

Bis(DL-alanine)tetraaquacobalt(II) dinitrate

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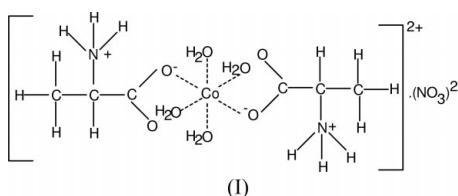
Key indicators

Single-crystal X-ray study
 $T = 273$ K
Mean $\sigma(\text{C}-\text{C}) = 0.005$ Å
 R factor = 0.048
 wR factor = 0.141
Data-to-parameter ratio = 17.1For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the title compound, $[\text{Co}(\text{C}_3\text{H}_7\text{NO}_2)_2(\text{H}_2\text{O})_4](\text{NO}_3)_2$, the Co^{II} atom lies on a crystallographic inversion centre and the asymmetric unit comprises the anion and one-half cation. Co^{II} is coordinated by six O atoms, two from alanine molecules and four from water molecules, forming an octahedron with minimal distortion. The O atoms of the nitrate group do not coordinate to cobalt but participate in hydrogen bonding.

Comment

Amino acids and their complexes are of great chemical and biological interest. Hence we have undertaken a systematic investigation of several complexes of amino acids, to study the geometry of amino acid molecules in different crystalline environments. This paper describes the crystal and molecular structure of a DL-alanine complex with $\text{Co}(\text{NO}_3)_2$, (I). Alanine, a non-essential amino acid commonly present in proteins, is hydrophobic and non-polar. A precise determination of the crystal structure of DL-alanine itself was recently carried out in our laboratory (Subha Nandhini *et al.*, 2001). The crystal structures of diaquabisglycinecobalt(II) bromide (Ravikumar *et al.*, 1985), DL-nickel alaninate tetrahydrate (Mostad & Natarajan, 1987), dichlorobis(DL-alanine)zinc(II) (Subha Nandhini, Krishnakumar & Natarajan, 2002) and β -alaninecadmium chloride (Subha Nandhini, Krishnakumar, Sivakumar & Natarajan, 2002) have already been reported.



The Co atom is coordinated by six O atoms, an O atom each from two alanine and four water molecules. The Co atom lies on a crystallographic inversion centre and, as a result, the asymmetric unit comprises one-half of the $[\text{Co}(\text{C}_3\text{H}_7\text{O}_2)_2(\text{H}_2\text{O})_4]^{2+}$ cation and an NO_3^- anion (Fig. 1). The Co atom is in an octahedral coordination environment and it is remarkably similar to those observed in the structures of the complexes of glycine with cobalt bromide, β -alanine with copper chloride (Papavinasam & Natarajan, 1985) and a nickel complex of DL-alanine (Mostad & Natarajan, 1987). The geometry of the octahedron is given in Table 1. The Co—O distances range from 2.070 (2) to 2.134 (2) Å.

The DL-alanine ligand exists as a zwitterion. This is evident from the fact that the C—O distances and the bond angles

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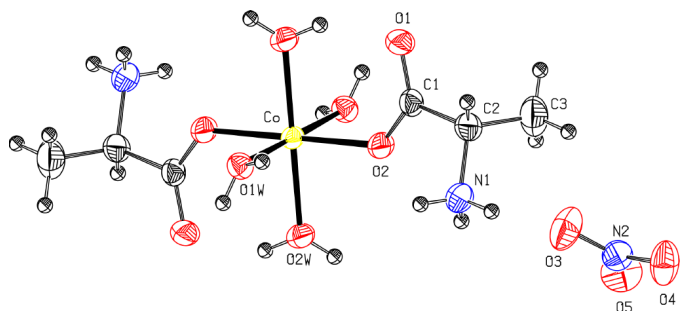


Figure 1
Molecular structure of (I), showing 50% probability displacement ellipsoids and atom-numbering scheme for the asymmetric unit.

around the C atom of the carboxylic acid group have expected values, and also three H atoms are attached to the N atom. The geometry of the DL-alanine molecule is normal, as found in other similar structures.

The geometries of the hydrogen bonds observed in (I) are listed in Table 2. The NH_3^+ group is a donor of three hydrogen bonds, the acceptors being two O atoms from the nitrate groups. Atom O5 of the nitrate group is not involved in hydrogen bonding. The carboxylate O atom, O1, which is not involved in the Co coordination environment is involved in hydrogen bonding. Apart from coordination, the water molecules are also found to mediate hydrogen-bonded interactions with the amino acid and nitrate molecules. The cations aggregate into a layered arrangement parallel to the *ab* plane. Adjacent layers are interlinked by the nitrate anions which are located between them, through $\text{N}-\text{H}\cdots\text{O}$ and $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds (Fig. 2).

Experimental

Single crystals of the title complex were grown as small pale pink plates, from a saturated aqueous solution containing DL-alanine and $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ with an excess of 10 percent of $\text{Co}(\text{NO}_3)_2$ in a 2:1:1 ratio.

