This work was supported by grants from PADCT, CNPq, FINEP, FAPESP and FUNCITEC. We thank Drs A. S. Ceccato and V. Kolm for their help with the preparation of the complex.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: LI1102). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Cobalt 1-Aminocyclohexanecarboxylate Complex

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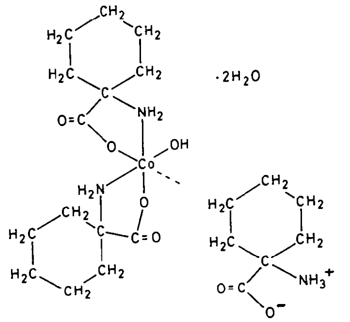
Abstract

The crystal structure of di-μ-hydroxo-bis[bis(1-aminocyclohexanecarboxylato-*N*,*O*)cobalt(III)]–1-aminocyclohexanecarboxylic acid–water (1/2/4), $[Co_2(C_7H_{12}NO_2)_4(OH)_2].2C_7H_{13}NO_2.4H_2O$, contains two asymmetric units related through a center of symmetry. Each molecule contains two hexacoordinate Co atoms, each of which is chelated to two bidentate 1-aminocyclohexanecarboxylato ligands. The Co atoms are linked by two hydroxo bridges. This results in two slightly distorted octahedral coordination polyhedra, which have an edge in common. In each polyhedron the N atoms are in *cis* positions. Each asymmetric unit is completed by an uncoordinated molecule of the ligand, in the zwitterionic form, and by two water molecules, which are involved in hydrogen bonding. The hydrogen-bonding scheme may also involve the amino groups of the free ligand molecule.

Comment

The structure analysis of the title compound (I) is a continuation of the investigation of metal complexes of aromatic and heterocyclic amino acids (Haendler, 1989, 1993; Boudreau & Haendler, 1992). 1-Aminocyclohexanecarboxylic acid can act as a bidentate ligand with several metals, forming a five-membered ring system. The amino and carboxyl groups are attached to the same C atom; their proximity results in some unexpected configurations. The Cu complex, for example, exhibits both planar and bipyramidal (or its rectangular pyramidal distortion) structures in the two molecules within each asymmetric unit. In the Ni complex, the Ni atom is hexacoordinate, coordinated by the two chelating bidentate ligands and by the O atoms of two water molecules, while a third water molecule forms part of a hydrogen-bond network.



(I)

In the Co complex studied here, the ligand is again bidentate, but two asymmetric units combine around the center of symmetry to form a dihydroxo-bridged molecule, the Co^{III} atoms being thus hexacoordinate. The resultant complex contains two slightly distorted octahedral coordination polyhedra sharing an O···O edge of 2.514 (4) Å, and having a Co···Co distance of 2.864 (1) Å. In addition, the unit cell contains two uncoordinated molecules of the ligand (in the zwitterionic form) and four water molecules. The result is an extensive hydrogen-bonding network, in which it is possible that the N atoms of the free ligand may also be involved.

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The N atoms in the Cu complex are in a *cis* position in the planar molecule and in a *trans* position in the pentacoordinate molecule. Those in the Ni complex are in a *trans* position, and those in the Co complex are in a *cis* position, as are the ether O atoms of the carboxyl group and the two hydroxo groups. In all cases, the amino groups are in axial positions on the cyclohexane rings and the carboxyl groups are in equatorial positions.

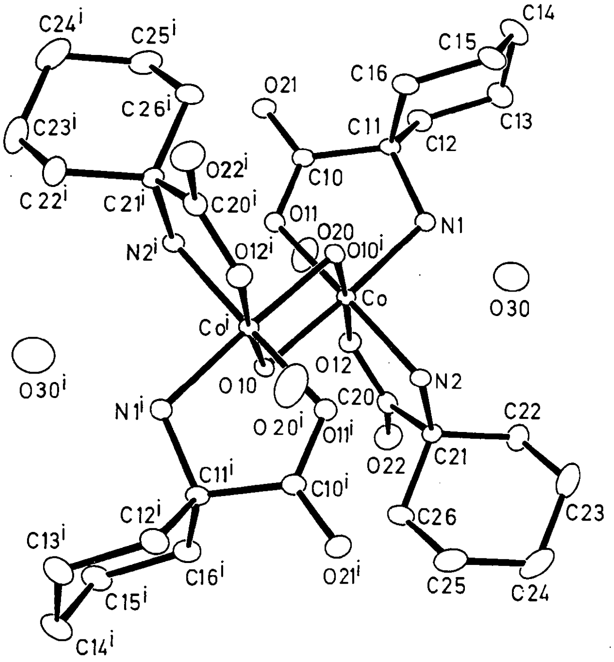

Fig. 1. A plot of the dicobalt complex showing displacement ellipsoids at the 20% probability level. H atoms are omitted for clarity.

