

MOLECULAR STRUCTURE OF *sym-fac*-[(1,5,9-TRIAZANONANE)-(R,S)-ASPARTATO]COBALT(III) PERCHLORATE MONOHYDRATE AND ITS RELATIONSHIP TO THE OPTICALLY ACTIVE [Co(dpt)(S)-Asp]⁺ ISOMERS

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Received January 19, 1990

Accepted March 14, 1990

The crystal and molecular structure of the title compound was determined by X-ray diffraction. The structure was solved by the heavy-atom method and refined to an *R* value of 0.118 for 997 observed reflections. The unit cell is monoclinic with $a = 11.980(1)$, $b = 12.130(1)$, $c = 12.641(1)$ Å, $\beta = 108.18(1)^\circ$, $Z = 4$. The space group is $P2_1/c$. The crystals are composed of *sym-fac*-[Co(dpt)(R,S)-Asp]⁺, ClO₄⁻, and H₂O held together probably in a network of hydrogen bonds. The structural data obtained allow an explanation of the *sym-fac*-[Co(dpt)(S)-Asp]⁺ isomer optical activity contributions which can arise from the distorted chair conformation of one of the two dpt fused chelate rings, the donor atom distortions from the defined plane, and the (S)-aspartic acid vicinal chirality.

In the course of our study of the stereochemistry of cobalt(III) complexes of ligands forming fused chelate ring systems, we have studied¹ cobalt(III) mixed-ligand complexes of N-2-aminoethyl-1,3-propanediamine (aepn) or 1,4,8-triazaoctane and (S)-aspartic acid. In view of the larger number of isomeric possibilities it was difficult to make unequivocal structural assignments to the isolated [Co(aepn)(S)-Asp]⁺ isomers purely on the basis of their chiroptical properties. An X-ray analysis of the first eluted [Co(aepn)(S)-Asp]⁺ isomer has been shown² to be the symmetrical facial (*sym-fac*) one with contributions to the optical activity arising from the *S* absolute configuration of the sec-N atom of the linear triamine, from the λ conformation of the five-membered chelate ring and from the vicinal effect of the (S)-aspartic acid. Similarly in the case of dipropylenetriamine (dpt) or 1,5,9-triazanonane, which forms two six-membered fused chelate rings in [Co(dpt)(S)-Asp]⁺, the isomers isolated³ show the same CD spectral patterns. In order to clarify the origin of the

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optical activity of the $[\text{Co}(\text{dpt})(\text{S})\text{-Asp}]^+$ isomer's we describe in this paper an X-ray structural analysis of the *sym-fac*- $[\text{Co}(\text{dpt})(\text{R,S})\text{-Asp}]^+$ isomer.

EXPERIMENTAL

Sym-fac- $[\text{Co}(\text{dpt})(\text{R,S})\text{-Asp}]\text{ClO}_4 \cdot \text{H}_2\text{O}$ was prepared by the reaction of an aqueous solution containing a 1 : 1 mole ratio of the disodium salt of (S)-aspartic acid and $[\text{Co}(\text{dpt})\text{Cl}_3]$ in the presence of charcoal at 60°C (ref.³). After 50 min of stirring, the reaction mixture was filtered and the filtrate was loaded on a cation exchange resin column (Dowex 50WX8, 100–200 mesh, Na^+ form). Elution with 0.15M- NaClO_4 produced several bands. From the first eluate, after concentration in vacuo and standing, red-violet crystals were formed. These were collected, washed with cold water and acetone, and dried in air. For $\text{C}_{10}\text{H}_{24}\text{ClCoN}_4\text{O}_9$ (438.7) calculated: 27.38% C, 5.51% H, 12.77% N; found: 27.41% C, 5.58% H, 12.70% N.