Crystal data

$[\text{Co}(\text{C}_3\text{H}_7\text{NO}_2)_2(\text{H}_2\text{O})_4](\text{NO}_3)_2$
 $M_r = 433.21$
 Monoclinic, $P2_1/n$
 $a = 5.5021$ (6) Å
 $b = 6.6396$ (8) Å
 $c = 23.821$ (3) Å
 $\beta = 96.22$ (1)°
 $V = 865.10$ (18) Å³
 $Z = 2$
 $D_x = 1.663$ Mg m⁻³
 $D_m = 1.67$ (1) Mg m⁻³

D_m measured by flotation in a mixture of bromoform and carbon tetrachloride
 Mo $K\alpha$ radiation
 Cell parameters from 3463 reflections
 $\theta = 3.2\text{--}28.0^\circ$
 $\mu = 1.07$ mm⁻¹
 $T = 273$ (2) K
 Plate, pale pink
 $0.23 \times 0.19 \times 0.13$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 1998)
 $T_{\min} = 0.791$, $T_{\max} = 0.874$
 5063 measured reflections

1968 independent reflections
 1854 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.014$
 $\theta_{\text{max}} = 28.0^\circ$
 $h = -5 \rightarrow 7$
 $k = -8 \rightarrow 8$
 $l = -27 \rightarrow 30$

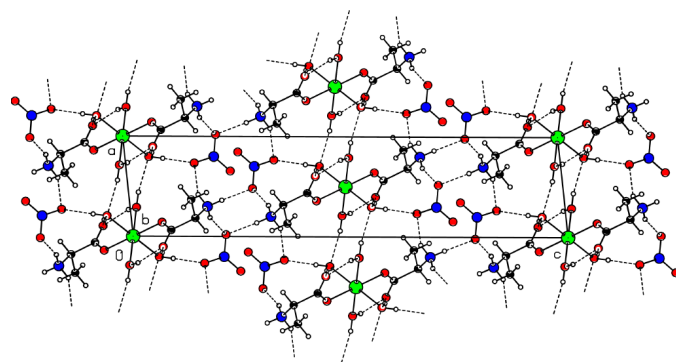


Figure 2
Packing of the molecules of (I), viewed down the *b* axis.

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.048$
 $wR(F^2) = 0.141$
 $S = 1.25$
 1968 reflections
 115 parameters
 H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0632P)^2 + 1.2873P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.70$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.34$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Co—O2W	2.070 (2)	O4—N2	1.256 (4)
Co—O2	2.096 (2)	O5—N2	1.220 (4)
Co—O1W	2.134 (2)	N1—C2	1.476 (4)
O1—C1	1.245 (4)	C1—C2	1.535 (4)
O2—C1	1.247 (4)	C2—C3	1.491 (6)
O3—N2	1.252 (4)		
O2W—Co—O2	90.07 (9)	O2—Co—O1W	88.48 (9)
O2W—Co—O1W	90.31 (9)		
O1—C1—C2—N1	157.4 (3)	O1—C1—C2—C3	−80.9 (4)
O2—C1—C2—N1	−21.7 (4)	O2—C1—C2—C3	100.1 (4)

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N1—H1A \cdots O3 ⁱ	0.89	2.06	2.912 (5)	159
N1—H1B \cdots O3	0.89	1.97	2.858 (4)	172
N1—H1C \cdots O4 ⁱⁱ	0.89	2.03	2.836 (4)	150
O1W—H1W1 \cdots O4 ⁱ	0.86	1.96	2.813 (4)	179
O1W—H2W1 \cdots O1 ⁱⁱⁱ	0.82	1.85	2.664 (3)	169
O2W—H2W2 \cdots O1 ^{iv}	0.85	1.87	2.630 (3)	149
O2W—H1W2 \cdots O1W ^v	0.85	2.02	2.857 (3)	166

Symmetry codes: (i) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (ii) $\frac{3}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (iii) $x, y - 1, z$; (iv) $-x, 1 - y, -z$; (v) $1 + x, y, z$.

H atoms of the alanine residue were positioned geometrically and were allowed to ride on their respective carrier atoms, with U_{iso} constrained to be $1.5U_{\text{eq}}$ of the carrier atom for the CH₃ and NH₃ groups and $1.2U_{\text{eq}}(C2)$ for H2. The C—H and N—H distances were set equal to 0.96 Å (0.98 Å for C2—H2) and 0.89 Å, respectively. H atoms of the water molecules were located from a difference Fourier map and their positional and isotropic displacement parameters (0.05 Å²) were not refined. Owing to the large fraction of weak data at higher angles, the completeness is only 94.5%. The highest peak was located at a distance of 0.85 Å from C2.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINTE* (Bruker, 2001); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1999); software used to prepare material for publication: *SHELXL97*.

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