)-C _E (2)	-40.8	1.24	C _R (1)-N(1)-C _G (1)-C' _G (1)	-77.1	1.80
C _G (1)-N(1)-C _E (1)-C _E (2)	-152.0	1.24	N(1)-C _G (1)-C' _G (1)-O _G (1)	-26.6	2.05
C _R (1)-N(1)-C _E (1)-C _E (2)	79.3	1.24	Co-O _G (1)-C' _G (1)-C _G (1)	-2.2	0.04
Co-N(1)-C _E (1)-C ^e	-171.2	1.24	Co-N(1)-C _R (1)-C' _R (1)	6.7	6.22
C _G (1)-N(1)-C _E (1)-C ^e	77.5	1.24	C _E (1)-N(1)-C _R (1)-C' _R (1)	-110.3	6.22
C _R (1)-N(1)-C _E (1)-C ^e	-51.2	1.24	C _G (1)-N(1)-C _R (1)-C' _R (1)	118.8	6.22
N(1)-C _E (1)-C _E (2)-N(2)	49.5	0.69	N(1)-C _R (1)-C' _R (1)-O _R (1)	0.0	0.02
N(1)-C _E (1)-C _E (2)-C ^a	-77.8	0.69	Co-O _R (1)-C' _R (1)-C _R (1)	-7.1	0.37
N(2)-C _E (2)-C _E (1)-C ^e	-179.8	0.69	Co-N(2)-C _G (2)-C' _G (2)	41.7	1.05
C ^e -C _E (1)-C _E (2)-C ^e	53.0	0.69	C _E (2)-N(2)-C _G (2)-C' _G (2)	160.1	1.05
Co-N(2)-C _E (2)-C _E (1)	-32.1	3.66	C _R (2)-N(2)-C _G (2)-C' _G (2)	-72.6	1.05
C _G (2)-N(2)-C _E (2)-C _E (1)	-147.4	3.66	N(2)-C _G (2)-C' _G (2)-O _G (2)	-26.8	2.05
C _R (2)-N(2)-C _E (2)-C _E (1)	86.0	3.66	Co-O _G (2)-C' _G (2)-C _G (2)	-4.4	0.15
Co-N(2)-C _E (2)-C ^a	95.1	3.66	Co-N(2)-C _R (2)-C' _R (2)	17.8	5.26
C _G (2)-N(2)-C _E (2)-C ^a	-20.2	3.66	C _E (2)-N(2)-C _R (2)-C' _R (2)	-100.1	5.26
C _R (2)-N(2)-C _E (2)-C ^a	-146.9	3.66	C _G (2)-N(2)-C _R (2)-C' _R (2)	128.3	5.26
Co-N(1)-C _G (1)-C' _G (1)	39.5	1.80	N(2)-C _R (2)-C' _R (2)-O _R (2)	-12.1	0.80
C _E (1)-N(1)-C _G (1)-C' _G (1)	151.7	1.80	Co-O _R (2)-C' _R (2)-C _R (2)	-0.5	0.00

Non-bonding interactions greater than 0.9 kJ mol⁻¹

Atoms	E^{NB} , kJ mol ⁻¹	Atoms	E^{NB} , kJ mol ⁻¹
C _E (1)...H _R ^a (1)	0.92	O _R (1)...H _G ^a (2)	1.05
C _E (2)...H _R ^a (2)	1.59	H _G ^a (1)...H _E ^a (1)	1.72
C _G (1)...O _R (2)	0.92	H _G ^a (1)...H _R ^a (1)	1.59
C _G (1)...H _R ^a (1)	2.51	H _R ^a (2)...H _G ^a (2)	0.88
C _G (1)...H _R ^a (1)	1.04	H _R ^a (2)...H _E ^a (2)	3.64
C _R (2)...C' _G (2)	1.21	H _G ^a (2)...C ^a	1.59
C _R (2)...H _E ^a (2)	1.67	H _G ^a (2)...H ³ (C ^a)	1.26
C _G (2)...O _R (1)	0.88	H _E ^a (2)...H ² (C ^a)	0.96
C _G (2)...H _R ^a (2)	2.55	H _R ^a (1)...C ^e	0.92
C _G (2)...C ^a	1.76	H _R ^a (1)...H ³ (C ^e)	4.06
C _R (1)...H _G ^a (1)	0.88	H _R ^a (1)...H ³ (C ^a)	0.92
C'(1)...H ³ (C ^e)	2.97	H ³ (C ^e)...H ¹ (C ^a)	1.88
O _R (2)...H _G ^a (1)	0.92		