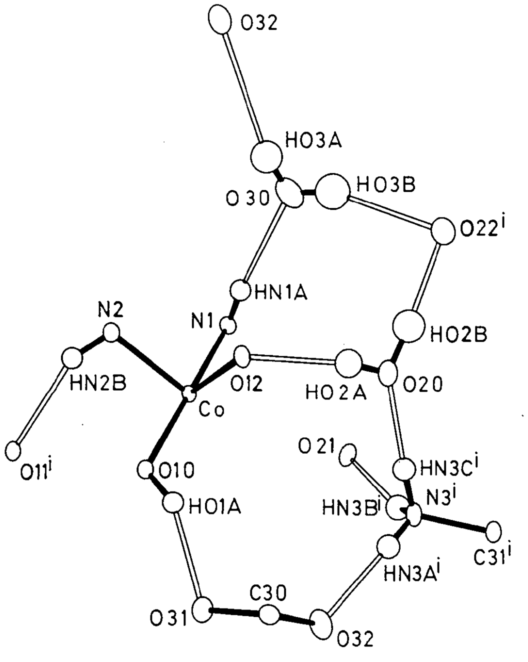

Fig. 2. A representation of the proposed hydrogen-bonding scheme. Hydrogen bonds are represented by open bonds.

In the structure of the classic diol cation, di-μ-hydroxo-bis[tetraamminecobalt(III)] (Prout, 1962), the Co···Co distance was found to be 2.932 (5) Å, the average Co—N distance 1.96 (2) Å, and the Co—OH distances 1.911 (15) and 1.913 (15) Å; the O—Co—O angle was 79.9 (5)°, which was described as being considerably less than that expected for an octahedral complex. In contrast, in the present structure the distances are shorter and the angles are closer to those expected for octahedral coordination.

Experimental

A suitable crystal formed over eight months on evaporation of a mixture of aqueous solutions of cobaltous acetate tetrahydrate and 1-aminocyclohexanecarboxylic acid in a molar ratio of 1:2 in the presence of air. A gradual intensification of color accompanied the oxidation to Co^{III}.

Crystal data

$[Co_2(C_7H_{12}NO_2)_4(OH)_2]$.-
$2C_7H_{13}NO_2.4H_2O$
$M_r = 1079.0$
Triclinic
$P\overline{1}$
$a = 11.090$ (3) Å
$b = 11.156$ (3) Å
$c = 11.952$ (3) Å
$\alpha = 97.07$ (2)°
$\beta = 93.26$ (2)°
$\gamma = 119.22$ (2)°
$V = 1269$ (1) $Å^3$
$Z = 1$
$D_x = 1.412$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 15 reflections
$\theta = 10$–25°
$\mu = 0.73$ mm^{-1}
$T = 293$ (1) K
Hexagonal prism
0.48 × 0.42 × 0.42 mm
Reddish purple

Data collection

Nicolet four-circle diffractometer
ω scans
Absorption correction: none
4908 measured reflections
4659 independent reflections
3724 observed reflections [$I > 2.5\sigma(I)$]
$R_{int} = 0.018$

$\theta_{max} = 25.35°$
$h = -13 \rightarrow 13$
$k = -13 \rightarrow 13$
$l = 0 \rightarrow 14$
6 standard reflections monitored every 300 reflections intensity variation: insignificant

Refinement

Refinement on F
$R = 0.034$
$wR = 0.041$
$S = 1.41$
3724 reflections
433 parameters

$(\Delta/\sigma)_{max} = 0.11$ for non-H atoms (mean 0.015), 0.67 for H atoms [H(26)A] (mean 0.042)
$\Delta\rho_{max} = 0.37$ e $Å^{-3}$
$\Delta\rho_{min} = -0.29$ e $Å^{-3}$

