# THE CRYSTAL STRUCTURE OF POTASSIUM <br> ^A-rac-2,3-BUTANEDIAMINE-N,N, $\mathbf{N}^{\prime}$, ${ }^{\prime}$ '-TETRAACETATECOBALTATE HEMIHYDRATE 

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#### Abstract

The crystal structure of $\Lambda \Delta-\mathrm{K}$ [ $\mathrm{Co}(\mathrm{rac}$-bdta) $] .1 / 2 \mathrm{H}_{2} \mathrm{O}$ was solved by the X-ray diffraction method and refined by the least squares method to $R=0.047$ on the basis of 3847 diffraction values. The substance crystallizes in a space group with symmetry $P \overline{1}$ with the following lattice parameters: $a=0.9412(5), \quad b=1.2166(6), \quad c=1.5370(9) \mathrm{nm}, \quad \alpha=70.68(4), \quad \beta=73.45(4)$, $\gamma=83 \cdot 24(4)^{\circ}$. The crystal structure consists of two symmetrically independent enantiomer pairs $\Delta-[\operatorname{Co}(R, R)$-bdta $]$ and $\Lambda-[\operatorname{Co}(S, S) \text {-bdta }]^{-}, \mathrm{K}^{+}$ions and molecules of water of crystallization. The $\mathrm{Co}(\mathrm{III})$ atom is octahedrally coordinated by $\operatorname{rac}(\mathrm{bdta})^{4-}$ forming four glycine and one ethylenediamine chelate ring. The stereospecific coordination of rac-(bdta) ${ }^{4-}$ is based on an energy preference for equatorially located methyl groups on the central ethylenediamine ring. Two types of strain in the $[\mathrm{Co}(\mathrm{rac} \text {-bdta })]^{-}$complex are derived from the three five-membered rings in the equatorial plane of the complex and repulsion between the methyl and methylene hydrogen atoms.


2,3-Butanediamine- $\mathrm{N}, \mathrm{N}, \mathrm{N}^{\prime}, \mathrm{N}^{\prime}$-tetraacetic acid $\left(\mathrm{H}_{4} \mathrm{bdta}\right)$ is the dimethyl derivative of ethylenediamine- $\mathrm{N}, \mathrm{N}, \mathrm{N}^{\prime}, \mathrm{N}^{\prime}$-tetraacetic acid ( $\mathrm{H}_{4}$ edta). The presence of two chiral centres in the molecule and the assumed hexadentate coordination (characteristic for edta ${ }^{4-}$ complexes), indicate that complexes of metals with bdta ${ }^{4-}$ can exist in three diastereoisomeric pairs. Using IUPAC notation for the absolute configuration of octahedral complexes ${ }^{1}$, these three diastereoisomers in the $\Delta \Lambda \Delta$ (pure chirality $\Delta)$ series are $\Delta-[\mathrm{M}((R, R)$-bdta $)], \Delta-[\mathrm{M}((R, S)$-bdta $)]$ and $\Delta-[\mathrm{M}((S, S)$-bdta $)]$. Thus the racemic form of $\mathrm{bdta}^{4-}$, rac-(bdta) ${ }^{4-}$ can form two diastereoisomers, $\Delta-[\mathrm{M}((R, R)$ --bdta $)]$ and $\Delta$ - $[\mathrm{M}((S, S)$-bdta $)]$, with ax-ax or eq-eq orientation of the methyl groups with respect to the central ethylenediamine chelate ring.

The complexes of bdta ${ }^{4-}$, similar to the analogous complexes of ptnta ${ }^{4-}\left(\mathrm{H}_{4}\right.$ ptnta $=2,4$-pentanediamine- $\mathrm{N}, \mathrm{N}, \mathrm{N}^{\prime}, \mathrm{N}^{\prime}$-tetraacetic acid), have often been extensively studied, especially considering the conformation of the chelate rings ${ }^{2-4}$, stereospecific coordination of the racemic or optically active $((R, R)$ - or ( $S, S$ )-) forms of $\mathrm{H}_{4}$ bdta and $\mathrm{H}_{4}$ ptnta ${ }^{4-6}$, as well as the stability constants of complexes in solution ${ }^{7-11}$. The first works ${ }^{7-11}$ indicated that the studied complexes of rac-bdta ${ }^{4-}$ exhibit higher stability than the corresponding meso-bdta ${ }^{4-}$ complexes. Analysis
of the $C D$ spectra of the $[\operatorname{Co}((R, R) \text {-ptnta })]^{-}$and $[\operatorname{Cr}((S, S) \text {-ptnta })]^{-}$complexes indicated that the methyl groups on the $\alpha$-carbon atoms are preferably located in equatorial positions during coordination leading to formation of a six-membered ethylenediamine chelate ring; thus the former complex is stereospecific ${ }^{5,6}$ with absolute configuration $\Delta \Lambda \Delta$ (pure chirality $\Delta$ ) and the latter with $\Lambda \Delta \Lambda$ (pure chirality $\Lambda$ ). Molecular-mechanics calculations carried out on the $\Lambda-[\mathrm{Co}((S, S) \text {-bdta })]^{-}$and $\Delta$ -$-[\mathrm{Co}((R, R) \text {-bdta })]^{-}$diastereoisomers (the formation of the latter stereoisomer is thermodynamically improbable $)^{4}$ yielded identical results. It thus appears that the determining factors in the stereospecific coordination of optically active or racemic forms of ptnta ${ }^{4-}$ and bdta $^{4-}$ are the steric effects of the methyl groups, acting on both the six-membered and five-membered rings.

In spite of this interest in the ptnta ${ }^{4-}$ and bdta $^{4-}$ complexes, so far the crystal structure of complexes of this type has not been described in the literature. Thus we decided to study the structure of the complex between Co (III) and rac-(bdta) ${ }^{4-}$ in an attempt to confirm assumptions on the stereospecific coordination of optically active complexes of bdta ${ }^{4-}$ and to determine the way in which the introduction of a methyl group and thus steric strain into the five-membered ethylenediamine chelate ring affects the bonding and stereo chemical parameters of the structurally well-known $[\mathrm{Co}(\mathrm{edta})]^{-}$complex ${ }^{12}$.

## EXPERIMENTAL

## Complex Preparation

Rac- $\mathrm{H}_{4}$ bdta was prepared by slight modification of the synthesis described by Majer ${ }^{7}$. Chloroacetic acid ( 4.5 mol ) was dissolved in a small amount of water and neutralized with ice cooling $\left(0-10^{\circ} \mathrm{C}\right)$ by slow addition of $7 \mathrm{~m}-\mathrm{NaOH}$ (the pH of the solution was $10-11$ ). After addition of rac-2,3-butanediamine hydrochloride the temperature of the water bath increased to $95^{\circ} \mathrm{C}$; the pH of the reaction mixture was maintained at a value of $10-11$ by dropping of the required amount of NaOH ( 6 mol of NaOH were added over 2.5 hours). The reaction mixture was further heated on the water bath for a further 9 hours. After cooling the mixture was acidified with concentrated HCl with cooling $\left(0-5^{\circ} \mathrm{C}\right)$ to a pH of $1.5-2$. The precipitated white, crystalline substance $\mathrm{rac}-\mathrm{H}_{4}$ bdta was filtered off and washed with water, ethanol and diethyl ether and then repeated recrystallized from boiling water. Analysis: for $\mathrm{C}_{12} \mathrm{H}_{20} \mathrm{~N}_{2} \mathrm{O}_{8} \cdot \mathrm{H}_{2} \mathrm{O}$ (338.3) calculated: $\mathbf{4 2} \cdot 60 \% \mathrm{C}, 8 \cdot 28 \% \mathrm{~N}$; found: $\mathbf{4 2} \cdot 56 \% \mathrm{C}, 8.31 \% \mathrm{~N}$.
( $\mathrm{Rac}-\mathrm{H}_{4}$ bdta). $\mathrm{H}_{2} \mathrm{O}$ was neutralized with potassium acetate and mixed with an equimolar amount of cobalt(III) acetate tetrahydrate. After addition of active carbon, a $5 \%$ solution of $\mathrm{H}_{2} \mathrm{O}_{2}$ was added twice, each time after bubbling the reaction mixture with air for 24 hours. After filtration and concentration of the filtrate, $c$. a 5 -fold (vol) amount of boiling absolute ethanol was added, until the solution began to become turbid with crystallized $\Lambda \Delta-K[C o(r a c-b d t a)]$. $.1 / 2 \mathrm{H}_{2} \mathrm{O}$. The solution was transferred to a tempered thermos flask and left to crystallize. Analysis: for $\mathrm{C}_{12} \mathrm{H}_{16} \mathrm{~N}_{2} \mathrm{O}_{8} \mathrm{KCo.1} / 2 \mathrm{H}_{2} \mathrm{O}(423.3)$ calculated: $34.05 \% \mathrm{C}, 4.05 \% \mathrm{H}, 6.62 \% \mathrm{~N}, 13.92 \%$ Co; found: $34.02 \% \mathrm{C}, 4.02 \% \mathrm{H}, 6.66 \% \mathrm{~N}, 13.97 \% \mathrm{Co}$.

