

[N-(Carboxylatomethyl)aspartato(3-)]-(ethylenediamine)cobalt(III) trihydrate

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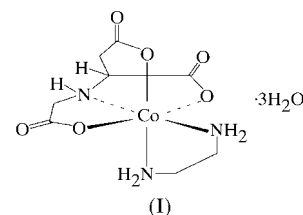
The mononuclear title complex, $[\text{Co}(\text{C}_6\text{H}_9\text{NO}_6)(\text{C}_2\text{H}_8\text{N}_2)] \cdot 3\text{H}_2\text{O}$, contains an octahedrally coordinated Co^{III} atom. The *N*-(carboxymethyl)aspartate moiety is coordinated as a tetradentate ligand, providing an OONO-donor set and forming two *trans* five-membered chelate rings and one six-membered chelate ring. A seven-membered chelate ring is also formed, which consists of part of the six-membered chelate ring and part of one of the five-membered chelate rings. The crystal structure of the complex is stabilized by hydrogen bonds with three water molecules.

Comment

The heteroligand complexes of cobalt(III) with polyamino-carboxylic acids have been studied extensively. These complexes are of interest not only for their stereochemistry (McLachlan *et al.*, 1995) but also for their applications in the bioinorganic field, as they provide simple structural models of

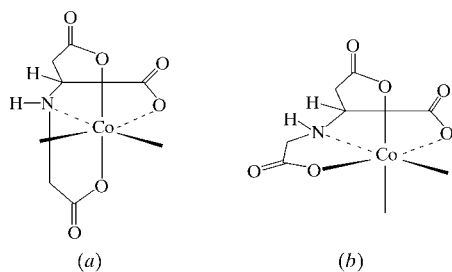
positions of the carboxyl groups forming the five-membered chelate rings, the tetradentate ligand can adopt two different geometries in the coordination octahedron of the Co atom, *viz.* (a) and (b) in *Scheme* above.

The crystal structure of the title compound, (I), contains discrete molecules, which have a slightly distorted octahedral coordination geometry around the Co atom, with cma^{3-} bonded as a tetradentate *trans*-*O,O,N,O*-ligand (see *Scheme* below and Fig. 1). The coordination about the Co atom can be considered to be meridional, with the three carboxyl O atoms (O2, O4 and O6) in one plane and the three N atoms (N5, N11 and N14) in another plane. The aspartic acid portion of the cma^{3-} ligand is coordinated to the Co atom through the α -amine N5, α -carboxyl O2 and β -carboxyl O4 atoms. This coordination mode is similar to that found for various bis(L-aspartato)cobalt(III) complexes previously reported in the literature (Oonishi *et al.*, 1973, 1975). The H atom attached to atom N5 is on the same (*syn*) side of the O2/N5/N14 plane as the coordinated β -carboxyl O4 atom. The glycinate group (N5—C6—C7—O6) is attached to the Co atom through the carboxyl O6 atom and occupies a position *trans* to the β -carboxyl O4 atom. The bidentate ethylenediamine ligand occupies the two remaining coordination sites about the Co atom.



Atom N11 is coordinated to the Co atom in a position *trans* to the α -amine N5 atom of cma^{3-} , and atom N14 is attached *trans* to the α -carboxyl O2 atom of the cma^{3-} ligand.

The bond distances observed within the cma^{3-} and ethylenediamine ligands are comparable to average values found in the structures of other complexes containing aspartic acid



metalloprotein active sites (Igi *et al.*, 1981). Tetradentate branched ligands of the aminopolycarboxylate type are used because they form stable complexes in solution (Bernauer, 1976). Recently, we have prepared a novel *O,O,N,O*-tetradentate ligand, namely *N*-(carboxymethyl)aspartic acid (H_3cma , $\text{C}_6\text{H}_9\text{NO}_6$; Maderova *et al.*, 2002). The formation of a complex between Co^{III} , cma^{3-} and glycine has been studied previously (Colomb & Bernauer, 1977), but the structure of the complex was not resolved. Depending on the relative