Only coordinates of H atoms refined
$w = 1/\sigma^2(F)$

Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	B_{eq}
Co	0.13989 (4)	0.11233 (4)	0.03488 (3)	1.645 (19)
O(11)	0.0784 (2)	0.2178 (2)	0.1269 (2)	2.16 (10)
O(12)	0.2583 (2)	0.2698 (2)	−0.0275 (2)	2.40 (11)
O(21)	0.1085 (3)	0.3359 (2)	0.2984 (2)	3.03 (12)
O(22)	0.3924 (3)	0.3424 (3)	−0.1618 (2)	3.88 (14)
O(31)	−0.2042 (3)	0.1382 (2)	−0.1177 (2)	3.38 (13)
O(32)	−0.1635 (3)	0.3304 (3)	−0.0023 (2)	3.80 (15)
O(10)	−0.0089 (2)	0.0510 (2)	−0.0861 (2)	1.86 (10)
O(20)	0.3212 (3)	0.5187 (3)	0.0993 (4)	5.27 (19)
O(30)	0.5762 (4)	0.3698 (4)	0.1181 (3)	5.63 (20)
N(1)	0.2809 (3)	0.1660 (3)	0.1649 (2)	2.10 (13)
N(2)	0.2080 (3)	0.0143 (3)	−0.0628 (2)	2.03 (13)
N(3)	−0.0768 (3)	0.4935 (3)	−0.1546 (3)	2.62 (16)
C(10)	0.1393 (3)	0.2667 (3)	0.2308 (3)	2.21 (16)
C(11)	0.2518 (3)	0.2326 (3)	0.2683 (2)	2.15 (15)
C(12)	0.3824 (4)	0.3677 (4)	0.3276 (3)	2.93 (18)
C(13)	0.4917 (4)	0.3429 (4)	0.3862 (4)	3.82 (20)
C(14)	0.4307 (5)	0.2446 (5)	0.4707 (4)	4.44 (25)
C(15)	0.3072 (5)	0.1078 (4)	0.4102 (3)	3.72 (23)
C(16)	0.1943 (4)	0.1289 (4)	0.3521 (3)	2.86 (18)
C(20)	0.3205 (3)	0.2497 (3)	−0.1092 (3)	2.50 (15)
C(21)	0.3001 (3)	0.1029 (3)	−0.1404 (3)	2.24 (14)
C(22)	0.4418 (4)	0.1092 (4)	−0.1249 (4)	3.36 (19)
C(23)	0.4305 (5)	−0.0299 (5)	−0.1710 (5)	4.78 (28)
C(24)	0.3646 (6)	−0.0819 (6)	−0.2938 (5)	5.66 (29)
C(25)	0.2230 (5)	−0.0930 (5)	−0.3083 (4)	4.37 (23)
C(26)	0.2309 (4)	0.0446 (4)	−0.2642 (3)	3.40 (20)
C(30)	−0.1623 (3)	0.2660 (3)	−0.0942 (3)	2.52 (15)
C(31)	−0.1008 (3)	0.3493 (3)	−0.1913 (3)	2.33 (16)
C(32)	−0.2038 (4)	0.2835 (4)	−0.3012 (3)	3.22 (19)
C(33)	−0.1403 (6)	0.3442 (5)	−0.4049 (3)	4.40 (28)
C(34)	−0.0052 (6)	0.3442 (5)	−0.4162 (4)	5.48 (33)
C(35)	0.0996 (5)	0.4217 (5)	−0.3096 (4)	4.90 (26)
C(36)	0.0390 (4)	0.3578 (4)	−0.2066 (4)	3.34 (20)

Table 2. *Selected geometric parameters* (Å, °)

The bond distances and angles for the cyclohexane rings are listed in the supplementary material.