Crystallographic Data
Preliminary rotation and Weissenberg patterns indicated a triclinic crystallographic system. The approximate values of the lattice parameters were refined on a Syntex $P 2_{1}$, diffractometer by the least squares method on the basis of 10 precisely centred reflections ( $\mathrm{MoK} \alpha$ ) radiation: $a=0.9412(5), \quad b=1.2166(6), \quad c=1.5370(9) \mathrm{nm}, \quad \alpha=70.68(4), \quad \beta=73.45(4), \quad y=83.24(4)^{\circ}$, $V=-1.5914 \mathrm{~nm}^{3}$. The crystal density $D_{0}=1.76 \mathrm{Mg} \mathrm{m}^{-3}$ measured in a bromoform-ethanol mixture is in good agreement with the calculated value of $D_{\mathrm{c}}=1.77 \mathrm{Mg} \mathrm{m}^{-3}$ assuming 4 formula units ( $Z=4$ ) per unit cell (one formula unit $=\mathrm{C}_{12} \mathrm{H}_{16} \mathrm{~N}_{2} \mathrm{O}_{8} \mathrm{KCo.1} / 2 \mathrm{H}_{2} \mathrm{O}, M_{\mathrm{r}}=423 \cdot 3$ ). The linear absorption coefficient $\mu(\mathrm{MoK} \alpha)=9.8 \mathrm{~cm}^{-1}$.

## Solution and Refinement of the Crystal Structure

Siructural analysis was carried out using a plate-shaped crystal with approximate dimensions $0.5 \times 0.3 \times 0.05 \mathrm{~mm}^{3}$. The integral intensity was measured using a computer-controlled four--circle Syntex $P 2_{1}$ diffractometer using graphite-monochromated $\mathrm{MoK} \alpha$ radiation ( $\lambda=0.07107$ nm ) and the scanning $2 \theta-0$ technique in the $0<\theta<50^{\circ}$. The program controlling the intensity measurement automatically controlled the scanning rate in the interval 4.88 to $29.3^{\circ} \mathrm{min}^{-1}$ on the basis of preliminary two-second measurement. In order to consider the crystal mosaic and peak splitting as a result of the presence of $\mathrm{K}_{\alpha 1}$ and $\mathrm{K}_{\alpha 2}$ components, the scanning range was selected automatically in dependence on the diffraction angle and corresponded to $1^{\circ}$ below the calculated $K_{\alpha 1}$ position to $1^{\circ}$ above the calculated $K_{\alpha 2}$ position (in $2 \theta$ ). The background was measured at both ends of the scan for a period of half of the reflection scanning time. The intensities of two standard reflections measured after each 98 recorded intensities did not exhibit significant fluctuation. Of a total number of 5324 recorded independent reflections, 3847 with $I>1.96 \sigma$ (I) were considered as observed. The intensities of all the reflections were corrected for the Lorentz and polarization factors. Correction was not carried out for absorption and secondary extinction.

In all the subsequent calculations connected with solution of the crystal structure, a space group of $P \overline{1}$ was assumed, and was finally confirmed by successful refinement of the structure in this group. The positions of the two Co atoms and two K atoms present in the assymetric crystal unit were found from three-dimensional Patterson synthesis calculated from all the observed reflections. The positions of the remaining non-hydrogen atoms were found and partially refined by step-wise Fourier synthesis of the electron density. The positional and isotropic thermal parameters of all the non-hydrogen atoms were refined in three cycles by the least squares method using a block-diagonal matrix and unit weights ( $w=1$ ) in the minimization function $M=$ $=u(\Delta F)^{2}$ for value $\mathrm{R}=0.09\left(R=\Sigma| | F_{0}\left|-\left|F_{\mathrm{c}}\right|\right| / \Sigma\left|F_{\mathrm{o}}\right|\right)$. The differential Fourier map of the residual electron density indicated the positions of all the hydrogen atoms in the structure (the two hydrogens of the molecule of water of crystallization present in the assymetric unit were also clearly discernible). The anisotropic thermal parameters of 49 independent non-hydrogen atoms and isotropic thermal parameters of 34 hydrogen atoms were refined together with the positional parameters by the least squares method in 6 cycles in a $9 \times 9$ block diagonal approximation using all 3847 observed reflections and relative weights $w^{-1}=\sigma^{2}\left(\left|F_{0}\right|\right)+\left(c\left|F_{0}\right|\right)^{2}$, where $\left.\sigma_{i}\left|F_{0}\right|\right)$ is derived from counting statistics and parameter $c$ is adjusted so that the average values of minimized function $M$ in the various $\left|F_{0}\right|$ intervals and of $|\sin \theta|$ are approximately identical (in the last cycle, $c=0.025$ ). The final value of $R$ was 0.047 and $R_{\mathrm{w}}=0.049$ ( $R_{\mathrm{w}}=$ $\left.==\sum w|\Delta F|^{2} / \sum w\left|F_{0}\right|^{2}\right)^{1 / 2}$ ). The shift required in the refined parameters in the last least squares cycle was not greater than 0.2 times its standard deviation. $F_{\mathrm{c}}$ was calculated using the scatter factors for the neutral atoms ${ }^{13}$. The maximal residual electron density in the differential Fourier synthesis was $170 \mathrm{en} \mathrm{m}^{-3}$. All the crystal structural calculations were carried out on a Siemens 4004/150 computer using published programs ${ }^{14,15}$.

## RESULTS AND DISCUSSION

Tables I and II give the final positional and anisotropic thermal parameters of the non-hydrogen atoms together with their standard deviations. Molecules $A$ and $B$ are two symmetrically independent molecules in a unit cell and $W$ is the oxygen atom of the molecule of water of crystallization. Designation of atoms in the $[\mathrm{Co}((R, R) \text {-bdta })]^{-}$complex ion is apparent from Fig. 1. The hydrogen atoms are

## Table I

The coordinates (. $10^{4}$ ) of the nonhydrogen atoms in the crystal structure of $\Lambda \Delta-\mathrm{K}[\mathrm{Co}(r a c$-bdta) $]$. $.1 / 2 \mathrm{H}_{2} \mathrm{O}$ with estimated standard deviations in parentheses

designated according to the atom to which they are bonded and Table III gives their refined positional parameters.