Data Collection, Structure Solution and Refinement

Preliminary elementary cell dimensions and its symmetry were determined from oscillation, Weissenberg and equiinclination patterns. The lattice parameter refinements (25 reflections $19 < \theta < 20^\circ$), space group determination and reflection intensity measurements were made on a four-circle Syntex P2₁ diffractometer. For the measurements a single crystal of dimension $0.1 \times 0.1 \times 0.1$ mm and the $\omega/2\theta$ scanning were used ($0 < h < 17$, $0 < k < 18$, $0 < l < 18$). Systematic absence of $h0l$, $l = 2n + 1$ and $0k0$, $k = 2n + 1$ reflections were found in the complete data set obtained from the diffractometer. The basic crystal data are summarized in Table I. Final atomic positional and thermal parameters are given in Table II.

For intensity measurements graphite monochromatic $\text{MoK}\alpha = 0.71073 \text{ \AA}$ radiation was used. A total of 1 527 reflections measurements in the range of $0^\circ < 2\theta < 60^\circ$ were carried out. The intensities of two standard diffractions which were controlled after each 98 reflections decreased to 50% of the original values. Only 997 reflections which fulfilled the condition $I > 1.96\sigma(I)$ were considered as observed. Reflection intensities were corrected using Lorentz polarization factors, but no absorption corrections were made.

The structure was solved by the heavy-atom method and the structural parameters (Table III) were refined by minimization of the function $\sum w(|F_o| - |F_c|)^2$. The weighting scheme $w = 6.40/(\sigma^2(F_o) + 0.0008|F_c|^2)$ was used. A total of 226 parameters including the scale factor, the positions and anisotropic temperature factors of the nonhydrogen atoms were refined. The final Fourier difference map had the highest peak 1.25 e/\AA^3 . In the final refining cycle, the maximum value was $(\Delta/\sigma)_{\text{max}} = 0.02$.

The final value of R and R_w factors is 0.118. It should be pointed out, however, that the locations of the hydrogen atoms to the positions expected with thermal parameters corresponding to their bonding parameters did not improve the R factors. Positions of the hydrogen atoms during refinement were not stabilized. The atomic scattering factor for cobalt, which is not included in the SHELX 76 program⁴, was taken from tables in ref.⁵. All calculations were carried out using SHELX 76 and PARST (ref.⁶) programs.

RESULTS AND DISCUSSION

As revealed by an X-ray analysis of the crystals obtained from the first eluant, the reaction of (S)-aspartic acid in alkaline solution with $[\text{Co}(\text{dpt})\text{Cl}_3]$ at elevated

TABLE I
Crystal data

| | |
|-----------------------------|-------------------------------------------------|
| $a = 11.980(1) \text{ \AA}$ | $V = 1\,745.4(3) \text{ \AA}^3$ |
| $b = 12.130(1) \text{ \AA}$ | $Z = 4$ |
| $c = 12.641(1) \text{ \AA}$ | $F(000) = 912$ |
| $\beta = 108.18(1)^\circ$ | $\rho_{\text{calc}} = 1\,669 \text{ kg m}^{-3}$ |
| $M_r = 438.7$ | $\mu = 11.846 \text{ cm}^{-1}$ |
| $P2_1/c$ | $\lambda = 0.71073 \text{ \AA}$ |

TABLE II
The fractional coordinates of the nonhydrogen atoms ($\cdot 10^4$) and their equivalent ($\cdot 10^3$) temperature coefficients. $U_{\text{eq}} = (U_{11} + U_{22} + U_{33} + 2U_{13} \cos \beta)/3$