Co—O(11)	1.900 (2)	Co—O(12)	1.884 (2)
Co—O(10)	1.914 (2)	Co—O(10^{i})	1.896 (2)
Co—N(1)	1.949 (3)	Co—N(2)	1.929 (3)
O(11)—C(10)	1.294 (4)	O(12)—C(20)	1.286 (4)
O(21)—C(10)	1.225 (4)	O(22)—C(20)	1.230 (4)
O(31)—C(30)	1.252 (4)	O(32)—C(30)	1.241 (4)
N(1)—C(11)	1.496 (4)	C(10)—C(11)	1.531 (5)
N(2)—C(21)	1.493 (4)	C(20)—C(21)	1.533 (5)
N(3)—C(31)	1.499 (4)	C(30)—C(31)	1.553 (4)
C(11)—C(12)	1.536 (5)	C(11)—C(16)	1.545 (5)
C(21)—C(22)	1.538 (5)	C(21)—C(26)	1.532 (5)
C(31)—C(32)	1.530 (5)	C(31)—C(36)	1.529 (5)
O(11)—Co—O(12)	90.9 (1)	O(10)—Co—O(10^{i})	82.6 (1)
O(11)—Co—O(10)	93.2 (1)	O(10)—Co—N(1)	175.7 (1)
O(11)—Co—O(10^{i})	89.7 (1)	O(10)—Co—N(2)	86.6 (1)
O(11)—Co—N(1)	85.3 (1)	O(10^{i})—Co—N(1)	93.4 (1)
O(11)—Co—N(2)	176.7 (1)	O(10^{i})—Co—N(2)	93.5 (1)
O(12)—Co—O(10)	92.4 (1)	O(12)—Co—O(10^{i})	174.9 (1)
O(12)—Co—N(1)	91.7 (1)	O(12)—Co—N(2)	85.8 (1)
N(1)—Co—N(2)	95.2 (1)	Co—O(10)—Co^{i}	97.4 (1)
Co—O(11)—C(10)	116.4 (2)	Co—O(12)—C(20)	116.6 (2)
Co—N(1)—C(11)	111.6 (2)	Co—N(2)—C(21)	112.0 (2)
O(11)—C(10)—O(21)	122.5 (3)	O(12)—C(20)—O(22)	122.4 (3)
O(11)—C(10)—C(11)	117.3 (3)	O(12)—C(20)—C(21)	117.1 (3)
O(21)—C(10)—C(11)	120.2 (3)	O(22)—C(20)—C(21)	120.5 (3)
N(1)—C(11)—C(10)	108.0 (2)	N(2)—C(21)—C(20)	108.1 (2)
N(1)—C(11)—C(12)	111.9 (3)	N(2)—C(21)—C(22)	109.5 (3)
N(1)—C(11)—C(16)	109.8 (3)	N(2)—C(21)—C(26)	110.2 (3)
C(10)—C(11)—C(12)	109.0 (3)	C(20)—C(21)—C(22)	109.9 (3)
C(10)—C(11)—C(16)	108.1 (3)	C(20)—C(21)—C(26)	108.4 (3)
O(31)—C(30)—O(32)	126.6 (3)	N(3)—C(31)—C(30)	107.3 (3)
O(31)—C(30)—C(31)	115.0 (3)	N(3)—C(31)—C(32)	108.3 (3)
O(32)—C(30)—C(31)	118.4 (3)	N(3)—C(31)—C(36)	109.1 (3)
C(30)—C(31)—C(32)	110.9 (3)	C(30)—C(31)—C(36)	108.8 (3)

Symmetry code: (i) $-x, -y, -z$.

Table 3. *Hydrogen-bonding geometry* (Å, °)

D	H	*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O(20)	H(O2*A*)	O(12)	2.729 (4)	0.77 (5)	1.97 (5)	167 (5)
O(20^{i})	H(O2*B*)	O(22)	2.773 (4)	0.95 (5)	1.83 (5)	169 (5)
O(30^{i})	H(O3*B*)	O(22)	3.029 (5)	0.82 (6)	2.26 (6)	156 (6)
O(10)	H(O1*A*)	O(31)	2.799 (3)	0.82 (4)	2.03 (4)	156 (3)
O(30^{i})	H(O3*A*)	O(32)	3.486 (5)	0.81 (5)	2.69 (5)	166 (5)
N(1)	H(N1*A*)	O(30)	3.076 (4)	0.81 (4)	2.27 (4)	173 (4)
N(2^{i})	H(N2*B*)	O(11)	2.930 (4)	0.87 (4)	2.14 (4)	151 (3)
N(3^{i})	H(N3*A*)	O(32)	2.809 (4)	0.84 (4)	1.97 (4)	173 (4)
N(3^{i})	H(N3*B*)	O(21)	2.844 (4)	0.95 (4)	1.98 (4)	151 (3)
N(3^{i})	H(N3*C*)	O(20)	2.769 (5)	0.95 (4)	1.83 (4)	169 (3)

Symmetry code: (i) $-x, -y, -z$.

The structure was solved using a combination of the VAX version of the *DIRDIF* system (Beurskens *et al.*, 1985) and the *NRCVAX* programs (Gabe, Lee & Le Page, 1985). In the absence of a chemical analysis, the compound was at first assumed to be a hydrated Co^{II} bis-bidentate complex. A Patterson map gave the location of the Co atom and a *DIRDIF* analysis showed the presence of a third, apparently unbonded, ligand cluster, a bonded hydroxo group and two water molecules in the asymmetric unit. Refinement was continued on that basis. The positions of the 30 ring H atoms were calculated, and the remaining 12 H atoms of the amino groups and the water molecules were then located on a difference Fourier map. The individual *U* values of the H atoms were fixed during the final full-matrix refinement.