It can be seen from Fig. 2 (schematically representing projection of the unit cell along the crystallographic $a$ axis) that the crystal structure consists of $\Delta-[\operatorname{Co}((R, R)-$ -bdta) $)]^{-}$and $\Lambda_{-}[\mathrm{Co}((S, S) \text {-bdta })]^{-}$enantiomers of paired complex anions, $\mathrm{K}^{+}$ cations and molecules of water of crystallization. Thus the diffraction experiment confirmed the assumption that the complex anion $[\mathrm{Co}((R, R) \text {-bdta })]^{-}$should be formed stereospecifically with absolute configuration $\Delta$ and complex anion $[\mathrm{Co}((S, S)$ --bdta) $]^{-}$with absolute configuration $\Lambda$. The absolute configurations of the complex anions are specified by the absolute configurations on the two chiral centres in the ligand molecule. The coordinates of the atoms of both symmetrically independent

Table II
The coefficients (. $10^{4}$ ) of the anisotropic thermal factors $\mathrm{T}=\exp \left[-\left(B_{11} h^{2}+\ldots+B_{12} h k+\right.\right.$ $+\ldots)]$. The estimated standard deviations are given in parentheses

| Atom | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Molecule $A$ |  |  |  |  |  |  |
| Co | 42(1) | 31(1) | $28(0)$ | 1(1) | $-17(1)$ | -24(1) |
| N(1) | 56(6) | 32(3) | 39(3) | 2(7) | $-26(6)$ | -32(5) |
| $\mathrm{N}(2)$ | 44(5) | 38(3) | 31(2) | $-1(7)$ | $-15(6)$ | --29(5) |
| $O(1)$ | $70(5)$ | 54(3) | 34(2) | 4(6) | $-11(5)$ | -45(4) |
| $O(2)$ | 67(5) | 45(3) | 42(2) | $-1(6)$ | -35(6) | $-15(4)$ |
| $\mathrm{O}(3)$ | $71(5)$ | 45(3) | 45(2) | 4(6) | $-31(6)$ | -42(4) |
| $\mathrm{O}(4)$ | 54(5) | 39(3) | 44(2) | $-8(6)$ | $-34(5)$ | $-24(4)$ |
| O(5) | 116(6) | $76(4)$ | 47(3) | -20(8) | --12(7) | -72(5) |
| $O(6)$ | $98(6)$ | 47(3) | 55(3) | 49(7) | $-73(6)$ | -35(5) |
| O(7) | 120(7) | $79(4)$ | 52(3) | $-30(8)$ | $-8(7)$ | -88(6) |
| $O(8)$ | 74(6) | 93(5) | 124(5) | $-31(9)$ | $-122(9)$ | 11(8) |
| C(1) | 52(6) | 34(4) | 36(3) | -6(8) | $-12(7)$ | -22(6) |
| $C(2)$ | 56(7) | 42(4) | 30(3) | 0(8) | $-9(7)$ | $-41(6)$ |
| C(3) | 69(8) | 53(5) | 59(4) | -26(10) | -42(9) | $-12(7)$ |
| C(4) | 67(7) | 39(4) | 38(3) | 6(9) | $-12(8)$ | $-17(6)$ |
| C(5) | 76(7) | $61(5)$ | 35(3) | -12(10) | - 29(8) | -41(7) |
| $C(6)$ | 91(8) | 36(4) | $31(3)$ | O(9) | -- 19(8) | $-14(6)$ |
| C(7) | 55(7) | 41(4) | 48(4) | 26(9) | - 29(8) | $-36(7)$ |
| C(8) | 76(7) | 46(5) | $39(3)$ | 0(9) | -40(8) | -40(6) |
| C(9) | 80(7) | 54(5) | 31(3) | $-17(9)$ | $-40(8)$ | $-28(6)$ |
| C(10) | 56(7) | 54(5) | 41 (3) | - 13(9) | $-20(8)$ | -43(7) |
| C(11) | 55(7) | 36(4) | 41(3) | 19(8) | --32(8) | -15(6) |
| C(12) | 64(7) | 62(5) | 49(4) | - 12(10) | - $44(8)$ | $-19(7)$ |

Table II
(Continued)

| Atom | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |

## Molecule $B$

| Co | $47(1)$ | $38(1)$ | $24(0)$ | $11(1)$ | $-27(1)$ | $-27(1)$ |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{N}(1)$ | $57(6)$ | $52(4)$ | $30(2)$ | $8(7)$ | $-17(6)$ | $-45(5)$ |
| $\mathrm{N}(2)$ | $58(5)$ | $41(4)$ | $24(2)$ | $9(7)$ | $-25(6)$ | $-24(5)$ |
| $\mathrm{O}(1)$ | $74(5)$ | $55(3)$ | $35(2)$ | $-4(7)$ | $-28(5)$ | $-40(4)$ |
| $O(2)$ | $69(5)$ | $69(4)$ | $47(2)$ | $41(7)$ | $-61(6)$ | $-52(5)$ |
| $O(3)$ | $64(5)$ | $48(3)$ | $32(2)$ | $21(6)$ | $-27(5)$ | $-47(4)$ |
| $O(4)$ | $78(5)$ | $45(3)$ | $39(2)$ | $2(6)$ | $-45(6)$ | $-21(4)$ |
| $\mathrm{O}(5)$ | $123(6)$ | $72(4)$ | $35(2)$ | $9(8)$ | $-20(6)$ | $-65(5)$ |
| $O(6)$ | $59(5)$ | $127(5)$ | $67(4)$ | $48(8)$ | $-52(7)$ | $-110(7)$ |
| $O(7)$ | $140(7)$ | $51(3)$ | $34(2)$ | $31(7)$ | $-49(6)$ | $-49(5)$ |
| $O(8)$ | $96(6)$ | $67(4)$ | $53(3)$ | $\cdots 5(8)$ | $10(7)$ | $-27(5)$ |
| $\mathrm{C}(1)$ | $72(7)$ | $42(4)$ | $28(3)$ | $1(9)$ | $-32(7)$ | $-31(6)$ |
| $\mathrm{C}(2)$ | $82(7)$ | $37(4)$ | $28(3)$ | $13(9)$ | $-33(7)$ | $-33(6)$ |
| $\mathrm{C}(3)$ | $144(10)$ | $55(5)$ | $47(4)$ | $-14(12)$ | $-55(10)$ | $-24(7)$ |
| $\mathrm{C}(4)$ | $121(9)$ | $55(5)$ | $55(4)$ | $76(11)$ | $-93(10)$ | $-43(7)$ |
| $\mathrm{C}(5)$ | $88(8)$ | $59(5)$ | $39(3)$ | $-6(10)$ | $-47(8)$ | $-55(7)$ |
| $\mathrm{C}(6)$ | $54(7)$ | $51(5)$ | $31(3)$ | $28(9)$ | $-37(7)$ | $-33(6)$ |
| $\mathrm{C}(7)$ | $62(7)$ | $69(5)$ | $36(3)$ | $--13(10)$ | $-4(8)$ | $-65(7)$ |
| $\mathrm{C}(8)$ | $66(7)$ | $84(6)$ | $46(4)$ | $25(10)$ | $-58(8)$ | $-\cdots 8(8)$ |
| $\mathrm{C}(9)$ | $68(7)$ | $50(5)$ | $33(3)$ | $12(9)$ | $-47(7)$ | $-44(6)$ |
| $\mathrm{C}(10)$ | $78(7)$ | $29(4)$ | $23(3)$ | $\cdots 6(8)$ | $-17(7)$ | $-9(5)$ |
| $\mathrm{C}(11)$ | $45(6)$ | $65(5)$ | $27(3)$ | $-20(9)$ | $-14(7)$ | $\cdots 33(6)$ |
| $\mathrm{C}(12)$ | $72(7)$ | $68(5)$ | $34(3)$ | $26(10)$ | $-24(8)$ | $-46(7)$ |
| $\mathrm{K}(1)$ | $91(2)$ | $72(1)$ | $35(1)$ | $12(2)$ | $-33(2)$ | $-30(2)$ |
| $\mathrm{K}(2)$ | $78(2)$ | $53(1)$ | $43(1)$ | $6(2)$ | $-25(2)$ | $-41(1)$ |
| $W$ | $169(8)$ | $64(4)$ | $62(3)$ | $-61(9)$ | $-10(8)$ | $-49(6)$ |

complex anions (molecules $A$ and $B$ ) given in Tables I and III correspond to the $\Delta-\left[\mathrm{Co}((R, R) \text {-bdta) }]^{-}\right.$enantiomer and are consistent with Fig. 1.