| Atom | x | y | z | $U_{\text{eq}}, \text{ \AA}^2$ |
|-------|-----------|-----------|----------|--------------------------------|
| Cl | 3523(6) | 5324(6) | 1189(4) | 57(3) |
| O(11) | 2391(14) | 4866(14) | 713(11) | 87(8) |
| O(22) | 3799(11) | 5398(14) | 2360(11) | 86(8) |
| O(33) | 4337(15) | 4641(14) | 917(11) | 85(8) |
| O(44) | 3561(19) | 6366(13) | 742(14) | 115(9) |
| W | 149(13) | 1851(11) | 4801(11) | 70(6) |
| Co | 1568(3) | 380(3) | 2533(2) | 64(1) |
| O(1) | 656(14) | -631(13) | 1519(11) | 55(7) |
| O(2) | -1148(12) | -1414(20) | 1099(10) | 53(6) |
| O(3) | 542(14) | 1538(13) | 1855(11) | 54(7) |
| O(4) | -1109(12) | 2547(12) | 1297(11) | 52(6) |
| N(1) | 2719(14) | -769(13) | 3185(12) | 49(7) |
| N(2) | 2330(13) | 732(13) | 1340(12) | 39(7) |
| N(3) | 2377(15) | 1482(12) | 3657(11) | 34(6) |
| N(4) | 605(13) | -6(14) | 3507(13) | 51(7) |
| C(1) | 2946(21) | -1594(16) | 2365(19) | 64(10) |
| C(2) | 3491(18) | -1056(18) | 1517(17) | 51(9) |
| C(3) | 2593(22) | -255(19) | 736(17) | 72(11) |
| C(4) | 3383(20) | 1518(18) | 1608(19) | 61(10) |
| C(5) | 3332(21) | 2478(17) | 2442(22) | 68(11) |
| C(6) | 3477(22) | 2012(18) | 3603(17) | 58(10) |
| C(7) | -274(27) | -796(16) | 1686(16) | 50(11) |
| C(8) | -547(19) | -140(21) | 2649(15) | 69(11) |
| C(9) | -1267(17) | 878(20) | 2306(17) | 47(9) |
| C(10) | -552(28) | 1700(19) | 1798(15) | 50(11) |

temperature (60°C) proceeds with the racemization of aspartic acid and *sym-fac*-[Co(dpt)(R,S)-Asp]⁺ isomers are formed. We had independently noted a circular dichroism change for the heated product eluant earlier⁷. With reference to the literature^{8,9}, stereochange at α-CH can occur only when aspartic acid is coordinated to metal atoms as a bidentate ligand. Accordingly, racemization has to occur during the early stages of coordination of Asp when it acts as a bidentate ligand, which is in accord with our proposed mechanism of [Co(ABA)(S)-Asp]⁺ (ABA is linear triamine) isomer formation^{1,3}.

The first eluted isomer has been isolated and exhibits symmetrical facial geometry. A perspective drawing for one of the two pseudoenantiomers, i.e., the *sym-fac*-[Co(dpt)(S)-Asp]⁺ isomer, together with the atom-numbering scheme is given in Fig. 1. The crystal structure consists of discrete *sym-fac*-[Co(dpt)(R,S)-Asp]⁺ and ClO₄⁻ ions linked together with water molecules in a network of possible hydrogen bonds, in which every N—H bond is probably involved in close contact with oxygen atoms of aspartic acid, water or perchlorate ions. Each carbonyl oxygen atom is

TABLE III

Possible hydrogen bonds (Å) apparent in *sym-fac*-[Co(dpt)(S)-Asp]ClO₄·H₂O and *sym-fac*-[Co(aepn)(S)-Asp]ClO₄

| <i>sym-fac</i> -[Co(dpt)(S)-Asp]ClO ₄ ·H ₂ O | | |
|--------------------------------------------------------------------|---------|------------------------------|
| N(1)····O(4 ⁱ) | 3·02(2) | Symmetry code: |
| N(1)····O(44 ⁱⁱ) | 3·16(2) | i -x, y - 1/2, -z + 1/2 |
| N(2)····O(3 ⁱⁱⁱ) | 3·08(2) | ii x, -y + 1/2, z + 1/2 |
| N(3)····O(11 ⁱⁱ) | 3·07(2) | iii -x, -y, -z |
| N(3)····O(2 ⁱⁱⁱⁱ) | 3·01(2) | iiii -x, y - 1/2, -z + 1/2 |
| N(4)····O(11 ⁱⁱ) | 2·94(2) | |
| N(4)····O(4 ⁱ) | 3·02(2) | |
| O(2)····W ⁱⁱⁱⁱ | 2·83(2) | |
| O(4)····W ⁱⁱ | 2·86(2) | |
| <i>sym-fac</i> -[Co(aepn)(S)-Asp]ClO ₄ ^a | | |
| N(1)····O(2 ⁱ) | 2·96(2) | Symmetry code: |
| N(2)····O(3 ⁱⁱ) | 2·97(2) | i x - 1/2, -y + 1/2, |
| | | -z - 1 |
| N(3)····O(3 ⁱⁱⁱ) | 2·95(2) | ii x + 1/2, -y - 1/2, |
| | | -z + 1 |
| N(4)····O(2 ⁱ) | 2·87(1) | iii x - 1/2, -y - 1/2, |
| | | -z + 1 |
| N(4)····O(3 ⁱⁱⁱ) | 2·93(1) | iiii -x, y - 1/2, -z + 3/2 |

