

Table 5. *Torsion angles* ($^{\circ}$)

Numbers in parentheses are e.s.d.'s.

| | |
|-----------------------------------|------------|
| O(1)—C(1)—C(2)—N | -31.1 (6) |
| O(2 ^b)—C(1)—C(2)—N | 150.5 (6) |
| O(1)—C(1)—C(2)—C(3) | 85.8 (6) |
| O(2 ^b)—C(1)—C(2)—C(3) | -92.5 (6) |
| C(1)—C(2)—C(3)—C(4) | -114.5 (7) |
| C(2)—C(3)—C(4)—C(5) | -29.0 (7) |
| C(3)—C(4)—C(5)—N | 40.1 (7) |
| C(4)—C(5)—N—C(2) | -36.5 (7) |
| C(5)—N—C(2)—C(3) | 18.5 (5) |
| N—C(2)—C(3)—C(4) | 6.4 (6) |

Bond lengths and angles in the tetrahedral SO_4^{2-} ion are normal.

A common property of polymeric Mn^{2+} complexes with α -amino acids with single carboxyl bridges (Głowiak & Ciunik, 1978; Ciunik & Głowiak, 1980) is the formation of *syn,anti* bonds by the bridging carboxyl groups. Only in one case were additional *anti,anti* bonds found (Głowiak & Ciunik, 1978).

$\text{Mn}\cdots\text{Mn}$ distances between the bridged atoms range from 5.36 to 5.52 Å. Distances of the Mn atoms from the $\text{C}^{\alpha}\text{COO}$ planes do not exceed 0.52 Å. In all cases the *syn* bonds are formed by the O atoms of carboxyl groups located closer to the N atoms (NH_3^+ or NH_2^+ groups). The $\text{C—O—Mn}(\textit{syn})$ angles range from 126 to 131 $^{\circ}$ (average 128.6 ± 2.7), $\text{C—O—Mn}(\textit{anti})$ angles from 139 to 143 $^{\circ}$ (average $140.6 \pm 2.4^{\circ}$).

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The Symmetrical-Facial Isomer of Ammine(diethylenetriamine)dinitrocobalt(III) Chloride, *s-fac*-[Co(dien)(NH_3)(NO_2) $_2$]Cl

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Abstract. $[\text{Co}(\text{C}_4\text{H}_{13}\text{N}_3)(\text{NH}_3)(\text{NO}_2)_2]\text{Cl}$, monoclinic, $P2_1/n$, $Z = 4$, $a = 7.993$ (2), $b = 10.893$ (2), $c = 12.969$ (2) Å, $\beta = 102.49$ (2) $^{\circ}$, $V = 1102.4$ (4) Å 3 , $D_c = 1.847$ Mg m $^{-3}$, $M_r = 306.60$, $\mu(\text{Mo } K\alpha) = 1.81$ mm $^{-1}$. Final $R_1 = 3.9\%$ for 1821 data with $F_o > \sigma(F_o)$. The Co^{III} ion has a slightly distorted octahedral geometry; the dien ligand occupies facial sites with $\text{Co—N}(4) = 1.985$ (3), $\text{Co—N}(5) = 1.950$ (3), and $\text{Co—N}(6) = 1.962$ (3) Å. The Co—NH_3 bond length is $\text{Co—N}(1) = 1.957$ (3) Å, while Co—NO_2 linkages are $\text{Co—N}(2) = 1.929$ (3) Å and $\text{Co—N}(3) = 1.932$ (3) Å.

Introduction. There are five possible isomers of the $[\text{Co}(\text{dien})(\text{NH}_3)(\text{NO}_2)_2]^+$ cation. The *trans* isomer (dien in meridional sites and NO_2 ligands mutually *trans*) is that whose synthesis in $\sim 90\%$ yield has been described in detail (Crayton, 1963). We are presently attempting to assign the stereochemistry to four isomers found in the filtrate from Crayton's procedure.

The *s-fac* (symmetrical facial) cation under study was isolated as the second of four bands from elution of the above filtrate with 0.15 *M* aqueous NaCl from an ion-exchange column (AG 50Wx8, 200–300 mesh, Na-type).

