

Structure of the Stable Isomer of the Bis(ethane-1,2-diamine)(*N*-methylethane-1,2-diamine)cobalt(III) Cation, [Co(meen)(en)₂]³⁺

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Abstract. Bis(ethane-1,2-diamine-*N,N'*)(*N*-methylethane-1,2-diamine-*N,N'*)cobalt(III) triperchlorate monohydrate, [Co(C₂H₈N₂)(C₂H₈N₂)₂](ClO₄)₃·H₂O, *M_r* = 569.6, monoclinic, *P*2₁/*n*, *a* = 10.280 (1), *b* = 13.905 (2), *c* = 14.533 (2) Å, β = 90.30 (1)°, *V* = 2077 (2) Å³, *Z* = 4, *D_x* = 1.821 g cm⁻³, λ(Mo *Kα*) = 0.7107 Å, μ = 12.84 cm⁻¹, *F*(000) = 1176, *T* = 293 (1) K, *R* = 0.051 for 2138 observed reflections. The Co atom in the cation is octahedrally coordinated by six N atoms from three chelating diamine ligands; Co—N 1.967 (5)–1.999 (5) Å, with Co—N(CH₃) the longest. The structure is a racemate and the conformational structure is *A-R-δ*λλ* (for one enantiomer). Comparisons are made with the structure calculated by molecular mechanics using an *MM2* force field. The crystal lattice is held together *via* hydrogen bonds involving the cation, perchlorate anions and the water molecule of crystallization.

Introduction. The separation and isolation of a number of isomers of Co^{III} complexes of *N*-methylethane-1,2-diamine (meen) has been reported recently (Searle & Keene, 1989). Aerial oxidation of a mixture of Co^{II}, 3meen and H⁺ in aqueous solution with charcoal at 353 K yields an equilibrium mixture of the complexes [Co(meen)₃]³⁺, [Co(meen)₂(en)]³⁺, [Co(meen)(en)₂]³⁺ and [Co(en)₃]³⁺, where the coordinated ethane-1,2-diamine (en) arises through demethylation of the Co^{III}–meen, brought about by the oxygen with charcoal catalysis. Each of these Co–meen complexes has a number of possible isomeric forms, arising from configurational (*A* or *Δ*, and *R* or *S*) and geometric (facial or meridional) isomerism.

The most stable of these complexes and isomers have been separated by cation-exchange chromatography on SP-Sephadex C25 using Na₃PO₄ as eluent,

and the complexes thus detected have been labelled (*A*) to (*H*) (Searle & Keene, 1989). They were isolated in crystalline form and were characterized by their ¹³C NMR spectra which allowed their isomeric identity to be established in most cases.

X-ray structures of several of these complexes have been reported previously: two [Co(meen)₃]³⁺ isomers labelled (*A*) and (*C*), and two [Co(meen)₂(en)]³⁺ isomers labelled (*F*) and (*H*) (Searle & Tiekink, 1989*a,b*). (*B*) is a third [Co(meen)₃]³⁺ isomer which has been isolated but not yet structurally characterized.

For the complex bis(ethane-1,2-diamine)(*N*-methylethane-1,2-diamine)cobalt(III) cation, two diastereoisomers are possible, *A-R/Δ-S* and *A-S/Δ-R* (as racemic pairs). Only one of these diastereoisomers has been evident experimentally, designated as complex (*E*), and the crystal structure of this isomer is now reported.

Experimental. Complex (*E*), [Co(meen)(en)₂]³⁺, was separated chromatographically and obtained as the perchlorate monohydrate salt by addition of HClO₄ to an HCl solution of the eluted complex. Crystals suitable for the X-ray study were grown by ethanol vapour diffusion into an aqueous solution of the complex under slight vacuum. Data were collected using an Enraf–Nonius CAD-4F diffractometer controlled by a PDP8/A computer, with graphite-monochromated Mo *Kα* radiation and ω–2θ scans. Cell parameters were determined by least squares on 25 reflections (9 ≤ θ ≤ 14°) (de Boer & Duisenberg, 1984) from a crystal 0.10 × 0.25 × 0.62 mm. An analytical absorption correction was applied with maximum and minimum transmission factors of 0.856 and 0.640 (*SHELX76*; Sheldrick, 1976). 5575 reflections (1.5 ≤ θ ≤ 25.0°) were measured in the range –12 ≤ *h* < 12, 0 ≤ *k* ≤ 16, –14 ≤ *l* < 5. No significant variation was observed in the net intensity