^a For atoms numbering see ref.².

interacting with two amine hydrogens and one water hydrogen as is evident from the interatomic contacts between ions and/or water (Table III), forming probably trifurcated hydrogen bonds, which had not been observed previously in other aspartic acid metal complexes. Thus, both carbonyl oxygens achieve a pseudo tetrahedral arrangement. Furthermore, the perchlorate ion is probably hydrogen bonded to an N—H of an adjacent complex cation. Similarly, the water molecules are involved in hydrogen bonds with C=O oxygen atoms of neighboring cations. As far as interatomic distances between atoms forming hydrogen bonds are concerned, the shortest ones are those between C=O and H atoms of water due to the greater attractive power of the more polar O—H bond for the carbonyl oxygen in comparison with the N—H case.

The remarkable feature of the *sym-fac*-[Co(dpt)(*R,S*)-Asp]⁺ cation, which seems common for all linear triamine-aspartic acid cobalt(III) complexes (see Table III), consists in the unusual C—O bond lengths within the carboxylate groups, especially in the one forming a five-membered chelate ring. Data presented in Table IV show that the C=O bond distance (1.31(3) Å) is apparently longer than the C—O (1.21(4) Å). It is reasonable to assume that this unexpected C—O bond lengths reversal is caused probably by the multiple hydrogen bonding. It is interesting to note that the carboxylate C—O bonds in the six-membered chelate ring are essentially equal (1.30(4) and 1.28(3) Å). The shorter C=O bond in carboxylic acids and carboxylate esters is typically about 1.23 Å and the longer C—O bond is typically about 1.36 Å long¹⁰. Regardless of the exact numbers, it is apparent that the hydrogen bonds lengthen the C=O bonds relative to simple carboxylates with concurrent shortening of the C—O bonded to the metal, and can even cause a reversal in bond lengths.

Both ligands, as expected, act as terdentate ligands with donor atoms forming a distorted octahedron around Co. The extent of this distortion becomes apparent

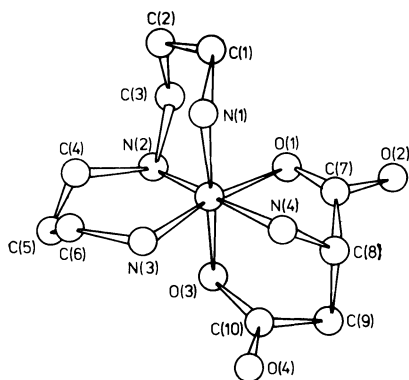


FIG. 1
Structure of the *sym-fac*-[Co(dpt)(*S*)-Asp]⁺ cation with the numbering system used for both the *R* and *S* cations

when bond angles (Table IV) are compared. The N(1)—Co—O(3), N(2)—Co—N(4) and N(3)—Co—N(1) bonds deviate from colinearity (with a mean value of 173.5°); the most significant one, 171.3° corresponds to the bond spanning the sec-N atom of the dpt with the N-atom of aspartic acid. It should be pointed out that in the structurally related *sym-fac*-[Co(aepn)(S)-Asp]⁺ isomer, only one NH₂. (five-membered ring)—Co—O bond deviates significantly from 180° (ref.²). As far as bond angles of six-membered fused chelate rings of dpt are concerned, all are