Cell dimensions and intensities were measured at 297 K with a Syntex $P2_1$ diffractometer (Churchill, Lashewycz & Rotella, 1977). The systematic absences $h0l$ for $h + l = 2n + 1$ and $0k0$ for $k = 2n + 1$ indicated the space group $P2_1/n$. Data with $3.5^{\circ} < 2\theta < 50^{\circ}$ (Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å) were collected from an orange crystal of size 0.25 \times 0.30 \times 0.30 mm using a θ - 2θ scan and the structure was solved *via* Patterson and difference-Fourier techniques. Full-matrix least-squares refinement led to convergence with $R_1 = 3.9\%$ and $R_2 = 3.5\%$ for 1821 reflections with $F_o > \sigma(F_o)$. [$R_1 = 4.4\%$ and $R_2 = 3.5\%$ for all 1954 unique data, none being rejected.] The strongest feature on a final difference-Fourier map was a peak of height 0.53 e Å $^{-3}$

Table 1. Atomic coordinates

| | x | y | z | B (Å ²) |
|--------|--------------|-------------|--------------|---------------------|
| Co | 0.23645 (5) | 0.22736 (4) | 0.09959 (3) | 1.10* |
| Cl | 0.13810 (11) | 0.48596 (8) | -0.12577 (7) | 2.2 |
| N(1) | 0.0041 (4) | 0.2572 (3) | 0.0176 (3) | 1.7 |
| N(2) | 0.2104 (3) | 0.0531 (3) | 0.0750 (2) | 1.6 |
| N(3) | 0.1517 (3) | 0.2107 (2) | 0.2276 (2) | 1.7 |
| N(4) | 0.3360 (4) | 0.2383 (3) | -0.0277 (2) | 1.6 |
| N(5) | 0.4739 (3) | 0.2075 (3) | 0.1750 (2) | 1.5 |
| N(6) | 0.2675 (4) | 0.4042 (3) | 0.1254 (3) | 1.6 |
| O(2A) | 0.1742 (3) | 0.0136 (2) | -0.0174 (2) | 2.4 |
| O(2B) | 0.2294 (4) | -0.0214 (2) | 0.1475 (2) | 3.1 |
| O(3A) | -0.0028 (3) | 0.2210 (3) | 0.2258 (2) | 3.1 |
| O(3B) | 0.2517 (3) | 0.1883 (2) | 0.3117 (2) | 2.4 |
| C(1) | 0.5263 (4) | 0.2224 (4) | -0.0028 (3) | 2.1 |
| C(2) | 0.5751 (4) | 0.1562 (4) | 0.1011 (3) | 1.8 |
| C(3) | 0.5390 (4) | 0.3281 (3) | 0.2234 (3) | 1.9 |
| C(4) | 0.4527 (4) | 0.4330 (3) | 0.1570 (3) | 2.0 |
| H(11)† | -0.057 (5) | 0.186 (4) | -0.002 (3) | 3.3 (9) |
| H(12) | -0.001 (5) | 0.301 (4) | -0.036 (3) | 3.5 (11) |
| H(13) | -0.055 (5) | 0.291 (4) | 0.061 (3) | 3.6 (10) |
| H(41) | 0.288 (4) | 0.184 (3) | -0.065 (3) | 1.5 (8) |
| H(42) | 0.300 (4) | 0.308 (4) | -0.060 (3) | 2.0 (8) |
| H(5) | 0.472 (4) | 0.157 (4) | 0.226 (3) | 2.1 (8) |
| H(61) | 0.228 (4) | 0.441 (3) | 0.070 (3) | 1.7 (8) |
| H(62) | 0.214 (5) | 0.429 (4) | 0.172 (3) | 3.0 (9) |
| H(1A) | 0.587 (4) | 0.308 (3) | -0.001 (3) | 2.0 (7) |
| H(1B) | 0.566 (4) | 0.184 (3) | -0.054 (3) | 2.3 (8) |
| H(2A) | 0.692 (5) | 0.163 (3) | 0.138 (3) | 2.4 (8) |
| H(2B) | 0.549 (4) | 0.071 (3) | 0.093 (2) | 1.4 (7) |
| H(3A) | 0.669 (5) | 0.331 (3) | 0.235 (3) | 2.6 (8) |
| H(3B) | 0.511 (4) | 0.332 (3) | 0.297 (3) | 2.0 (7) |
| H(4A) | 0.493 (4) | 0.444 (3) | 0.092 (3) | 1.9 (7) |
| H(4B) | 0.474 (4) | 0.510 (4) | 0.194 (3) | 2.4 (8) |

* Equivalent isotropic thermal parameters are given for the non-hydrogen atoms. These are calculated as $B_{eq} = \frac{1}{3}(B_{11} + B_{22} + B_{33} + 2B_{13} \cos \beta)$.