The Co atom is octahedrally coordinated by two N atoms and a single O atom of each of the four carboxyl groups of the coordinating ligand, forming five-membered rings. The notation given by Hoard ${ }^{12}$ is employed in designation of these chelate rings (Fig. 1): the NCoN system defines the "equatorial plane" of the complex and the corresponding ethylenediamine ring is designated by symbol $E$; the $G$ rings ( $G_{1}$ and $G_{2}$ ) are those with central plane roughly parallel with the equatorial plane,
in contrast to the $R$ rings ( $R_{1}$ and $R_{2}$ ) whose central planes are roughly perpendicular to the NCoN plane.
Table IV lists the bond lengths and valence angles in the complex anions ( $A$ and $B$ ). It follows from this data that both the interatomic distances and the valence angles for two independent molecules ( $A$ and $B$ ) are approximately identical, i.e. do not differ by more than $3 \sigma$ ( $\sigma=$ estimated standard deviation). The only exception is the length of the $\mathrm{N}(2)-\mathrm{C}(9)$ bond, which is 1.488 in molecule $A$ and $1.514 .10^{-10}$ in molecule $B$ (a difference of greater than $3 \sigma,(\sigma=0.007)$, the length of the $\mathrm{C}(12)$ -$-\mathrm{O}(8)$ bond which equals $1 \cdot 198(A)$ and $1 \cdot 228.10^{-10} \mathrm{~m}(B)$ and valence angles $\mathrm{N}(2)-\mathrm{Co}-\mathrm{O}(1)$, with values of $94 \cdot 8(A)$ and $93 \cdot 1^{\circ}(B), \mathrm{O}(2)-\mathrm{Co}-\mathrm{O}(4)$ with values of $100.0(A)$ and $100.9^{\circ}(B), \mathrm{O}(3)-\mathrm{Co}-\mathrm{O}(2)$ with values of $86.0(A)$ and $86.9^{\circ}(B)$ and $\mathrm{Co}-\mathrm{N}(2)-\mathrm{C}(11)$ with values of $103 \cdot 8(A)$ and $105 \cdot 0^{\circ}(B)$. In addition, con-


Fig. 1
Perspective projection of $\Delta-[\operatorname{Co}((R, R) \text {-bdta })]^{-}$with designation of the atoms and chelate rings
sidering the distances and angles in Table IV, it follows that both independent complex anions have approximately $C_{2}$ symmetry, where the $C_{2}$ axis passes through the Co atom and the centre of the $\mathrm{N} . . . \mathrm{N}$ connecting line. Thus an average value can be found for each bonding parameter from the four corresponding values, as given in Fig. 3. Here the atoms are designated by indices in agreement with the above--mentioned chelate ring notation and the atoms forming primarily double bonds (i.e. the uncoordinated $O$ atom and the $C$ atom of the carboxyl group) are designated by dotted lines.

Of the three independent coordination bonds, the longest is the $\mathrm{Co}-\mathrm{N}$ bond, with a length of $1.925 .10^{-10} \mathrm{~m}$. The $\mathrm{Co}-\mathrm{O}$ bonds are longer in the $G$ rings than in the $R$ rings, with average values of 1.913 and $1.890 .10^{-10} \mathrm{~m}$, respectively. Similar values were also found for edta ${ }^{4-}$ or edta $^{4-}$-analogous complexes of Co (III) (refs 12,16,17).

## Table III

The coordinates (. $10^{3}$ ) of the hydrogen atoms in the crystal structure of $\Lambda \Delta[\mathrm{KCo}($ rac-bdta $)] .1 / 2$ $\mathrm{H}_{2} \mathrm{O}$ with estimated standard deviations in parentheses

| Atom | Molecule $A$ |  |  | Molecule $B$ |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | $x$ | $y$ | $z$ |  | $x$ | $y$ | $z$ |
| $\mathrm{H}(\mathrm{Cl})$ | 1037(6) | 77(5) | 638(4) |  | 521(6) | 636(5) | 591(4) |
| H(C2) | 835(5) | 206(4) | 722(3) |  | 315(5) | 669(4) | 750(3) |
| $\mathrm{H}^{1}(\mathrm{C} 3)$ | 1215 (8) | 141(6) | 689(5) |  | 649(6) | 808(5) | 581(4) |
| $\mathrm{H}^{2}$ (C3) | $1174(6)$ | 235(5) | 603(4) |  | 486(6) | 829(5) | 548(4) |
| $\mathrm{H}^{3}(\mathrm{C} 3)$ | $1110(6)$ | 253(5) | 708(4) |  | 500(5) | 837(4) | 642(3) |
| $\mathrm{H}^{1}(\mathrm{C} 4)$ | 780 (7) | 316(5) | 579(4) |  | 223(6) | 792(5) | 624(4) |
| $\mathrm{H}^{2}$ (C4) | 952(6) | 259(4) | 531(4) |  | 254(8) | 708(6) | 571(5) |
| $\mathrm{H}^{3}(\mathrm{C} 4)$ | 938(7) | 351(5) | 592(4) |  | 123(7) | 693(5) | 662(5) |
| $\mathrm{H}^{1}(\mathrm{C} 5)$ | $1001(6)$ | 135(5) | 846(4) |  | 569(6) | 729(5) | 774(4) |
| $\mathrm{H}^{2}$ (C5) | 991(7) | 1(5) | 916(4) |  | 673(5) | 638(4) | 803(3) |
| $\mathrm{H}^{1}(\mathrm{C} 7)$ | $1134(5)$ | -103(4) | 733(3) |  | 754(5) | 557(4) | 610(3) |
| $\mathrm{H}^{2}(\mathrm{C} 7)$ | $1167(6)$ | - 74(5) | 810(4) |  | 800(5) | 640(4) | 652(3) |
| $\mathrm{H}^{1}(\mathrm{C} 9)$ | 862(5) | 97(4) | 546(3) |  | 240(5) | 419(4) | 672(3) |
| $\mathrm{H}^{2}(\mathrm{C} 9)$ | 710(7) | 56(5) | 574(4) |  | 300(8) | 543(6) | 585(5) |
| $\mathrm{H}^{1}(\mathrm{C} 11)$ | 584(6) | 165(4) | 759(4) |  | 169(5) | 505(4) | 858(3) |
| $\mathrm{H}^{2}(\mathrm{C} 11)$ | 568(5) | 173(4) | 656(3) |  | 99(5) | 479(4) | 787(3) |
|  |  |  |  | $y$ |  |  |  |
|  |  |  |  | $\begin{aligned} & 392(6) \\ & 460(6) \end{aligned}$ |  |  |  |

The values of the valence angles in Table IV indicate that connection of the three five-membered chelate rings in the equatorial plane yields a system with high strain, which does not permit location of the $\mathrm{O}_{\mathrm{G}}$ donor atoms in the corners of an ideal square. This is reflected in the average value of the $\mathrm{O}_{\mathrm{G}}-\mathrm{Co}-\mathrm{O}_{\mathrm{G}}$ angle of $100.4^{\circ}$, which is very different from the ideal value of $90^{\circ}$. The inter-ring valence angle, $\mathrm{C}_{\mathrm{G}}-\mathrm{N}-\mathrm{C}_{\mathrm{E}}$, with a value of $115 \cdot 7^{\circ}$, exhibits marked deformation from the standard tetrahedral value $\left(109 \cdot 5^{\circ}\right)$. The described strain in the equatorial plane can be unambiguously assigned to the energetically unfavourable connection of 5-5-5-membered rings, as this deformation is not observed in complexes containing a system of $5-6-5$ or $6-5-6-\mathrm{membered}$ chelate rings ${ }^{16-19}$. In the studied complex $\Lambda \Delta-[\mathrm{Co}(\mathrm{rac}-$ -bdta) $]^{-}$, as in $[\mathrm{Co}(\mathrm{edta})]^{-}$, the equatorial strain is partially energetically compensated by intramolecular nonbonding interactions between the methylene hydrogens in the $E, G$ and $R$ rings (Table $V$ ), that line in the region of the minimum on the H... H potential curve as described by Tosi and coworkers ${ }^{20}$.