† Deceased 24 July, 1992.

of three reference reflections ($\bar{4}24$, $\bar{3}25$ and $\bar{4}36$) measured every 7200 s. 3668 unique reflections were measured ($R_{\text{merge}} = 0.021$) of which 2138 satisfied $I \geq 2.5\sigma(I)$. The structure was solved by Patterson methods, with full-matrix least-squares refinement on 292 parameters based on F (SHELX76; Sheldrick, 1976). Refinement included anisotropic thermal parameters for non-H atoms, and H atoms were included at their calculated positions with a common isotropic thermal parameter. The ClO_4^- anions with the Cl(2) and Cl(3) atoms were found to be disordered such that an O atom in each, *i.e.* O(8) and O(12), was situated over two positions; these were modelled with 50% site occupancy factors. At convergence $R = 0.051$, $wR = 0.060$ $\{w = 1.76/[\sigma^2(F) + 0.0008F^2]\}$, $S = 3.32$, $(\Delta/\sigma)_{\text{max}} \leq 0.02$ (for cation), $\Delta\rho_{\text{max}} = 0.75$, $\Delta\rho_{\text{min}} = -0.57 \text{ e } \text{\AA}^{-3}$. An extinction correction was applied such that the value of $nz = 0.0001(3)$ (SHELX76; Sheldrick, 1976). Scattering factors for Co^{3+} corrected for f' and f'' , were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 99, 149) and for the remaining atoms as incorporated in SHELX76 (Sheldrick, 1976). All calculations were performed on a SUN4/280 computer system. Atomic coordinates are given in Table 1, selected interatomic parameters are in Table 2,* and the atom-numbering scheme used for the cation is shown in Fig. 1, which was drawn with ORTEPII (Johnson, 1976) at 25% probability levels.

Discussion. The complex (*E*) crystallizes as the perchlorate monohydrate salt in the space group $P2_1/n$, with two pairs of enantiomeric molecules in the unit cell. The octahedral cation geometry is defined by six N atoms derived from three chelating diamine ligands. The six Co—N bond distances are all similar, lying in the range 1.967(5)–1.999(5) Å; the longest distance is formed by the methylated N atom. Distortions from ideal octahedral geometry may be related to the restricted bite distance of the chelating ligands, with the maximum deviation manifested in the N(5)—Co—N(6) angle of 84.7(2)°.

In the crystal lattice of [Co(meen)(en)₂](ClO₄)₃·H₂O there are a large number of hydrogen-bonding contacts between the cation, the perchlorate anions and the water molecule of crystallization. These contacts are summarized as follows [details in

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, all interatomic parameters, hydrogen-bonding contacts and details of *MM2* results have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55430 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS0569]

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å²)