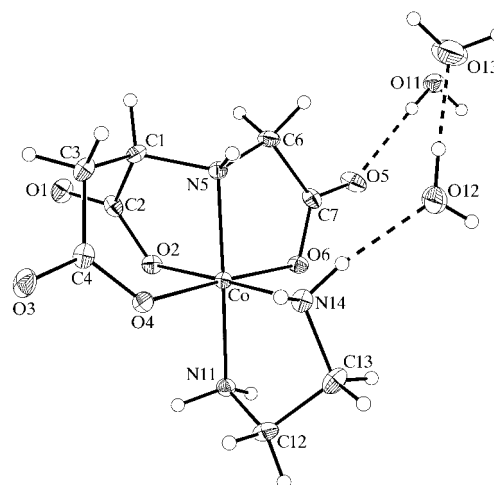


Figure 1
ORTEPIII (Johnson & Burnett, 1996) plot of (I). Displacement ellipsoids are drawn at the 50% probability level.

(Oonishi *et al.*, 1973, 1975). The bond lengths and angles within the ethylenediamine ligand are normal (Templeton *et al.*, 1979). The Co–N and Co–O bond distances are similar to the corresponding distances in other cobalt(II) complexes containing polyamine, amino acid or aminopolycarboxylate ligands (Herak *et al.*, 1974; Halloran *et al.*, 1975; Thorup, 1975, 1977; Voss *et al.*, 1978).

The O2–Co–N14 angle is closed slightly, to 178.61 (8)°, and the C1–N5–C6 angle is opened to 114.16 (17)°, which is evidence of some strain in the arrangement of the chelate rings. The O6–C7–C6 angle of 116.8 (2)° is larger than the ideal tetrahedral value of 109°, a feature also found in complexes (Hammershoi *et al.*, 1984) and free aspartates (Oonishi *et al.*, 1973; Sekizaki, 1978). The average Co–O(carboxyl) bond length is 1.896 Å and the average Co–N bond length is 1.937 Å.

The maximum deviation of bond angles around the Co atom from an ideal octahedral geometry is 7.07°. The greatest deviation from 90° occurs for the angles in the two five-membered chelate rings (N5–Co–O2, N5–Co–O6, and O4–Co–N11; N14–Co–N5, O4–Co–N5 and O2–Co–N11; see Table 1). The smallest angular deviation from ideal geometry is for the O6–Co–O2 angle.

The ethylenediamine ligand does not appear to interact sterically with any part of the cma³⁻ ligand. There are virtually no differences in bond lengths and angles within the Co–O2–C2–C1–N5 and Co–O6–C7–C6–N5 chelate rings.

In the crystal structure, the Co^{III} complex and three water molecules are stabilized by an infinite three-dimensional framework of strong O–H···O and N–H···O hydrogen bonds (Table 2).

Experimental

rac-N-(Carboxymethyl)aspartic acid, H₃cma, was prepared according to the method of Maderova *et al.* (2002), and the title complex, (I), was prepared according to the method of Shibata (1983). All chemicals were of analytical grade. A mixture of H₃cma (5 mmol) in water (5 ml) and freshly prepared K₃[Co(CO₃)₃]·3H₂O was placed in water (50 ml) and heated with stirring at 323 K for 20 min. The colour of the solution changed from green to wine-red. After addition of ethylenediamine (5 mmol), the mixture was heated to 333 K and stirred for 3 h. After cooling to room temperature, the reaction mixture was filtered. Crystals of (I) were grown by slow evaporation of an aqueous solution at room temperature. After 3 d, red crystals were obtained. Compound purity was tested by examination of FT-IR and ¹H NMR spectra and by elemental analysis (Elemental Analyzer Carlo Erba 1106). Analysis calculated for (I): C 26.6, H 5.5, N 11.6%; found: C 26.3, H 5.3, N 11.5%.

Crystal data

[Co(C ₆ H ₆ NO ₆)(C ₂ H ₈ N ₂)]·3H ₂ O	<i>D</i> _x = 1.672 Mg m ⁻³
<i>M</i> _r = 361.20	Mo Kα radiation
Monoclinic, <i>Cc</i>	Cell parameters from 1591 reflections
<i>a</i> = 11.6265 (13) Å	<i>θ</i> = 3.7–26.5°
<i>b</i> = 14.5467 (9) Å	<i>μ</i> = 1.25 mm ⁻¹
<i>c</i> = 10.0565 (11) Å	<i>T</i> = 120 (2) K
<i>β</i> = 122.475 (15)°	Prism, dark red
<i>V</i> = 1434.9 (3) Å ³	0.50 × 0.20 × 0.20 mm
<i>Z</i> = 4	

Table 1

Selected geometric parameters (Å, °).