Fig. 2
Projection of the structure of $\Lambda \Delta-\mathrm{K}\left[\mathrm{Co}(\mathrm{rac}\right.$-bdta) $] .1 / 2 \mathrm{H}_{2} \mathrm{O}$ along crystallographic axis $a$. The dipole-ion and hydrogen bonds within the chain along the $b$ axis are designated by dashed lines. Molecules $A$ and $B$ are two independent $\Delta-\left[\operatorname{Co}((R, R) \text {-bdta) }]^{-}\right.$anions within a unit cell, consistent with the atomic coordinates in Table $\mathrm{I}, \circ \mathrm{Co}, \circ \mathrm{O}, \bullet \mathrm{C}, \oplus \mathrm{N}, \otimes \mathrm{K}, \circ \mathrm{W}$

The bonding conditions in the carboxyl groups can be analyzed on the basis of the data in Tables IV and VI. It is apparent from Fig. 2 that the oxygen atoms of the carboxyl groups participate in the formation of ionic interactions with $\mathrm{K}^{+}$ ions and are acceptors of hydrogen bonds with water molecules (W). The number and type of these interactions are given for each carboxyl group in Table VI (second and third columns). In all cases, the $\mathrm{C}-\mathrm{O}$ bonds are much longer for coordinated oxygen atoms $(\mathbf{O})$ than for uncoordinated oxygen atoms ( $\mathrm{O}^{\prime}$ ) (Table IV), where the differences vary from 0.034 to $0.116 .10^{-10} \mathrm{~m}$ (fourth column in Table VI). However, these differences are not correlated with the lengths of the $\mathrm{Co}-\mathrm{O}$ coordination bond and are also not dependent on the number of interactions of the carboxyl groups with $\mathrm{K}^{+}$and W . For example, the O atom of the carboxyl group of ring $R_{1}$ of mole-


Fig. 3
The average values of the bonding parameters in $\Lambda \Delta-[\operatorname{Co}(r a c \text {-bdta })]^{-}$employing pseudo- $C_{2}$ symmetry of the complex. The individual atoms are designated by indices according to the Hoard notation of chelate rings ${ }^{12}$. Atoms forming essentially a double bond are denoted by dashed lines. N Co $\mathrm{N} 90 \cdot 8, \mathrm{O}_{\mathrm{G}} \mathrm{CoO}_{\mathrm{G}} 100 \cdot 4$
cule $A$ interacts with one $\mathrm{K}^{+}$ion and the $\mathrm{O}^{\prime}$ atom with two $\mathrm{K}^{+}$ions, while the carboxyl group of ring $R_{2}$ of molecule $B$ does not participate in the formation of either ionic or hydrogen bonds. Nonetheless, both groups are characterized by almost identical $\Delta(\mathrm{C}-\mathrm{O})$ values: 0.068 and $0.069 .10^{-10} \mathrm{~m}$. On the other hand, the carboxyl group of ring $G_{2}$ of molecule $A$ and of ring $G_{1}$ of molecule $B$ have the largest and smallest $\Delta(\mathrm{C}-\mathrm{O})$ values, but their ionic vicinity differs only in a single interaction with $\mathrm{K}^{+}$. This situation is completely different from that for the complexes of $\mathrm{Ni}(\mathrm{II})$ with edta ${ }^{4-}$ or isomeric edds ${ }^{4-}\left(\mathrm{H}_{4}\right.$ edds $=$ ethylenediamine- $\mathrm{N}, \mathrm{N}^{\prime}$-disuccinic acid $)$, where a dependence of $\Delta(\mathrm{C}-\mathrm{O})$ on the strength of the $\mathrm{Ni}-\mathrm{O}$ bond was observed ${ }^{21,22}$. The complexes of $\mathrm{Co}(\mathrm{II})$ with edta ${ }^{4-}$ and phdta ${ }^{4-}$ (phenylenediamine- $\mathrm{N}, \mathrm{N}, \mathrm{N}^{\prime}, \mathrm{N}^{\prime}-$ -tetraacetate) are examples of complexes in which the secondary ionic and hydrogen bonds of the carboxyl groups affect the $\Delta(\mathbf{C}-\mathrm{O})$ value ${ }^{23}$. The insensitivity of the bonding parameters of the carboxyl groups and of the $\mathrm{Co}-\mathrm{O}$ distances to their crystallographic neighbourhood in the studied $\Lambda \Delta-\left[\mathrm{Co}(\mathrm{rac} \text {-bdta) }]^{-}\right.$complex reflects the relative rigidity of the coordination sphere of Cc (III) and the high degree of covalency of the $\mathrm{Co}-\mathrm{O}$ coordination bonds. However, the $\mathrm{C}-\mathrm{O}$ and $\Delta(\mathrm{C}-\mathrm{O})$ distances correlate with the valence angles on the $\mathrm{C}^{\prime}$ atoms of the carboxyl groups and closely obey the systematic relationships described by Borthwick ${ }^{24}$. The sum of the valence angles on the $\mathrm{C}^{\prime}$ atom is equal to $360^{\circ}$ for all 8 carboxyl groups, within experimental error (Table IV), where the individual angles are uncqually deformed as a result of coordination so that the $\mathrm{C}-\mathrm{C}^{\prime}-\mathrm{O}$ angle is smaller and the $\mathrm{O}^{\prime}-\mathrm{C}^{\prime}-\mathrm{O}$ angle is larger than the ideal trigonal value of $120^{\circ}$ (the $\mathrm{C}-\mathrm{C}^{\prime}-\mathrm{O}^{\prime}$ angle is practically undeformed).

The overall conformation of the $\Delta-[\operatorname{Co}((R, R) \text {-bdta })]^{-}$complex can be described according to Lee ${ }^{25}$ as $\lambda-\delta \delta-\delta \delta$. The conformations of the individual chelate rings are apparent from Table VII. The torsion parameters corresponding to two symmetric independent molecules are identical at the $7 \sigma$ level, but in an individual molecule are not connected by pseudo- $C_{2}$ symmetry, in contrast to the bonding parameters. The main difference lies in the conformation of the $G$ ring; the $G_{1}$ rings are in the gauche form, where the $C_{2}$ symmetry around the $C(8)$ atom is much higher in molecule $A$ than in molecule $B$, reflected in the asymmetry parameters ${ }^{26} \Delta C_{2}[C(8)]$ $3.6^{\circ}$ (molecule $A$ ) and $8.4^{\circ}$ (molecule $B$ ). In contrast, in the crystal the $G_{2}$ rings have a relatively symmetrical envelope conformation with low values of asymmetry parameters $\Delta C_{\mathrm{s}}[\mathrm{N}(2)] 3.5^{\circ}(A)$ and $3.6^{\circ}(B)$. The $\mathrm{N}(2)$ atom lies outside the central plane defined by $\mathrm{Co}, \mathrm{O}(4), \mathrm{C}(11), \mathrm{C}(12)\left(\chi^{2} 195\right.$ and 166$)$ by $0.710 .10^{-10} \mathrm{~m}$ in the $G_{2 \mathrm{~A}}$ ring and by $0.681 .10^{-10} \mathrm{~m}$ in the $G_{2 \mathrm{~B}}$ ring. The twist conformation of the $G_{1}$ rings observed in the $\Lambda \Delta-[\mathrm{Co}((r a c) \text {-bdta })]^{-}$structure is a result of the distortion of the energetically more favourable envelope form by deviation of the $\mathbf{O}(2)$ donor atom from the $\mathrm{Co}, \mathrm{O}(2), \mathrm{C}(7), \mathrm{C}(8)$ plane towards the $\mathrm{N}(1)$ atom. The above distortion is due to dipole-ion interaction between the lone electron pair of the $O(2)$ atom with the $\mathrm{K}(1)^{+}$ion in the $A$ complex anion or $\mathrm{K}(2)^{+}$ion in the $B$ complex anion,
which is approximately oriented due to the $s p^{3}$ hybridization of the $O(2)$ atom in the direction of the normal to the best plane of the $G_{1}$ rings. (The $O(4)$ atoms of the $G_{2 \mathrm{~A}}$ and $G_{2 \mathrm{~B}}$ rings are similarly involved in dipole-ion interaction with $\mathrm{K}^{+}$ions, but this interaction lies in the opposite direction.) The deviation of the $\mathrm{O}(2)$ atom from the $\mathrm{Co} \mathrm{O}(2) \mathrm{C}(7) \mathrm{C}(8)$ plane with simultaneous attempt of the $\mathrm{C}(7), \mathrm{C}(8)$, $\mathrm{O}(2), \mathrm{O}(6)$ fragment to retain its planarity leads to a change in the conformation of all the bonds of the $G_{1}$ ring, except for the $\mathrm{Co}-\mathrm{N}(1)$ bond (Table VII). This observation reflects the considerable flexibility of the $G$ ring in $\Lambda \Delta-[\mathrm{Co}(\mathrm{rac}) \text {-bdta) }]^{-}$. In contrast, although the $R_{1}$ and $R_{2}$ rings have very different crystallographic surroundings in molecules $(A)$ and $(B)$, these rings have the same conformation in the crystal (Table VI). The latter conformation can be described on the basis of the torsion angles given in Table VII as the Co-envelope conformation with very small puckering. The higher planarity of the $R$ ring compared to the $G$ ring is also apparent from the mean deviation of the five atoms of the given chelate ring from its mean central plane. The mean deviation of the $G$ rings in $\Lambda \Delta-[\mathrm{Co}((\mathrm{rac})-\mathrm{bdta})]^{-}$is 0.232 . $.10^{-10} \mathrm{~m}$ and of the $R$ rings $0.086 .10^{-10} \mathrm{~m}$. The value $0.086 .10^{-10} \mathrm{~m}$ is comparable with the mean deviation of other edta ${ }^{4-}$ or edta ${ }^{4-}$-analogous complexes according to the data given by Lingafelter and coworkerks ${ }^{21}$, but the distortion