$$B_{\text{eq}} = (8\pi^2/3)(U_{11} + U_{22} + U_{33}).$$

| | x | y | z | B_{eq} |
|--------|--------------|-------------|--------------|-----------------|
| Co | -0.01083 (7) | 0.25098 (6) | 0.70115 (5) | 1.92 |
| N(1) | -0.1533 (5) | 0.2664 (3) | 0.7897 (4) | 2.66 |
| N(2) | 0.0021 (5) | 0.3944 (3) | 0.7048 (4) | 2.74 |
| N(3) | -0.1353 (5) | 0.2586 (4) | 0.5974 (3) | 2.58 |
| N(4) | 0.1238 (5) | 0.2397 (4) | 0.6042 (4) | 3.11 |
| N(5) | 0.1163 (5) | 0.2356 (3) | 0.8017 (4) | 2.66 |
| N(6) | -0.0242 (5) | 0.1095 (3) | 0.7066 (4) | 2.79 |
| C(1) | -0.1953 (6) | 0.3685 (5) | 0.7938 (5) | 3.37 |
| C(2) | -0.0716 (6) | 0.4292 (5) | 0.7867 (5) | 3.34 |
| C(3) | 0.1301 (6) | 0.4428 (5) | 0.7015 (6) | 3.92 |
| C(4) | -0.0661 (7) | 0.2741 (6) | 0.5091 (5) | 4.53 |
| C(5) | 0.0598 (8) | 0.2235 (7) | 0.5129 (6) | 5.42 |
| C(6) | 0.1078 (7) | 0.1362 (5) | 0.8389 (5) | 3.84 |
| C(7) | 0.0836 (7) | 0.0691 (5) | 0.7615 (6) | 4.11 |
| Cl(1) | 0.2598 (2) | 0.4732 (2) | 0.4346 (1) | 4.58 |
| O(1) | 0.2777 (8) | 0.4362 (6) | 0.3459 (5) | 8.42 |
| O(2) | 0.1297 (7) | 0.4940 (7) | 0.4490 (6) | 10.48 |
| O(3) | 0.3127 (8) | 0.4154 (7) | 0.5054 (6) | 11.16 |
| O(4) | 0.3175 (10) | 0.5652 (6) | 0.4322 (7) | 11.19 |
| Cl(2) | 0.2508 (3) | 0.4707 (1) | -0.0237 (2) | 5.40 |
| O(5) | 0.2749 (7) | 0.4514 (5) | 0.0682 (4) | 6.82 |
| O(6) | 0.2225 (8) | 0.3900 (6) | -0.0735 (5) | 9.63 |
| O(7) | 0.2287 (12) | 0.5522 (8) | -0.0498 (8) | 15.08 |
| O(8) | 0.3948 (13) | 0.4837 (12) | -0.0587 (13) | 11.53 |
| O(8') | 0.0956 (12) | 0.4952 (11) | -0.0085 (10) | 8.45 |
| Cl(3) | -0.0201 (2) | 0.2515 (1) | 0.2282 (1) | 3.53 |
| O(9) | 0.0875 (6) | 0.2892 (7) | 0.1868 (6) | 9.19 |
| O(10) | -0.0949 (9) | 0.1979 (8) | 0.1648 (7) | 12.29 |
| O(11) | -0.1086 (8) | 0.3197 (6) | 0.2558 (10) | 16.06 |
| O(12) | 0.0091 (10) | 0.1791 (8) | 0.2973 (7) | 4.74 |
| O(12') | 0.0325 (20) | 0.2774 (25) | 0.3002 (14) | 30.50 |
| O(H1) | 0.4565 (7) | 0.2204 (5) | 0.4761 (4) | 7.00 |

Table 2. Selected interatomic distances (Å) and bond angles (°)