† Those H atoms labeled with numbers only are attached to N atoms [e.g. H(11) is attached to N(1) and H(61) is attached to N(6) etc.]. H atoms labeled with a number and a letter are attached to C atoms [e.g. H(1A) is attached to C(1), H(3B) is attached to C(3) etc.].

near the Co atom; the structure is thus correct and complete. All calculations were performed on a Nova 1200 minicomputer using a locally modified version of the Syntex XTL program package. Analytical scattering factors for neutral atoms from *International Tables for X-ray Crystallography* (1974) were corrected for both f' and f'' terms. The function minimized during least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where $w = \{[\sigma(F_o)]^2 + (0.01F_o)^2\}^{-1}$. Data were corrected for secondary extinction using the formula: $F_{o,cor.} = F_{o,uncor.} (1 + kI_o)$. The value of k (obtained graphically) is 6.8×10^{-8} .

Atomic coordinates are given in Table 1.*

* Lists of structure factor amplitudes and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35793 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. Bond distances and angles are collected in Table 2. The labeling of non-hydrogen atoms in the cation is shown in Fig. 1; a stereoscopic view of the cation appears as Fig. 2.

The Co^{III} ion is in a slightly distorted octahedral environment with the dien ligand occupying three facial sites. The dien ligand has a $\lambda\delta$ conformation and the central N atom (*i.e.* that *trans* to the ammine ligand) is associated with the shortest of the three Co-N(dien) linkages, *viz.* Co-N(5) = 1.950 (3) *vs* Co-N(4) = 1.985 (3) and Co-N(6) = 1.962 (3) Å. The Co-NO₂ linkages are equivalent and the Co atom is essentially coplanar with each of the nitro ligands (see Table 3).

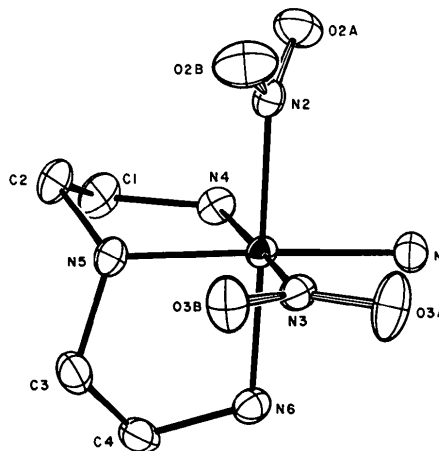


Fig. 1. Labeling of non-hydrogen atoms in the *s*-fac-[Co(dien)(NH₃)(NO₂)₂]⁺ cation.

Table 2. Bond distances (Å) and selected angles (°)

| | | | |
|-----------------------|-------------------|------------------|-------------|
| Co-N(1) | 1.957 (3) | Co-N(4) | 1.985 (3) |
| Co-N(2) | 1.929 (3) | Co-N(5) | 1.950 (3) |
| Co-N(3) | 1.932 (3) | Co-N(6) | 1.962 (3) |
| N(2)-O(2A) | 1.247 (4) | N(3)-O(3A) | 1.235 (4) |
| N(2)-O(2B) | 1.226 (4) | N(3)-O(3B) | 1.230 (4) |
| N(4)-C(1) | 1.495 (5) | N(5)-C(3) | 1.500 (5) |
| C(1)-C(2) | 1.504 (5) | C(3)-C(4) | 1.505 (5) |
| C(2)-N(5) | 1.489 (5) | C(4)-N(6) | 1.482 (5) |
| N-H(NH ₃) | 0.83 (4)-0.92 (4) | | |
| N-H(dien) | 0.81 (4)-0.89 (4) | | |
| C-H(dien) | 0.90 (4)-1.05 (4) | | |
| N(1)-Co-N(2) | 91.03 (13) | N(2)-Co-N(6) | 178.95 (13) |
| N(1)-Co-N(3) | 90.84 (13) | N(3)-Co-N(4) | 176.43 (12) |
| N(1)-Co-N(4) | 92.42 (13) | N(3)-Co-N(5) | 92.44 (12) |
| N(1)-Co-N(5) | 175.62 (13) | N(3)-Co-N(6) | 90.06 (12) |
| N(1)-Co-N(6) | 89.97 (13) | N(4)-Co-N(5) | 84.37 (12) |
| N(2)-Co-N(3) | 90.23 (12) | N(4)-Co-N(6) | 91.38 (13) |
| N(2)-Co-N(4) | 88.28 (12) | N(5)-Co-N(6) | 87.13 (12) |
| N(2)-Co-N(5) | 91.85 (12) | | |
| Co-N(4)-C(1) | 112.7 (2) | Co-N(5)-C(3) | 108.9 (2) |
| N(4)-C(1)-C(2) | 107.6 (3) | N(5)-C(3)-C(4) | 110.6 (3) |
| C(1)-C(2)-N(5) | 109.0 (3) | C(3)-C(4)-N(6) | 107.8 (3) |
| C(2)-N(5)-Co | 108.9 (2) | C(4)-N(6)-Co | 109.7 (2) |
| C(2)-N(5)-C(3) | 114.2 (3) | | |
| Co-N(2)-O(2A) | 119.5 (2) | Co-N(3)-O(3A) | 120.7 (2) |
| Co-N(2)-O(2B) | 122.3 (2) | Co-N(3)-O(3B) | 120.0 (2) |
| O(2A)-N(2)-O(2B) | 118.3 (3) | O(3A)-N(3)-O(3B) | 119.3 (3) |