Table IV
The interatomic distances $\left(.10^{-10} \mathrm{~m}\right)$ and valence angles $\left(^{\circ}\right)$ (estimated standard deviations are given in parentheses) in the $\Delta-\left[\mathrm{Co}(R, R \text {-bdta) }]^{-}\right.$complex ions (molecule $A$ and $B$ )

Interatomic distances

| Bond | A | B | Bond | A | B |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Co - $\mathrm{N}(1)$ | 1.927(5) | 1.929(5) | $\mathrm{C}(2)-\mathrm{C}(4)$ | 1.517(8) | 1.523(9) |
| $\mathrm{Co}-\mathrm{N}(2)$ | 1.924(4) | 1.918(4) | $\mathrm{C}(5)-\mathrm{C}(6)$ | 1.513(8) | 1.497(8) |
| $\mathrm{Co}-\mathrm{O}(1)$ | 1.898(4) | 1.890 (4) | $\mathrm{C}(6)-\mathrm{O}(1)$ | 1-294(7) | 1-291(7) |
| $\mathrm{Co}-\mathrm{O}(3)$ | 1.885(4) | 1.884(4) | $\mathrm{C}(6)-\mathrm{O}(5)$ | 1.226(7) | 1-226(7) |
| $\mathrm{Co}-\mathrm{O}(2)$ | 1-904(4) | $1.918(4)$ | $\mathrm{C}(7)-\mathrm{C}(8)$ | 1.536(8) | 1.544(9) |
| $\mathrm{Co}-\mathrm{O}(4)$ | 1.918(4) | 1.912(4) | $\mathrm{C}(8)-\mathrm{O}(2)$ | 1-294(7) | 1-272(7) |
| $\mathrm{N}(1)-\mathrm{C}(1)$ | $1 \cdot 500(7)$ | 1.504(7) | $\mathrm{C}(8)-\mathrm{O}(6)$ | 1.226(7) | 1.238(8) |
| $\mathrm{N}(1)-\mathrm{C}(5)$ | 1.491(7) | $1.505(7)$ | $\mathrm{C}(9)-\mathrm{C}(10)$ | $1 \cdot 516(8)$ | 1.510(8) |
| $\mathrm{N}(1)-\mathrm{C}(7)$ | 1.495(7) | $1.495(7)$ | $\mathrm{C}(10)-\mathrm{O}(3)$ | 1.287(7) | 1.289(7) |
| $\mathrm{C}(1)-\mathrm{C}(2)$ | $1 \cdot 552(8)$ | 1.543(8) | $\mathrm{C}(10)-\mathrm{O}(7)$ | 1-217(7) | 1.220(6) |
| $\mathrm{C}(1)-\mathrm{C}(3)$ | 1.529(8) | 1.523(9) | $\mathrm{C}(11)-\mathrm{C}(12)$ | 1.527(9) | 1.537(9) |
| $\mathrm{N}(2)-\mathrm{C}(2)$ | 1.522(7) | 1.512(8) | $\mathrm{C}(12)-\mathrm{O}(4)$ | 1.314(7) | 1-307(7) |
| $\mathrm{N}(2)-\mathrm{C}(9)$ | 1.488(7) | 1.514(7) | $\mathrm{C}(12)-\mathrm{O}(8)$ | 1-198(8) | 1-228(8) |
| $\mathrm{N}(2)-\mathrm{C}(11)$ | 1.507(7) | 1.500(7) |  |  |  |

Table IV
(Continued)