| | | | |
|----------------|-----------|----------------|-----------|
| Co—N(1) | 1.967 (5) | Co—N(2) | 1.999 (5) |
| Co—N(3) | 1.976 (5) | Co—N(4) | 1.986 (5) |
| Co—N(5) | 1.967 (5) | Co—N(6) | 1.974 (5) |
| N(1)—C(1) | 1.486 (8) | N(2)—C(2) | 1.495 (9) |
| N(2)—C(3) | 1.480 (7) | N(3)—C(4) | 1.486 (8) |
| N(4)—C(5) | 1.50 (1) | N(5)—C(6) | 1.487 (8) |
| N(6)—C(7) | 1.473 (8) | C(1)—C(2) | 1.529 (8) |
| C(4)—C(5) | 1.47 (1) | C(6)—C(7) | 1.48 (1) |
| N(1)—Co—N(2) | 85.6 (2) | N(1)—Co—N(3) | 90.7 (2) |
| N(1)—Co—N(4) | 175.5 (2) | N(1)—Co—N(5) | 91.1 (2) |
| N(1)—Co—N(6) | 91.7 (2) | N(2)—Co—N(3) | 90.5 (2) |
| N(2)—Co—N(4) | 92.9 (2) | N(2)—Co—N(5) | 92.6 (2) |
| N(2)—Co—N(6) | 176.2 (2) | N(3)—Co—N(4) | 85.1 (2) |
| N(3)—Co—N(5) | 176.5 (2) | N(3)—Co—N(6) | 92.3 (2) |
| N(4)—Co—N(5) | 93.2 (2) | N(4)—Co—N(6) | 89.9 (2) |
| N(5)—Co—N(6) | 84.7 (2) | Co—N(1)—C(1) | 110.3 (4) |
| Co—N(2)—C(2) | 108.1 (4) | Co—N(2)—C(3) | 120.8 (4) |
| Co—N(3)—C(4) | 110.8 (4) | Co—N(4)—C(5) | 109.7 (4) |
| Co—N(5)—C(6) | 109.3 (4) | Co—N(6)—C(7) | 110.4 (4) |
| C(2)—N(2)—C(3) | 109.4 (5) | N(1)—C(1)—C(2) | 106.4 (5) |
| N(2)—C(2)—C(1) | 107.5 (5) | N(3)—C(4)—C(5) | 108.9 (6) |
| N(4)—C(5)—C(4) | 110.1 (6) | N(5)—C(6)—C(7) | 108.6 (5) |
| N(6)—C(7)—C(6) | 107.1 (5) | | |

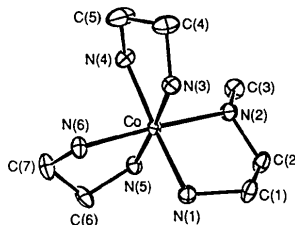


Fig. 1. Molecular structure and crystallographic numbering scheme employed for the cation in [Co(meen)(en)₂](ClO₄)₃·H₂O (Johnson, 1976).

supplementary table S(7):† each of the N-bound H atoms is involved in at least one contact with an O atom from either a perchlorate anion or the water molecule. The water molecule of crystallization forms two close contacts with the cation and two close contacts with the symmetry-related perchlorate groups, presumably *via* the water molecule H atoms which were not located in the difference map. Each of the perchlorate O atoms is thus involved in the hydrogen-bonding network. It is unknown how such hydrogen bonding might determine the ring conformations, although such bonding forces *acting cooperatively* must be a major factor in accounting for any differences between the detailed structures found in the solid state and those calculated by energy minimization for the cation only.

The particular diastereoisomer is the *A-R* isomer (as racemate), and is illustrated in Fig. 1. The conformational structure is uniquely defined as *A-R- $\delta^*\lambda\lambda$* ,‡ with the methyl substituent being equatorial (to the mean plane of its chelate ring). This diastereoisomer, which is isolated, should be the thermodynamically more stable, since the two diastereoisomers should interconvert at the asymmetric N atom in solution, *A-R* \rightleftharpoons *A-S*, under the basic conditions of the chromatographic separation, and these two configurations should then be fixed in their equilibrium ratio on the subsequent acidification. That only one of the diastereoisomeric pairs *A-R/A-S* has been observed experimentally under all conditions, indicates that *K* [equilibrium ratio of the two diastereoisomeric pairs (*A-R/A-S*) and (*A-S/A-R*)] for the two diastereoisomers must be large (say *K* > 12, for which $\Delta G > 6 \text{ kJ mol}^{-1}$).

For the $[\text{Co}(\text{meen})(\text{en})_2]^{3+}$ system, the steric energies of the sixteen possible geometrically different conformations, eight for *A-R* and eight for *A-S*, have been calculated using the *MM2* force field (Atkinson, Keene & Searle, 1991).§ From this recent analysis, the isomer having the lowest calculated steric energy was *A-R- $\delta^*\delta\delta$* (steric energy 44.5 kJ mol^{-1}). Thus, the *MM2* calculations correctly predicted the particular diastereoisomer and the equatorial methyl in the meen δ^* ring, but the conformations of the two en rings ($\delta\delta$) differed from

