This work was supported by the National Natural Scientific Foundation of China and the Natural Scientific Foundation of Fujian Province.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KH1111). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C**52**, 2693–2695

Hexaaquacobalt(II) Bis[(2-Hydroxy-1,3-propanediamine-*N*,*N*,*N*′,*N*′-tetraacetato)cobalt(III)]

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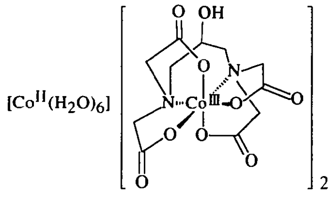
(*Received 14 February 1996; accepted 13 June 1996*)

Abstract

The structure of the title complex, $[Co(H_2O)_6][Co(C_{11}H_{14}N_2O_9)]_2$, is comprised of discrete $[Co(hpdta)]^-$ anions (H_4hpdta is 2-hydroxy-1,3-propanediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid) and $[Co(H_2O)_6]^{2+}$ cations in a 2:1 molar ratio. The trivalent Co atom in the anion is coordinated by the hexadentate hpdta chelate ligand, with two amino-N atoms [Co—N 1.948 (3) Å] and four O atoms of the four monodentate carboxylato groups [Co—O 1.869 (2)–1.914 (2) Å] in a distorted octahedral arrangement, whereas the divalent Co atom in the cation is coordinated in an octahedral manner by six aqua ligands [Co—O 2.078 (2)–2.124 (2) Å]. The crystal structure is stabilized by extensive hydrogen bonding. Each aqua ligand forms two donor hydrogen bonds with the carboxyl O atoms from adjacent anions and the hydroxyl group forms a hydrogen bond with an adjacent carboxyl O atom.

Comment

2-Hydroxy-1,3-propanediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid (H_4hpdta) is a structural analogue of the widely used chelate ligand ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid. Hence, it is somewhat surprising that metal complexes of H_4hpdta have received little attention. Only a few metal complexes of hpdta have been structurally characterized, including two cobalt(III) complexes (Kalina, Pavelčik & Majer, 1978; Sato & Yano, 1989) and one palladium(II) complex (Song, Zhang, Li, Jin & Jin, 1992). In this paper, we report the preparation and structure of a mixed-valent cobalt complex of hpdta, namely $[Co(H_2O)_6][Co(hpdta)]_2$, (I). The complex was obtained from a mixture of $Co(NO_3)_2$ and H_4hpdta in a weakly acidic aqueous solution.



(I)

The crystal structure of the mixed-valent complex comprises discrete $[Co(H_2O)_6]^{2+}$ cations and $[Co(hpdta)]^-$ anions in a 1:2 molar ratio. The Co^{III} atom in the anion is coordinated by a hexadentate hpdta chelate ligand, being surrounded by two N atoms [Co—N 1.948 (3) Å] and four O atoms from the four monodentate carboxylato groups [Co—O 1.869 (2)–1.914 (2) Å] in a distorted octahedral arrangement, with the most distorted bond angle being N1—Co1—N2 at 97.7 (1)° (Fig. 1). The bond lengths and angles of this anion are strikingly similar to those of the cobalt(III) complexes of hpdta reported previously (Kalina, Pavelčik & Majer, 1978; Sato & Yano, 1989). It is noteworthy that the Co1—O8 [1.869 (2) Å] and Co1—O4 [1.894 (2) Å] bonds are significantly shorter than the Co1—O2 [1.904 (2) Å] and Co1—O6 [1.914 (2) Å] bonds, which are *trans* with respect to the Co—N bonds, demonstrating clearly that nitrogen has a much greater *trans* effect than oxygen. In the $[Co(H_2O)_6]^{2+}$ cation, the Co^{II} atom is located at an inversion centre and is surrounded by six centrosymmetrically related aqua ligands [Co—O 2.078 (2)–2.124 (2) Å] in a slightly distorted octahedral

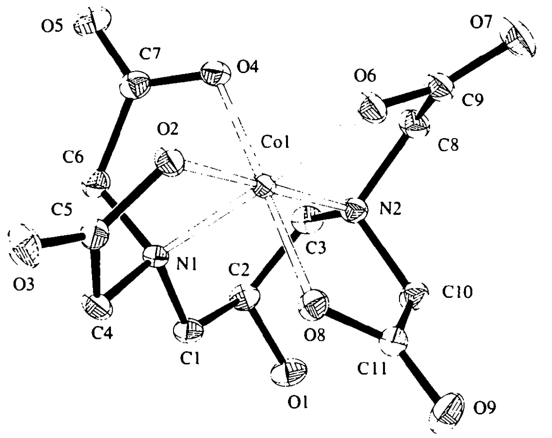


Fig. 1. An *ORTEP* (Johnson, 1965) plot (30% probability) of the $[Co(hpdta)]^-$ anion.

arrangement, where the most distorted bond angle is O1*W*—Co2—O2*W* at 93.34 (9)°. The geometry of this cation is similar to those of $[M(H_2O)_6]^{2+}$ (M = Zn, Mn; Auerbach, Stockheim, Weyhermüller, Wieghardt & Nuber, 1993).