TABLE III
Minimized geometry and deformation energy of $A\text{-[Co}((R,R)\text{-DBTA)]}^-$

Bond lengths					
Bond	R, nm	E^R , kJ mol $^{-1}$	Bond	R, nm	E^R , kJ mol $^{-1}$
Co-N	0.1938	0.17	C _G -C' _G	0.1529	0.13
Co-O _G	0.1894	0.04	C' _G -O _G	0.1293	0.04
Co-O _R	0.1893	0.04	N-C _R	0.1494	1.00
N-C _E	0.1496	1.21	C _R -C' _R	0.1516	0.00
C _E -C _E	0.1555	0.96	C' _R -O _R	0.1284	0.08
N-C _G	0.1485	0.38			

Bond angles					
Angle	θ , deg	E^θ , kJ mol $^{-1}$	Angle	θ , deg	E^θ , kJ mol $^{-1}$
N-Co-N	90.0	0.00	Co-N-C _G	101.8	2.18
N-Co-O _G	86.9	0.62	N-C _G -C' _G	105.8	1.00
N-Co-O _R	87.4	0.42	C _G -C' _G -O _G	118.0	0.38
N-Co-O _R ^s	97.1	3.10	Co-O _G -C' _G	109.2	4.27
O _G -Co-O _R ^s	85.7	1.17	Co-N-C _R	108.7	0.04
O _G -Co-O _R	90.2	0.00	N-C _R -C' _R	109.9	0.00
O _G -Co-O _G	97.1	3.18	C _R -C' _R -O _R	118.2	0.29
Co-N-C _E	108.8	0.00	Co-N-C' _R	113.9	1.38
N-C _E -C _E	109.8	0.00	C _E -N-C _G	117.4	5.69
N-C _E -C ^a	114.4	2.22	C _E -N-C _R	110.9	0.17
C _E -C _E -C ^a	110.7	0.13	C _G -N-C _R	108.7	0.04

Torsion angles					
Angle	ϕ , deg	E^ϕ , kJ mol $^{-1}$	Angle	ϕ , deg	E^ϕ , kJ mol $^{-1}$
Co-N-C _E -C _E	-30.0	3.84	C _E -N-C _G -C' _G	160.2	1.03
C _G -N-C _E -C _E	-144.8	3.84	C _R -N-C _G -C' _G	-72.9	1.03
C _R -N-C _E -C _E	89.4	3.84	N-C _G -C' _G -O _G	-28.7	2.09
Co-N-C _E -C ^a	95.2	3.84	Co-O _G -C' _G -C _G	-1.7	0.02
C _G -N-C _E -C ^a	-19.6	3.84	Co-N-C _R -C' _R	12.0	5.96
C _R -N-C _E -C ^a	-145.4	3.84	C _E -N-C _R -C' _R	-107.5	5.96
N-C _E -C _E -N	39.8	3.99	C _G -N-C _R -C' _R	122.0	5.96
N-C _E -C _E -C ^a	-87.4	3.99	N-C _R -C' _R -O _R	-4.1	0.15
C ^a -C _E -C _E -C ^a	145.4	3.99	Co-O _R -C' _R -C _R	-6.4	0.31
Co-N-C _G -C' _G	41.7	1.03			

TABLE III
(Continued)