those in the observed structure ($\lambda\lambda$). The calculated steric energy for this observed structure (49.0 kJ mol^{-1}) was 4.5 kJ mol^{-1} higher, which corresponds to a ratio of *K ca* 6. No specific crystal forces can be identified in the structure which might account for the $\lambda\lambda$ arrangement being favoured. There are two other conformers which have lower calculated steric energies than the observed structure: *A-R- $\delta^*\lambda\delta$* (45.0 kJ mol^{-1}) and *A-R- $\delta^*\delta\lambda$* (48.8 kJ mol^{-1}). Despite there being several conformers of similar energy, the complex crystallizes readily in only one form, perhaps because of the lability of the en ring conformations. In solution the conformers present are unknown and the ^{13}C NMR spectrum gives only a time average of any conformer mixture.

While the 4.5 kJ mol^{-1} steric-energy gap between the observed and calculated structures is not large by *MM2* standards, we did observe better correlations for the $[\text{Co}(\text{meen})_2(\text{en})]^{3+}$ and $[\text{Co}(\text{meen})_3]^{3+}$ systems (Atkinson, Keene & Searle, 1991). It is therefore unlikely that the origin of the discrepancy lies solely with the force field employed in the calculations. Structural comparisons between the minimized *A-R- $[\text{Co}(\text{meen})(\text{en})_2]^{3+}$* conformations where the methyl group is equatorial reveal that the molecular shapes [as determined by the root-mean-square (r.m.s.) differences of atomic positions] are very similar irrespective of the conformations of the two en chelate rings. This situation is different from the $[\text{Co}(\text{meen})_2(\text{en})]^{3+}$ and $[\text{Co}(\text{meen})_3]^{3+}$ systems, where there are additional ring substituents. It is therefore possible that in this special case of $[\text{Co}(\text{meen})(\text{en})_2]^{3+}$, the molecular structures are too closely related to be reliably discriminated with a general *MM2* force field.

Comparison of the details of the determined structure with those of the calculated (minimized) structure for the *A-R- $\delta^*\lambda\lambda$* shows close agreement between the structures: r.m.s. differences are 0.029 \AA for 16 bond lengths, 1.39° for 29 bond angles, 2.41° for 40 torsional angles, and 0.042 \AA for all interatomic distances [supplementary tables S(5) and S(6)].†

The energy difference from the determined structure to that calculated for the other diastereoisomer *A-S- $\lambda^*\delta\delta$* (51.4 kJ mol^{-1}) is only 2.4 kJ mol^{-1} (*K ca* 2.6). This does not seem sufficiently large to account for the apparent stereospecificity as the *A-S* isomer was not observed experimentally. It is likely, therefore, that hydrogen bonding in the solid state is important in discriminating these isomers.

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† See deposition footnote.

‡ Each of the five-membered chelate rings formed by the bidentate ligands meen and en can exist in alternative conformations, δ or λ . The unique meen ring is specified first and designated with an asterisk (Atkinson, Keene & Searle, 1991). The discussion here is presented for only the *A* configurations of complexes, but in all cases there is an equivalent Δ form in the racemate that constitutes each diastereoisomeric pair.

§ An early conformational analysis of $[\text{Co}(\text{meen})(\text{en})_2]^{3+}$ used non-bonded interactions only (Sargeson, 1966). Although the broad structure predicted for the more stable isomer was correct (*A-R- δ^**), the results of such limited analyses are generally unreliable.

† See deposition footnote.

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Complexes Between Uranyl Nitrate and Benzo-15-crown-5: Structures of the (2/1) and (1/1) Complexes of Benzo-15-crown-5–Diaquadintratodioxouranium(VI)