TABLE IV
Intramolecular distances (Å) and bond angles (°) for *sym-fac*-[Co(dpt)(S)-Asp]⁺ cation

| Interatomic distances | | | |
|-----------------------|-----------|-----------------|-----------|
| Co—N(1) | 1.95(2) | C(1)—C(2) | 1.56(4) |
| Co—N(2) | 2.04(2) | C(2)—C(3) | 1.55(3) |
| Co—N(3) | 1.97(1) | C(4)—C(5) | 1.58(4) |
| Co—N(4) | 1.99(2) | C(5)—C(6) | 1.53(3) |
| Co—O(1) | 1.86(1) | O(1)—C(7) | 1.21(4) |
| Co—O(3) | 1.89(2) | O(2)—C(7) | 1.31(3) |
| N(1)—C(1) | 1.53(3) | O(3)—C(10) | 1.30(4) |
| N(2)—C(3) | 1.51(3) | O(4)—C(10) | 1.28(3) |
| N(2)—C(4) | 1.53(3) | C(7)—C(8) | 1.57(3) |
| N(3)—C(6) | 1.49(3) | C(8)—C(9) | 1.49(3) |
| | | C(8)—N(4) | 1.48(2) |
| | | C(9)—C(10) | 1.58(4) |
| Bond angles | | | |
| O(3)—Co—N(4) | 92.0(7) | N(1)—C(1)—C(2) | 113.2(16) |
| O(1)—Co—N(4) | 86.7(7) | C(1)—C(2)—C(3) | 110.0(19) |
| O(1)—Co—O(3) | 91.1(7) | N(2)—C(3)—C(2) | 112.8(16) |
| N(3)—Co—O(3) | 85.8(7) | N(2)—C(4)—C(5) | 113.9(19) |
| N(3)—Co—O(1) | 173.6(8) | C(4)—C(5)—C(6) | 110.5(17) |
| N(3)—Co—N(4) | 87.9(7) | Co—O(1)—C(7) | 111.2(13) |
| N(2)—Co—N(4) | 171.3(7) | O(1)—C(7)—O(2) | 127.2(22) |
| N(2)—Co—O(3) | 83.5(6) | O(1)—C(7)—C(8) | 118.4(22) |
| N(2)—Co—O(1) | 86.0(6) | C(7)—C(8)—C(9) | 115.8(16) |
| N(2)—Co—N(3) | 99.1(7) | O(3)—C(10)—O(4) | 120.5(25) |
| N(1)—Co—N(4) | 92.3(7) | C(8)—C(9)—C(10) | 107.7(20) |
| N(1)—Co—O(3) | 175.5(7) | O(3)—C(10)—C(9) | 123.1(21) |
| N(1)—Co—O(1) | 90.3(7) | Co—N(4)—C(8) | 99.3(11) |
| N(1)—Co—N(3) | 93.2(6) | N(3)—C(6)—C(5) | 111.5(20) |
| N(1)—Co—N(2) | 92.4(7) | Co—O(3)—C(10) | 129.6(14) |
| Co—N(1)—C(1) | 115.7(12) | O(2)—C(7)—C(8) | 113.9(21) |
| Co—N(2)—C(4) | 119.7(12) | C(7)—C(8)—N(4) | 104.6(17) |
| Co—N(2)—C(3) | 115.0(12) | C(9)—C(8)—N(4) | 116.5(20) |
| C(3)—N(2)—C(4) | 108.6(17) | O(4)—C(10)—C(9) | 116.4(21) |
| Co—(3)—C(6) | 120.2(12) | | |

widened from their nominal value (Table IV). The most marked angular distortion occurs in the Co—O(3)—C(10), Co—N(2)—C(4) and Co—N(3)—C(6) bond angles, which are thus more strained relative to Co—N(2)—C(3) and Co—N(1)—C(1). The Co—N—C angles, similar to other dpt cobalt(III) complexes^{11,12}, show deviations from tetrahedral angles (Table IV).

The mean Co—N(H₂) distance (1.96 Å) of the dpt is of the same magnitude as in the *sym-fac*-[Co(aepn)(S)-Asp]⁺ isomer. On the other hand, the Co—N(H) bond length of 2.04(2) Å agrees well with those of 2.033(5) and 2.010(8) Å observed in the *sym-fac*- and *unsym-fac*-[Co(dien)(dpt)]³⁺ isomers, respectively^{11,12}, and is significantly longer than the Co—N(H) bond in the *sym-fac*-[Co(aepn)(S)-Asp]⁺ isomer², in which the Co—N(H) bond is the shortest Co—N distance (1.900(1) Å).