| Valence angles |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Bond | A | B | Bond | A | B |
| $\mathrm{N}(1)-\mathrm{Co}-\mathrm{N}(2)$ | $90 \cdot 9(2)$ | 90.6(2) | $\mathrm{N}(1)-\mathrm{C}(1)-\mathrm{C}(3)$ | 115.3(5) | 115.2(5) |
| $\mathrm{N}(1)-\mathrm{Co}-\mathrm{O}(1)$ | $87 \cdot 7(2)$ | 87-4(2) | $\mathrm{C}(2)-\mathrm{C}(1)-\mathrm{C}(3)$ | 112.6(5) | 113.5(5) |
| $\mathrm{N}(1)-\mathrm{Co}-\mathrm{O}(2)$ | 84.8(2) | 84.3(2) | $\mathrm{N}(2)-\mathrm{C}(2)-\mathrm{C}(1)$ | 105•3(4) | 105.4(4) |
| $\mathrm{N}(1)-\mathrm{Co}-\mathrm{O}(3)$ | 94.4(2) | 93.9(2) | $\mathrm{N}(2)-\mathrm{C}(2)-\mathrm{C}(4)$ | 114.4(4) | 113.5(4) |
| $\mathrm{N}(2)-\mathrm{Co}-\mathrm{O}(3)$ | 87.5(2) | 87.5(2) | $\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{C}(4)$ | 114-1(5) | $113 \cdot 8(5)$ |
| $\mathrm{N}(2)-\mathrm{Co}-\mathrm{O}(4)$ | 84.8(2) | 84.6(2) | $\mathrm{N}(1)-\mathrm{C}(5)-\mathrm{C}(6)$ | $111.7(5)$ | $111 \cdot 8(5)$ |
| $\mathrm{N}(2)-\mathrm{Co}-\mathrm{O}(1)$ | 94.8(2) | 93.1(2) | $\mathrm{C}(5)-\mathrm{C}(6)-\mathrm{O}(1)$ | $115 \cdot 7(5)$ | $115 \cdot 8(5)$ |
| $\mathrm{O}(2)-\mathrm{Co}-\mathrm{O}(4)$ | 100.0(2) | 100.9(2) | $\mathrm{C}(5)-\mathrm{C}(6)-\mathrm{O}(5)$ | 120.1(5) | 120.2(5) |
| $\mathrm{O}(1)-\mathrm{Co}-\mathrm{O}(2)$ | 91.9(2) | 92.5(2) | $\mathrm{O}(1)-\mathrm{C}(6)-\mathrm{O}(5)$ | 124.1(5) | 124.0(5) |
| $\mathrm{O}(1)-\mathrm{Co}-\mathrm{O}(4)$ | 87.0(2) | 87•8(2) | $\mathrm{Co}-\mathrm{O}(1)-\mathrm{C}(6)$ | 114.8(3) | 115.3(3) |
| $\mathrm{O}(3)-\mathrm{Co}-\mathrm{O}(2)$ | 86.0(2) | $86 \cdot 9$ (2) | $\mathrm{N}(1)-\mathrm{C}(7)-\mathrm{C}(8)$ | $107 \cdot 8(4)$ | 106.4(4) |
| $\mathrm{O}(3)-\mathrm{Co}-\mathrm{O}(4)$ | 91.1(2) | 90.8(2) | $\mathrm{C}(7)-\mathrm{C}(8)-\mathrm{O}(2)$ | 116.0(4) | 116.4(5) |
| $\mathrm{Co}-\mathrm{N}(1)-\mathrm{C}(1)$ | 105.4(3) | 105.3(3) | $\mathrm{C}(7)-\mathrm{C}(8)-\mathrm{O}(6)$ | 120.3(5) | 119.2(5) |
| $\mathrm{Co}-\mathrm{N}(1)-\mathrm{C}(5)$ | 107.6(3) | 107.0(3) | $\mathrm{O}(2)-\mathrm{C}(8)-\mathrm{O}(6)$ | 123.6(5) | $124.5(5)$ |
| $\mathrm{Co}-\mathrm{N}(1)-\mathrm{C}(7)$ | 103.9(3) | 103.9(3) | $\mathrm{Co}-\mathrm{O}(2)-\mathrm{C}(8)$ | 110.4(4) | 111.5(4) |
| $\mathrm{C}(1)-\mathrm{N}(1)-\mathrm{C}(5)$ | 114.4(4) | 113.8(4) | $\mathrm{N}(2)-\mathrm{C}(9)-\mathrm{C}(10)$ | 112.1(5) | 111.4(5) |
| $\mathrm{C}(1)-\mathrm{N}(1)-\mathrm{C}(7)$ | 115-2(4) | 116.1(4) | $\mathrm{C}(9)-\mathrm{C}(10)-\mathrm{O}(3)$ | 115.3(5) | 115.5(5) |
| $\mathrm{C}(5)-\mathrm{N}(1)-\mathrm{C}(7)$ | 109.4(4) | 109.6(4) | $\mathrm{C}(9)-\mathrm{C}(10)-\mathrm{O}(7)$ | $120 \cdot 1(5)$ | 119.6(5) |
| $\mathrm{Co}-\mathrm{N}(2)-\mathrm{C}(2)$ | $105 \cdot 5(3)$ | 105.5(3) | $\mathrm{O}(3)-\mathrm{C}(10)-\mathrm{O}(7)$ | 124.6(5) | 124.9(5) |
| $\mathrm{Co}-\mathrm{N}(2)-\mathrm{C}(9)$ | 107.8(3) | 108.1(3) | $\mathrm{Co}-\mathrm{O}(3)-\mathrm{C}(10)$ | 115.0(4) | 115.3(4) |
| $\mathrm{Co}-\mathrm{N}(2)-\mathrm{C}(11)$ | 103.8(3) | 105.0(3) | $\mathrm{N}(2)-\mathrm{C}(11)-\mathrm{C}(12)$ | 106.1(5) | 106.0(5) |
| $\mathrm{C}(2)-\mathrm{N}(2)-\mathrm{C}(9)$ | 114.0(4) | $113.2(4)$ | $\mathrm{C}(11)-\mathrm{C}(12)-\mathrm{O}(4)$ | 115.1(5) | $114.9(5)$ |
| $\mathrm{C}(2)-\mathrm{N}(2)-\mathrm{C}(11)$ | 115.5(4) | 115.8(4) | $\mathrm{C}(11)-\mathrm{C}(12)-\mathrm{O}(8)$ | 121-4(6) | $120 \cdot 5(5)$ |
| $\mathrm{C}(9)-\mathrm{N}(2)-\mathrm{C}(11)$ | 109.2(4) | 108.6(4) | $\mathrm{O}(4)-\mathrm{C}(12)-\mathrm{O}(8)$ | $123 \cdot 5(6)$ | $124.5(5)$ |
| $\mathrm{N}(1)-\mathrm{C}(1)-\mathrm{C}(2)$ | 106.9(4) | 106.3(4) | $\mathrm{Co}-\mathrm{O}(4) \cdots \mathrm{O}(12)$ | 112.3(4) | 112.8(4) |

of the $G$ rings from planarity observed in $\Lambda \Delta-[\mathrm{Co}((\mathrm{rac}) \text {-bdta })]^{-}$is much greater. The $E$ ring in $A$ and $B$ lies in the gauche form of $\lambda$ chirality with almost exactly $C_{2}$ symmetry (the corresponding asymmetry parameter $\Delta C_{2}(\mathrm{Co})$ equals $0.6^{\circ}$ in $A$ and $1.9^{\circ}$ in $B$ ). The puckering of the ring, expressed by torsion angle $\mathrm{N}(1)-\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{N}(2)$, equal to $-55 \cdot 5^{\circ}(A)$ and $-56.4^{\circ}(B)$ is, in agreement with the results of molecular--mechanics calculations ${ }^{4}$, significantly larger than in the $[\mathrm{Co}(\text { edta })]^{-}$complex, where this torsion angle has a value of $47.8^{\circ}$ (ref. ${ }^{12}$ ).

As mentioned, the deformation of some bonding parameters in the equatorial plane of the $\Lambda \Delta-[\mathrm{Co}((\mathrm{rac}) \text {-bdta })]^{-}$anion has also been observed in other edta ${ }^{4-}$ complexes and reflects strain resulting from the bonding of three five-membered chelate
rings. It is thus interesting to compare this deformation to that produced by replacing the equatorial H atoms (on the $E$ ring) in the [ $\mathrm{Co}(\mathrm{edta})]^{-}$complex by methyl groups. Investigation of the molecular model has demonstrated that the "additional" strain in $\Lambda \Delta-[\mathrm{Co}((r a c) \text {-bdta })]^{-}$compared with $[\mathrm{Co}(\mathrm{edta})]^{-}$is due to the very short intramolecular nonbonding distances $\mathrm{H}^{3}(\mathrm{C} 3) \ldots \mathrm{H}^{2}(\mathrm{C} 5)$ or $\mathrm{H}^{3}(\mathrm{C} 4) \ldots \mathrm{H}^{2}(\mathrm{C} 9)$ with respect to pseudo- $C_{2}$ symmetry of the complex. The relaxed values of these distances observed in the crystal structure are listed in Table V. However, as the centres of gravity of the electron clouds of the H atoms recorded in the diffraction experiment are shifted by bonding forces towards the C atoms, the internuclear $\mathrm{H} . . \mathrm{H}$ distances are probably even shorter. The shift of the corresponding hydrogen atoms along the

Table V
Intramolecular nonbonding interactions $\mathrm{H} \ldots \mathrm{H}<2 \cdot 5 \cdot 10^{-10} \mathrm{~m}$ in the crystal structure of $\Lambda \Delta-\mathrm{K}[\mathrm{Co}(\mathrm{rac}-\mathrm{bdta})] .1 / 2 \mathrm{H}_{2} \mathrm{O}$ with estimated standard deviations in parentheses

| Interaction | Molecule $A$ | Molecule $B$ |
| :---: | :---: | :---: |
|  |  |  |
| $\mathrm{H}^{3}(\mathrm{C} 3) \ldots \mathrm{H}^{2}(\mathrm{C} 5)$ | $2 \cdot 16(8)$ | $2 \cdot 26(7)$ |
| $\mathrm{H}^{3}(\mathrm{C} 4) \ldots \mathrm{H}^{2}(\mathrm{C} 9)$ | $2 \cdot 15(7)$ | $1 \cdot 95(9)$ |
| $\mathrm{H}^{1}(\mathrm{C} 5) \ldots \mathrm{H}^{2}(\mathrm{C} 7)$ | $2 \cdot 31(8)$ | $2 \cdot 29(6)$ |
| $\mathrm{H}^{1}(\mathrm{C} 9) \ldots \mathrm{H}^{2}(\mathrm{C} 11)$ | $2 \cdot 28(8)$ | $2 \cdot 18(7)$ |
| $\mathrm{H}(\mathrm{Cl}) \ldots \mathrm{H}^{1}(\mathrm{C} 7)$ | $2 \cdot 43(8)$ | $2 \cdot 34(7)$ |
| $\mathbf{H}(\mathrm{C} 2) \ldots \mathrm{H}^{1}(\mathrm{C} 11)$ | $2 \cdot 34(7)$ | $2 \cdot 40(7)$ |