The author wishes to acknowledge receipt of a grant from the University of New Hampshire Research Office that made possible the use of the University Computation Center. The intensity data were collected by Dr Cynthia Day of Crystalytics Company, Lincoln, Nebraska, to whom the author is also indebted for suggestions concerning the structure. Dr Gary Weisman of the Department of Chemistry was most helpful in arranging the production of the illustrations.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, bond distances and angles involving H atoms, least-squares-planes data, torsion angles, and bond distances and angles for the cyclohexane rings, along with a projection of the unit cell, have been deposited with the IUCr (Reference: CD1058). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Potassium *trans*-Tetraaquadicarbonatonickelate(II), $K_2[Ni(CO_3)_2(H_2O)_4]$

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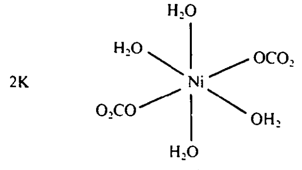
Abstract

The structure of potassium tetraaquadicarbonatonickelate(II), $K_2[Ni(CO_3)_2(H_2O)_4]$, can be described as a close-packed arrangement of $[Ni(CO_3)_2(H_2O)_4]^{2-}$ anions at the corners and the body centre of the monoclinic unit cell with K^+ cations located in the interstices. Each Ni atom is coordinated by four water O atoms and two monodentate carbonate O atoms arranged in a *trans* configuration at the corners of a slightly distorted octahedron, with Ni—O bond distances in the range 2.046 (2)–2.094 (3) Å. Hydrogen bonding takes place between water molecules and carbonate groups within and between the anions. The anions are linked into a three-dimensional network by the hydrogen bonding. Each K^+ ion has seven neighbouring O atoms at normal distances ranging from 2.699 (3) to 3.094 (3) Å. The carbonate group exhibits a deviation from D_{3h} symmetry [O—C 1.275 (4)–1.292 (5) Å; O—C—O 119.5 (3)–120.5 (3)°].

Comment

The title compound, (I), was first identified by Deville (1851) and was at first reported to be orthorhombic (Deville, 1852). On the basis of powder X-ray diffraction patterns, it was suggested that the compound was isostructural with $K_2[Co(CO_3)_2(H_2O)_4]$ (Harlow & Simonsen, 1976). However, no comment was made on the fact that the latter is isostructural with baylissite, $K_2Mg(CO_3)_2.4H_2O$ (Walenta, 1976; Bucat, Patrick, White & Willis, 1977). In order to investigate carbonates of the baylissite type systematically, the crystal structure of $K_2[Ni(CO_3)_2(H_2O)_4]$ has been determined by single crystal X-ray diffraction and confirmed to be isostructural with the analogous Co and Mg compounds.



(I)

The $[Ni(CO_3)_2(H_2O)_4]^{2-}$ anions in the title compound, in which each centrosymmetric Ni atom is bound to four water O atoms and two monodentate carbonate O atoms to form a slightly distorted octahedron in a *trans* configuration, occupy the centre and corners of the unit cell. In comparison with the water molecules, the better donor ability of the CO_3^{2-} anions is reflected by the shorter Ni—O bond length of 2.046 (2) Å to the carbonate group. The Ni—O bond length to the water O atom O5 is found to be longer than that to the water O atom O4, which is in contrast to the bond lengths observed in $K_2[Co(CO_3)_2(H_2O)_4]$ (Harlow & Simonsen, 1976). The longer Ni—O5 bond distance may result from the stronger repulsion between the carbonate group and water O atom O5, since the electron clouds of the $p\pi$ orbitals of the carbonate group are oriented roughly towards the O5 water O atoms. The water O atoms are strongly hydrogen bonded to the carbonate O atoms O2 and O3, which are not coordinated to the central Ni atom, with O···O distances in the range 2.565 (4)–2.727 (4) Å and nearly linear O—H···O angles varying from 164 to 168°. One hydrogen bond per asymmetric unit is formed within the anion, while the others are formed between adjacent anions, linking them into a three-dimensional network. The K^+ cations are located within cavities in the structure, each of which is formed by five complex anions, resulting in seven K···O contact distances in the range 2.699 (3)–3.094 (3) Å, the four shorter ones involving carbonate O atoms and the others water O atoms. The carbonate groups in the title compound deviate more significantly from the D_{3h} symmetry of the CO_3^{2-} ions in calcite (Sass, Vidale & Donohue, 1957) than those in the isostructural Co and Mg analogues; for these, the C—O bond distances are in the range 1.282 (4)–1.298 (3) Å

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