Co–O4	1.8849 (17)	Co–N14	1.9300 (19)
Co–O6	1.8860 (17)	Co–N11	1.939 (2)
Co–O2	1.9172 (16)	Co–N5	1.9407 (19)
O4–Co–O6	177.43 (7)	O6–Co–N5	87.86 (8)
O4–Co–O2	91.15 (7)	O2–Co–N5	84.31 (7)
O6–Co–O2	90.11 (7)	N14–Co–N5	97.07 (8)
O4–Co–N14	88.82 (8)	N11–Co–N5	176.33 (8)
O6–Co–N14	89.87 (8)	C2–O2–Co	112.99 (13)
O2–Co–N14	178.61 (8)	C4–O4–Co	128.07 (16)
O4–Co–N11	86.94 (8)	C7–O6–Co	115.12 (16)
O6–Co–N11	90.78 (8)	C6–N5–Co	108.60 (13)
O2–Co–N11	92.28 (8)	C1–N5–Co	103.33 (13)
N14–Co–N11	86.33 (8)	C12–N11–Co	109.26 (15)
O4–Co–N5	94.50 (8)	C13–N14–Co	109.14 (13)

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
N5–H5···O5 ⁱ	0.93	1.92	2.832 (3)	168
N11–H11A···O11 ⁱⁱ	0.92	2.12	2.937 (3)	148
N11–H11B···O3 ⁱⁱⁱ	0.92	2.29	3.086 (3)	144
N14–H14A···O12	0.92	1.90	2.812 (3)	171
N14–H14B···O2 ⁱ	0.92	2.31	3.057 (2)	139
N14–H14B···O6 ⁱ	0.92	2.45	3.243 (3)	145
O11–H11W···O5	0.89 (7)	1.90 (2)	2.747 (3)	157 (4)
O11–H11V···O1 ^{iv}	0.88 (2)	1.88 (2)	2.752 (3)	171 (4)
O12–H12W···O13	0.88 (5)	1.85 (5)	2.719 (3)	168 (4)
O12–H12V···O3 ^{iv}	0.87 (2)	1.92 (2)	2.783 (3)	172 (4)
O13–H13V···O3 ^v	0.90 (2)	2.09 (3)	2.941 (3)	156 (4)
O13–H13W···O11 ⁱ	0.89 (2)	1.88 (2)	2.757 (3)	166 (5)

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

Data collection

Kuma KM-4-Plus CCD diffractometer	<i>R</i> _{int} = 0.035
<i>ω</i> scans	<i>θ</i> _{max} = 26.0°
3217 measured reflections	<i>h</i> = –8 → 14
1763 independent reflections	<i>k</i> = –17 → 17
1746 reflections with <i>I</i> > 2σ(<i>I</i>)	<i>l</i> = –12 → 10

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.045P)^2 + 0.35P]$
<i>R</i> (<i>F</i>) = 0.022	where $P = (F_o^2 + 2F_c^2)/3$
<i>wR</i> (<i>F</i> ²) = 0.057	(Δ/ <i>σ</i>) _{max} = 0.001
<i>S</i> = 1.04	Δ <i>ρ</i> _{max} = 0.48 e Å ⁻³
1763 reflections	Δ <i>ρ</i> _{min} = –0.43 e Å ⁻³
209 parameters	Absolute structure: Flack (1983),
H atoms treated by a mixture of independent and constrained refinement	374 Friedel reflections
	Flack parameter = 0.010 (12)

H atoms attached to C or N atoms were positioned geometrically, with *U*_{iso} values derived from *U*_{eq} of the corresponding C or N atoms. The H atoms attached to atoms O11, O12 and O13 were refined freely, except for the O–H distances, which were restrained to 0.9 Å, and a common free variable was used to describe simultaneously the *U*_{iso} values of all six water H atoms.

Data collection: *CrysAlis* (Oxford Diffraction, 2002); cell refinement: *CrysAlis*; data reduction: *CrysRed* (Oxford Diffraction, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997);

molecular graphics: *ORTEPIII* (Johnson & Burnett, 1996); software used to prepare material for publication: *SHELXL97* and *PARST* (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1619). Services for accessing these data are described at the back of the journal.

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