## Table VI

Participation of oxygen atoms (coordinated O or uncoordinated $\mathrm{O}^{\prime}$ ) of the carboxyl groups in the formation of ionic bonds with $\mathrm{K}^{+}$and hydrogen bonds with molecules of water of crystallization $W . \Delta(\mathrm{C}-\mathrm{O})=\mathrm{d}\left(\mathrm{C}^{\prime}-\mathrm{O}\right)-\mathrm{d}\left(\mathrm{C}^{\prime}-\mathrm{O}^{\prime}\right)$

| Ring | O | $0^{\prime}$ | $\Delta(\mathrm{C}-\mathrm{O}) \cdot 10^{-10} \mathrm{~m}$ |
| :---: | :---: | :---: | :---: |
| $R_{1 \mathrm{~A}}$ | $1 \mathrm{~K}^{+}$ | $2 \mathrm{~K}^{+}$ | 0.068 |
| $G_{1 \mathrm{~A}}$ | $1 \mathrm{~K}^{+}$ | $1 \mathrm{~K}^{+}, W$ | 0.068 |
| $R_{2 A}$ | - | - | 0.070 |
| $G_{2 A}$ | $1 \mathrm{~K}^{+}$ | + | $0 \cdot 116$ |
| $R_{1 \mathrm{~B}}$ | W | $2 \mathrm{~K}^{+}$ | 0.065 |
| $G_{18}$ | $1 \mathrm{~K}^{+}$ | $1 \mathrm{~K}^{+}$ | 0.034 |
| $R_{2 B}$ |  |  | 0.069 |
| $G_{2 \mathrm{~B}}$ | $1 \mathrm{~K}^{+}$ | $1 \mathrm{~K}^{+}$ | 0.079 |

$\mathrm{C}-\mathrm{H}$ bonds to a distance of $1.09 .10^{-10} \mathrm{~m}$ leads to shortening of the given $\mathrm{H} \ldots \mathrm{H}$ distance to: $\mathrm{H}^{3}(\mathrm{C} 3) \ldots \mathrm{H}^{2}(\mathrm{C} 5) 2.04(A)$ and $2.11(B), \mathrm{H}^{3}(\mathrm{C} 4) \ldots \mathrm{H}^{2}(\mathrm{C} 9) 2.00(A)$

## Table VII

Torsion angles $\left(^{\circ}\right)$ in the $\Delta-[\operatorname{Co}(R, R) \text {-bdta) }]^{-}$complex anion with estimated standard deviations in parentheses

and $1 \cdot 86.10^{-10} \mathrm{~m}(B)$. Use of the $\mathrm{H} \ldots \mathrm{H}$ nonbonding potential function given by Tosi and coworkers ${ }^{20}$ yields a mean repulsion energy for these interactions of $3.14 \mathrm{~kJ} \mathrm{~mol}^{-1}$. This value is very similar to the value of $3.52 \mathrm{~kJ} \mathrm{~mol}^{-1}$ obtained from molecular-mechanics calculations ${ }^{4}$. In the relaxation process the repulsion energy of the given $\mathrm{H} \ldots \mathrm{H}$ interactions is distributed over the following bonds and torsion parameters: 1) the $\mathrm{N}-\mathrm{C}_{\mathrm{E}}$ and $\mathrm{N}-\mathrm{C}_{\mathrm{R}}$ bonds (Fig. 3) are lengthened from the values of 1.49 and $1.47 .10^{-10} \mathrm{~m}$ observed in $[\mathrm{Co}(\mathrm{edta})]^{-}$(ref. ${ }^{12}$ ) to 1.51 and 1.50 . $.10^{-10} \mathrm{~m}$ in $\Lambda \Delta-[\mathrm{Co}((\mathrm{rac}) \text {-bdta })]^{-}$; these values are very different from the standard length of the $\mathrm{N}\left(s p^{3}\right)-\mathrm{C}\left(s p^{3}\right)$ bond, $\left.1 \cdot 47.10^{-10} \mathrm{~m} ; 2\right)$ the $\mathrm{C}_{\mathrm{E}}-\mathrm{N}-\mathrm{C}_{\mathrm{R}}$ valence angle increases to $113.8^{\circ}$ compared to the value of $108.6^{\circ}$ in $[\mathrm{Co}(\mathrm{edta})]^{-}$(ref. ${ }^{12}$ ) (the angles $\mathrm{N}-\mathrm{C}_{\mathrm{E}}-\mathrm{CH}_{3} 114.6^{\circ}$ and $\mathrm{C}_{\mathrm{E}}-\mathrm{C}_{\mathrm{E}}-\mathrm{CH}_{3} 113.5^{\circ}$ are not comparable with the corresponding angles in [Co(edta) $]^{-}$but are nonetheless significantly deformed compared to the tetrahedral value of $109.5^{\circ}$ ); 3) as mentioned above, the puckering of the $E$ ring increases. The remaining interatomic distances, valence and torsion angles (Fig. 3 and Table VII) that are not directly affected by minimization of the H...H repulsion energy are "normal" within experimental error.

It can be seen from Fig. 2 that the $\Lambda \Delta-[\mathrm{Co}((R, R) \text {-bdta })]^{-}$and $[\mathrm{Co}((S, S) \text {-bdta })]^{-}$ complex anions are connected in infinite chains along the $b$ axis through the $\mathrm{K}^{+}$ions and molecules of water of crystallization, $W$. The oxygen atom, $W$, is a donor of two hydrogen bonds, $W-\mathrm{H}^{1} \ldots \mathrm{O}(6 A) 2 \cdot 941(7)$ and $W-\mathrm{H}^{2} \ldots \mathrm{O}(1 B) 2 \cdot 932(6) .10^{-10} \mathrm{~m}$. The remaining bonds in the chains formed by the oxygen atoms of the complex ions and $W$ with the $\mathrm{K}^{+}$ions are of the dipole-ion type. Of the two $\mathrm{K}^{+}$ions in the asymmetrical crystal unit, $\mathrm{K}(1)^{+}$is hexa-coordinated by the $\mathrm{O}(1 A), \mathrm{O}(2 A), \mathrm{O}(4 A), \mathrm{O}(5 A)$, $\mathrm{O}(2 B)$ and $\mathrm{O}(5 B)$ atoms and the $\mathrm{K}(2)^{+}$ion is hepta-coordinated by the $\mathrm{O}(5 A)$, $\mathrm{O}(6 A), \mathrm{O}(2 B), \mathrm{O}(5 B), \mathrm{O}(6 B)$ and $\mathrm{O}(8 B)$ atoms and $W$. The spatial arrangement around the $\mathrm{K}^{+}$ions is stringly deformed and cannot be expressed by any defined coordination polyhedron. The $\mathrm{K}(1)^{+} \ldots \mathrm{O}$ distances varies from 2.748 to 2.969 . $.10^{-10} \mathrm{~m}$ and the $\mathrm{K}(2)^{+} \ldots \mathrm{O}$ distance from 2.633 to $2.998 .10^{-10} \mathrm{~m}$. The average value of $\mathrm{K}(1)^{+} \ldots \mathrm{O}$ of $2.833(4) .10^{-10} \mathrm{~m}$ corresponds to the ionic radius of $\mathrm{K}^{+}$ for coordination numbers of six and seven ${ }^{27}$ and the van der Waals radius of the O atom. The average value of $\mathrm{K}(2)^{+} \ldots \mathrm{O}$ of $2.773(5) .10^{-10} \mathrm{~m}$ corresponds to the sum of the ionic radius of $\mathrm{K}^{+}$for a coordination number of six and the van der Waals radius of $O$.

All the calculations were carried out on a Siemens 4004/150 computer at the Comenius University, Computer Centre, Bratislava. The authors wish to thank Dr J. Soldan for measuring the intensities on the Syntex $P 2_{1}$ diffractometer.

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