Non-bonding interactions greater than 0.8 kJ mol ⁻¹			
Atoms	E^{NB} , kJ mol ⁻¹	Atoms	E^{NB} , kJ mol ⁻¹
$C_E \dots H_R^e$	1.72	$H_G^a \dots O_R^s$	1.21
$C_G \dots O_R^s$	0.92	$H_G^a \dots C^a$	1.84
$C_G \dots H_R^a$	2.81	$H_G^a \dots H^2(C^a)$	1.05
$C_G \dots C^a$	2.05	$H_G^a \dots H^3(C^a)$	1.38
$C'_G \dots C_R$	1.13	$H_G^e \dots H_R^a$	1.21
$C_R \dots H_G^e$	0.84	$H_R^e \dots H_E^e$	3.56
$C_R \dots H_E^e$	1.59	$C^a \dots H_E^{es}$	0.96
$C'_R \dots H^3(C^a)^s$	2.64	$H_E^a \dots H^1(C^a)^s$	0.84

steric strain caused by non-bonding interactions between the equatorial methyl group and the H_R^e atom, ($H_R^e \dots H^3(C^e)$) which is the largest non-bonding interaction in the complex (3.52 kJ mol⁻¹). This steric strain is reflected in large deformation of the bonding angles $N-C_E-C^e$ and $C_E-C_E-C^e$ (1.76 and 1.00 kJ mol⁻¹) and is one of the reasons for the increased length of the $N-C_R$ bond by 0.0022 nm compared with the "ideal" value.

Introduction of one methyl group into the axial position of the E ring in Λ -[Co((R,S)-DBTA)]⁻ (Fig. 3) leads to repulsion between the axial methyl group and the atoms of the R ring, which has no analogy in the Λ -[Co((S,S)-DBTA)]⁻ isomer. As a result of the relaxation process, the magnitude of this interaction decreased during the minimization compared with the initial model, but at the cost of deformation of some of the bonding parameters. The $C_E(2)$ atom approached the plane $N(1)-Co-N(2)$, decreasing the $Co-N(2)-C_E(2)-C_E(1)$ torsion angle to 32.1° (torsion energy 3.66 kJ mol⁻¹) compared with 40.8° in $Co(EDTA)^-$ and the $N(1)-C_E(1)-C_E(2)-N(2)$ angle decreased to 49.5° (it equals 55.6° in the EDTA complex). Through rotation around the $N(2)-C_E(2)$ bond, the $H_E^e(2)$ and $H_R^e(2)$ atoms approached each other and their repulsion energy increased from a value of 1.72 in the [Co(EDTA)]⁻ complex to 3.64 kJ mol⁻¹. The $C_E(2)-N(2)-C_G(2)$ angle increased to 118.3° and the corresponding deformation energy is 7.08 kJ mol⁻¹. As a result of these changes, the torsion strain in the R(2) ring is somewhat decreased. The $Co-N(2)-C_R(2)-C'_R(2)$ torsion angle has a value of 17.8°, which is significantly greater than the analogous value 11.5° in the EDTA complex or the value of 6.7° for the $Co-N(1)-C_R(1)-C'_R(1)$ angle in the second R ring of the same complex.

In the Δ -[Co((*R,R*)-DBTA)]⁻ isomer (Fig. 4) there are large repulsion interactions between the axial methyl groups and the atoms of the R and G rings. Partial compensation of this strain is connected with a large decrease in the torsion angles in the E ring. The Co-N-C_E-C_E torsion angle decreased to -30.0° and the N-C_E-C_E-N angle to 39.8° with torsion energies of 3.84 and 3.99 kJ mol⁻¹. The analogously calculated torsion angles for the [Co(EDTA)]⁻ complex are 40.8 and 55.6°.

Table IV lists the results of statistical-thermodynamic calculations for the [Co(DBTA)]⁻ complex anions. The vibrational contributions to the enthalpy and the vibrational entropy contributions are not significant for the overall free energy. A decisive factor for the relative stabilities of the complexes of DBTA is non-bonding energy. The axial methyl group on the ethylenediamine ring is a destabilizing factor, especially for repulsion interactions with atoms of the R ring. Consequently, formation of the Δ -[Co((*R,R*)-DBTA)]⁻ isomer in solution is thermodynamically improbable. DBTA exhibits high, possibly absolute diastereoselectivity. (*R,R*)-DBTA will coordinate to form a complex with absolute Δ configuration and (*S,S*)-DBTA with absolute Λ configuration.