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Abstract. (1) [UO₂(NO₃)₂(H₂O)₂].2C₁₄H₂₀O₅, *M_r* = 966.69, monoclinic, *P*2₁/*n*, *a* = 10.891 (3), *b* = 8.312 (2), *c* = 20.507 (6) Å, β = 97.21 (2)°, *V* = 1842 (1) Å³, *Z* = 2, *D_x* = 1.74 g cm⁻³, λ(Mo *K*α) = 0.71073 Å, μ = 42.56 cm⁻¹, *F*(000) = 956, *T* = 295 K, *R* = 0.024 for 1994 unique reflections. (2) [UO₂(NO₃)₂(H₂O)₂].C₁₄H₂₀O₅, *M_r* = 698.38, triclinic, *P*1̄, *a* = 8.477 (2), *b* = 8.809 (2), *c* = 16.700 (3) Å, α = 105.18 (2)°, β = 82.42 (2)°, γ = 110.08 (2)°, *V* = 1129 (1) Å³, *Z* = 2, *D_x* = 2.05 g cm⁻³, λ(Mo *K*α) = 0.71073 Å, μ = 68.86 cm⁻¹, *F*(000) = 668, *T* = 295 K, *R* = 0.033 for 2431 unique reflections. In both complexes, the crown ether molecules are hydrogen bonded to the two water molecules of the hexagonal bipyramidal [UO₂(NO₃)₂(H₂O)₂]. In complex (1), two crown ether molecules are linked to one U complex to form a molecular structure whereas in complex (2), each crown ether molecule is shared by two U complexes to form polymer chains.

Introduction. Most *f*-element salts, and particularly U salts, are known to form a large variety of adducts with crown ethers (Moody & Ryan, 1979; Rogers, 1988; Rogers, Kurihara & Benning, 1987). During the recrystallization of the adducts of uranyl nitrate with benzo-15-crown-5 from ethanol solution, well shaped crystals with different morphology and colour were obtained. These crystals have been studied by X-ray diffraction and shown to be the 1/1 and 1/2 adducts.

Experimental. Suitable crystals of both complexes were obtained by slow evaporation from ethanol solution of uranyl nitrate and benzo-15-crown-5.

Table 1. Data collection and refinement parameters for [UO₂(NO₃)₂(H₂O)₂](benzo-15-crown-5)₂ (1) and [UO₂(NO₃)₂(H₂O)₂](benzo-15-crown-5) (2)

| | Complex (1) | Complex (2) |
|--|--------------------|--------------------|
| Crystal colour | Yellow | Yellow |
| Crystal size (mm) | 0.35 × 0.35 × 0.20 | 0.40 × 0.35 × 0.20 |
| 2θ range for data collection (°) | 2–50 | 2–44 |
| Standard reflections | 330, 404, 305 | 033, 133, 236 |
| Variation (%) of standard reflections over period (h) of data collection | 0.2, 44 | 0.3, 43 |
| <i>hkl</i> range, <i>h</i> | 0, 12 | 8, –8 |
| <i>k</i> | 0, 9 | 9, –9 |
| <i>l</i> | –24, 24 | 0, 17 |
| Absorption corrections (maximum/minimum transmission) | 0.996/0.792 | 0.999/0.491 |
| Total No. of reflections measured | 3676 | 2871 |
| No. of unique reflections | 3233 | 2755 |
| <i>R_{int}</i> | 0.018 | 0.015 |
| No. of reflections with <i>I</i> > 3σ(<i>I</i>) | 1994 | 2431 |
| No. of parameters | 162 | 219 |
| <i>R</i> | 0.024 | 0.033 |
| <i>wR</i> (<i>w</i> = 1) | 0.030 | 0.051 |
| <i>S</i> | 2.23 | 3.52 |
| (Δ/ <i>σ</i>) _{max} | 0.02 | 0.03 |
| Maximum electron density (e Å ⁻³) in final difference map | 0.849 | 0.658 |

Details of data collection and structure refinement for both compounds are summarized in Table 1. All data were collected at room temperature on an Enraf–Nonius CAD-4 diffractometer by the ω/2θ-scan method using variable scan speed (1.54–10° min⁻¹), scan width of (0.80 + 0.35tanθ)° and graphite monochromator. Lattice parameters were determined from the setting angles of 25 selected reflections with θ between 8 and 12°. Three standard reflections were measured after each hour to monitor crystal decay; no significant variations were observed for both compounds. The data were corrected for Lorentz–polarization effects, as well as absorption using an empirical correction based on ψ scans