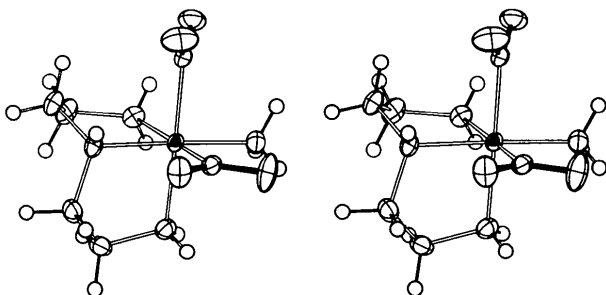


Fig. 2. Stereoscopic view of the *s-fac*-[Co(dien)(NH₃)(NO₂)₂]⁺ cation. (Note the relative orientations of the nitro groups about their Co—N axes; it is this feature that destroys the possible C₃ symmetry of this cation.)

Table 3. Deviations (in Å) of atoms from planes

| Plane | Atom, with deviation |
|------------------|-----------------------------------|
| N(4)—Co—N(5) | C(1), 0.046 (4); C(2), 0.601 (4) |
| N(5)—Co—N(6) | C(3), -0.203 (4); C(4), 0.382 (4) |
| O(2A)—N(2)—O(2B) | Co, 0.0153 (4) |
| O(3A)—N(3)—O(3B) | Co, 0.0228 (4) |

The N—O distances average 1.234 (9) Å, agreeing well with those found in *mer*-[Co(NH₃)₃(NO₂)₃] (Laing, Baines & Sommerville, 1971) and *fac*-[Co(NH₃)₃(NO₂)₃] (Nuber, Siebert, Weidenhammer, Weiss & Ziegler, 1979).

The chloride ion is involved in hydrogen bonding *via* various N—H...Cl interactions.

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Structure of Lithium Hydrogen Acetylenedicarboxylate Monohydrate

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Abstract. C₄H₄LiO₄·H₂O, LiHC₄O₄·H₂O, triclinic, *P*1̄, *a* = 6.296 (3), *b* = 6.545 (2), *c* = 7.877 (2) Å, α = 66.87 (2), β = 83.92 (3), γ = 70.82 (3)°, *V* = 281.8 Å³, *Z* = 2, *D_m*(flotation) = 1.61 (2), *D_x* = 1.63 Mg m⁻³, *F*(000) = 140; *R* = 0.034 and *R*' = 0.069 for 1201 reflections. In this compound the hydrogen acetylenedicarboxylate anions form infinite chains *via* intermolecular hydrogen bonds. The O—H...O distance is 2.537 (1) Å, the longest so far observed in the acid salts of acetylenedicarboxylic acid.

Introduction. Acid salts of acetylenedicarboxylic acid (H₂ADC) form polymeric structures with strong hydrogen bonds (Blain, Speakman, Stamp, Golić & Leban, 1973; Leban, Golić & Speakman, 1973; Leban, 1974; Gupta & Mahata, 1976). The O...O distances lie in the range 2.43–2.47 Å. The structures of all alkali-metal acid salts of H₂ADC except LiHADC

have been reported previously. As a small cation, lithium usually favours very short hydrogen bonds in similar compounds (Follner, 1970; Thomas, 1972; Küppers, 1978). LiHADC crystallizes as the monohydrate from a solution of H₂ADC and Li₂CO₃ in the ratio 2:1 at room temperature. A crystal 0.20 × 0.25 × 0.4 mm was used for data collection at 123 K on a Syntex P₂ diffractometer with graphite-monochromated Mo *K*α radiation. With the θ/2θ scan and variable scan speeds (4.86–29.3° min⁻¹), 1219 reflections were measured to θ_{max} = 27°. Backgrounds were measured at each end of the scan for a total time of 0.8 times the scan time. No absorption correction was applied (μ = 0.16 mm⁻¹). The structure determination is based on 1201 reflections with *I* > 3.92σ(*I*). The structure was solved using the Syntex *E-XTL* program system by a combination of direct methods, and Patterson and Fourier methods, in space group *P*1,