Although experimental stability constants for Co(III) complexes are not available, it appears that the theoretical calculations at least qualitatively explain the difference in the stabilities of the complexes of the *meso* and racemic forms of DBTA. The calculated difference (in units of the logarithm of the stability constant) for co-

TABLE IV

Results of the calculation of the deformation energy and statistical thermodynamic functions of the Δ -[Co(DBTA)]⁻ complexes for a temperature of 298.15 K. For comparison⁶, the values for the Co(EDTA)⁻ anion are also given (Results are given in kJ mol⁻¹)

Function	(<i>R,R</i>)-DBTA	(<i>R,S</i>)-DBTA	(<i>S,S</i>)-DBTA	EDTA
<i>E</i> (R)	7.83	6.49	5.32	3.01
<i>E</i> (θ)	60.12	64.85	55.18	43.04
<i>E</i> (ϕ)	31.07	25.71	26.71	23.49
<i>E</i> (NB)	0.21	-5.78	-13.15	-12.56
<i>E</i> _{total}	99.19	91.31	74.06	56.98
<i>H</i> _{v,r.}	53.51	54.43	55.14	47.48
<i>ZPE</i>	807.63	802.92	800.62	654.29
<i>T</i> [*] <i>S</i> _{v,r.T.}	171.58	175.64	178.11	161.57
<i>G</i>	788.75	773.01	751.70	597.16
ΔG	37.05	21.31	0.00	—
$\Delta \log K$	-6.51	-3.74	0.00	—

balt(III) complexes, 3.7, is comparable with the values in the range 2.0–2.7 for complexes of the alkaline earths⁷, 1.5–2.6 for some transition metals^{8,10} or 1.8 to 3.2 for lanthanoids. Assuming that DBTA acts as a hexadentate ligand in the complex, the complexes of the meso form are less stable because of steric strain. It is possible that this strain will be so large in some octahedral complexes of the meso form that one glycine ring will be opened, similarly as in some EDTA complexes^{17,18}. The enthalpy change will be more favourable for complex formation, but the translational entropy contribution to the free energy will be smaller, because one less water molecule is freed during chelation¹⁹. Further study is necessary to decide whether the G ring is opened as in EDTA complexes, or the R ring.

REFERENCES

1. Altona C., Faber D. H.: *Topics Current Chem.* **45**, 1 (1974).
2. Ermer O.: *Struct. Bond.* **27**, 161 (1976).
3. Allinger N. L.: *Advan. Phys. Org. Chem.* **13**, 1 (1976).
4. Niketić S. R., Rasmussen K.: *The Consistent Force Field. A Documentation. Lecture Notes in Chemistry* **3**, p. 1–12. (G. Berthier, Ed.), Springer-Verlag, Berlin 1977.
5. Pavelčík F., Majer J.: *This Journal* **43**, 1450 (1978).
6. Pavelčík F., Majer J.: *This Journal* **43**, 239 (1978).
7. Majer J., Dvořáková E.: *Chem. Zvesti* **17**, 402 (1963).
8. Majer J., Novák V., Svičeková M.: *Chem. Zvesti* **18**, 481 (1964).
9. Novák V., Majer J., Svičeková M.: *Chem. Zvesti* **19**, 817 (1965).
10. Dvořáková E., Majer J.: *Chem. Zvesti* **20**, 233 (1966).
11. Novák V., Svičeková M., Majer J.: *Chem. Zvesti* **20**, 252 (1966).
12. Pavelčík F.: Unpublished results.
13. Boyd R. H.: *J. Chem. Phys.* **49**, 2574 (1968).
14. Buckingham D. A.: *J. Amer. Chem. Soc.* **96**, 1713 (1974).
15. Weakliem H. A., Hoard J. L.: *J. Amer. Chem. Soc.* **81**, 549 (1959).
16. Pavelčík F.: Unpublished results.
17. Lee B.: *Inorg. Chem.* **11**, 1072 (1972).
18. Porai-Koshits M. A.: *Proc. of the IVth Conf. on Coord. Chem.*, Smolenice 1973, p. 76.
19. Chung Chung-Sun: *Inorg. Chem.* **18**, 1321 (1979).
20. Brown M. F., Cook B. R., Sloan T. E.: *Inorg. Chem.* **14**, 1273 (1975).
21. IUPAC: *Inorg. Chem.* **9**, 1 (1970).

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