As follows from the positions of the C(1), C(2), C(3), C(4), C(5) and C(6) carbon atoms relative to the plane formed by the N—Co—N atoms (Table V), both six-membered fused dpt chelate rings are chair conformers related by an approximate two-fold axis of symmetry folded in the same rotational direction. In the absence of distortions, the two chair geometries should be similar. However, a comparison of both Co—N(H₂) bond lengths and bond angles (Table IV) shows some structural differences between the two dpt chelate rings (cf., Fig. 2). The distortion from a regular chair conformation is evident from the deviations of carbon atoms C(4) and C(6) from the N(2)—Co—N(3) plane (Table V). From these deviations it is apparent that the six-membered dpt chelate ring *trans* to the five-membered aspartic acid chelate ring forms a distorted chair (Fig. 2), with atoms C(4) and C(6) making a contribution to the CD spectrum³ of the *sym-fac*-[Co(dpt)-(S)-Asp]⁺ isomer. This conformation is not identical with the flattened or distorted chair found in other complexes containing facially coordinated dpt (refs^{11,12}); therefore, the conformation of dpt is controlled by the geometry of the second ligand.

Lest-square calculated deviations listed in Table VI show that each donor atom of the properly defined plane is skewed away from the mean plane. Donor atoms N(2)N(3)—O(1)N(4), N(1)N(3)—O(1)O(3) give rise to a δ chirality in the *sym-fac*-[Co(dpt)(S)-Asp]⁺ isomer shown in Fig. 1, while N(1)N(2)—O(3)N(4) are skewed in the opposed sense. The net contribution from the (S)-Asp isomer should be δ (cf. ref.¹³).

From the comparison of the geometric data obtained (Table V) with those described in the literature^{2,14}, it follows that the aspartic acid chelate rings assume a symmetrical envelope and skew-boat conformation typical of complexes in which aspartic acid acts as terdentate ligand. Thus, it can be concluded that conformations of aspartic acid chelate rings together with the vicinal contribution from the (S)-carbon atom are additional sources of optical activity in the *sym-fac*-[Co(dpt)(S)-Asp]⁺ isomer³. We assume that aspartic acid rigidity causes all of these noted contributions to the optical activity to be preserved in the unsymmetrical *unsym-fac*-[Co(dpt)(S)-Asp]⁺ isomer.

Finally, the geometry of the *sym-fac*-[Co(dpt)(S)-Asp]⁺ isomer can be described as *exo* with respect to the proton of the *sec*-N atom. In principle, this proton can be oriented in two ways, which can give rise to two conformational isomers related by

TABLE V

Deviations (Å) of atoms from the optimal plane fitted through atoms of chelate rings in *sym-fac*-[Co(dpt)(S)-Asp]⁺ cation

| Atom | Distance, Å | Atom | Distance, Å |
|-------------------|-------------|-------------------|-------------|
| N(1) ^a | 0 | N(2) ^b | 0 |
| Co | 0 | Co | 0 |
| N(2) | 0 | N(3) | 0 |
| C(1) | 1.02(2) | C(4) | -0.23(2) |
| C(2) | 0.79(2) | C(5) | 0.38(2) |
| C(3) | 1.02(2) | C(6) | -0.38(2) |
| O(3) ^c | 0 | N(4) ^d | 0 |
| Co | 0 | Co | 0 |
| N(4) | 0 | O(1) | 0 |
| C(10) | 0.35(2) | C(8) | 0.88(2) |
| C(9) | 0.92(2) | C(7) | 0.41(2) |
| C(8) | 1.17(2) | | |

The plane fitted through the ^a N(1)-Co-N(2) atoms: $-0.418(8) X - 0.677(6) Y - 0.606 Z = -2.522(15) = 0, \chi^2 = 0$; ^b N(2)-Co-N(3) atoms: $-0.629(7) X + 0.661(7) Y - 0.410(6) Z - 1.495(2) = 0, \chi^2 = 0$; ^c O(3)-Co-N(4) atoms: $-0.337(8) X - 0.634(6) Y - 0.696(6) Z - 2.71(1) = 0, \chi^2 = 0$; ^d N(4)-Co-O(1) atoms: $-0.543(7) X + 0.726(6) Y - 0.423(7) Z - 1.43(2) = 0, \chi^2 = 0$.

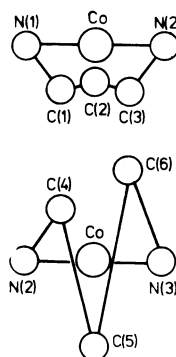


FIG. 2
Conformations of the six-membered dpt fused chelate rings

TABLE VI
Selected least squares planes, displacements from the plane are given

| Atom | Distance, Å | Atom | Distance, Å |
|-------------------|-------------|-------|-------------|
| O(1) ^a | 0.04(2) | C(4) | -0.07(2) |
| N(4) | 0.08(2) | C(5) | 0.55(2) |
| N(3) | 0.05(2) | C(6) | -0.26(2) |
| N(2) | 0.07(2) | C(7) | 0.51(2) |
| Co | -0.011(3) | C(8) | 1.00(2) |
| O(1) ^b | -0.01(2) | C(4) | -0.13(2) |
| N(4) | 0.01(2) | C(5) | 0.49(2) |
| N(3) | -0.01(2) | C(6) | -0.32(2) |
| N(2) | 0.01(2) | C(7) | 0.45(2) |
| Co | 0.072(4) | C(8) | 0.94(2) |
| N(1) ^c | -0.03(2) | C(1) | 1.04(2) |
| N(2) | 0.11(2) | C(2) | 0.90(2) |
| O(3) | -0.03(2) | C(3) | 1.16(2) |
| N(4) | 0.13(2) | C(8) | 1.30(2) |
| Co | -0.007(3) | C(9) | 0.04(2) |
| | | C(10) | 1.37(2) |
| N(1) ^d | -0.07(2) | C(1) | 1.00(2) |
| N(2) | 0.08(2) | C(2) | 0.86(2) |
| O(3) | -0.08(2) | C(3) | 1.12(2) |
| N(4) | 0.08(2) | C(8) | 1.26(2) |
| Co | -0.049(3) | C(9) | 0.99(2) |
| | | C(10) | 0.33(2) |
| N(1) ^e | 0.07(2) | N(3) | -0.09(2) |
| O(1) | -0.09(2) | Co | 0.001(3) |
| O(3) | 0.08(2) | | |
| N(1) ^f | 0.08(2) | N(3) | -0.08(2) |
| O(1) | -0.08(2) | Co | 0.009(3) |
| O(3) | 0.08(2) | | |

The plane fitted through the ^a O(1)-N(4)-N(3)-N(2)-Co atoms: $-0.585X + 0.697Y - 0.415Z = -1.445$; ^b O(1)-N(4)-N(3)-N(2) atoms: $-0.585X + 0.696Y - 0.416Z = -1.387$; ^c N(1)-N(2)-O(3)-N(4)-Co atoms: $-0.382X - 0.658Y - 0.649Z = -2.606$; ^d N(1)-N(2)-O(3)-N(4) atoms: $-0.381X - 0.657Y - 0.651Z = -2.568$; ^e N(1)-O(1)-O(3)-N(3)-Co atoms: $0.768X + 0.232Y - 0.597Z = -1.307$; ^f N(1)-O(1)-O(3)-N(3) atoms: $0.768X + 0.232Y - 0.597Z = -1.044$.

the inversion of the sec-N atom. This type of isomerism is known for meridionally coordinated dien (diethylenetriamine or 1,4,7-triazaheptane) and dpt (ref.¹⁵). Whereas dpt has increased flexibility relative to dien, Dreiding models infer that these isomers could exist when dpt is coordinated in a *facial* manner, too. The crystal structure shows the proton as *exo* with the proton of the sec-N atom directed toward the plane defined by the O(1)—Co—O(3) atoms.

The authors acknowledge Prof. Ronald D. Archer, University of Massachusetts, Amherst for his valuable discussion of the manuscript.

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Translated by the author (F.J.).