Hydrogen bonding plays a vital role in stabilizing the crystal structure. The hydroxyl group forms a donor hydrogen bond with a carboxyl O atom [O1···O9 2.912 (4) Å] from an adjacent anion. Each aqua ligand also forms two donor hydrogen bonds [O···O 2.703 (3)–2.782 (4) Å] with carboxyl O atoms from adjacent anions, resulting in each $[Co(H_2O)_6]^{2+}$ cation forming 12 donor hydrogen bonds with six adjacent $[Co(hpdta)]^-$ anions (Fig. 2). Extensive hydrogen bonding similar to that in the title complex has been found in metal complexes containing analogous $[M(H_2O)_6]^{2+}$ cations (M = Zn, Mn; Auerbach, Stockheim, Weyhermüller, Wieghardt & Nuber, 1993). The hydrogen bonds in the title complex extend the structure into two-dimensional layers parallel to the *yz* plane.

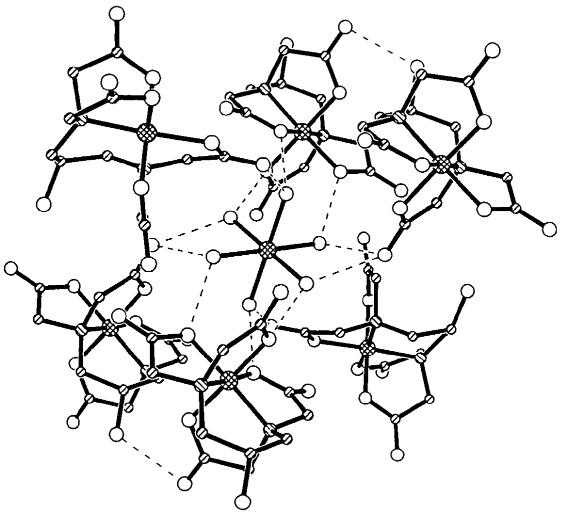


Fig. 2. Perspective view showing the hydrogen-bonding scheme. The cross-hatched circles, open circles, bottom left-to-top right lined circles and bottom right-to-top left lined circles represent the Co, O, N and C atoms, respectively.

Finally, it is noteworthy that complexes containing $[Co(hpdta)]^-$ anions were commonly prepared by oxidation of Co^{II} ions with hydrogen peroxide. In contrast, the title complex was prepared by auto-oxidation of Co^{II} with air in a weakly acidic aqueous solution (pH 5).

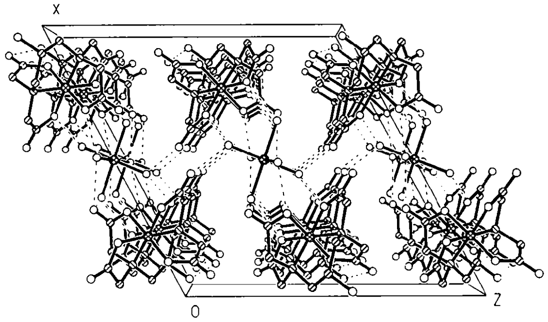


Fig. 3. The molecular packing of the title complex in the lattice.

Experimental

An aqueous solution (2 ml) of $Co(NO_3)_2.6H_2O$ (0.29 g, 2.0 mmol) was added to an aqueous solution (8 ml) of H_4hpdta (0.51 g, 1.0 mmol). The mixture was heated at 323 K, stirred for 10 min and the resulting solution adjusted to pH 5 with an aqueous solution of 2 *N* NaOH and allowed to stand in air. Reddish brown crystals of the title compound were deposited after a week.

Crystal data

$[Co(H_2O)_6][Co(C_{11}H_{14}N_2O_9)]_2$
$M_r = 921.37$
Monoclinic
$P2_1/c$
$a = 16.434\ (2)$ Å
$b = 6.990\ (3)$ Å
$c = 16.204\ (2)$ Å
$\beta = 117.83\ (1)°$
$V = 1646.1\ (8)$ Å^3
$Z = 2$
$D_x = 1.859$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 8–13°$
$\mu = 1.600$ mm^{-1}
$T = 293\ (2)$ K
Polyhedral
0.42 × 0.36 × 0.28 mm
Reddish brown

Data collection

Siemens *P*4 diffractometer
ω scans

$R_{int} = 0.027$
$\theta_{max} = 27.5°$

Absorption correction:
ψ scan (Kopfmann & Huber, 1968)
$T_{\min} = 0.58$, $T_{\max} = 0.64$
3880 measured reflections
3744 independent reflections
3165 observed reflections
$[I > 2\sigma(I)]$

$h = -21 \rightarrow 18$
$k = -9 \rightarrow 0$
$l = 0 \rightarrow 21$
3 standard reflections
monitored every 100 reflections
intensity decay: 0.017%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0452$
$wR(F^2) = 0.1225$
$S = 1.075$
3744 reflections
241 parameters
H(C) atoms riding and H(O) atoms located and fixed
$w = 1/[\sigma^2(F_o^2) + (0.082P)^2 + 1.287P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = -0.001$
$\Delta\rho_{\max} = 0.730$ e Å^{-3}
$\Delta\rho_{\min} = -0.697$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Co1	0.76246 (2)	0.18929 (6)	0.48580 (3)	0.0182 (1)
Co2	1/2	0	0	0.0243 (2)
O1	0.9244 (2)	−0.2656 (4)	0.4447 (2)	0.0355 (6)
C1	0.9195 (2)	−0.0650 (5)	0.5570 (2)	0.0249 (6)
C2	0.8687 (2)	−0.2266 (5)	0.4888 (2)	0.0266 (6)
C3	0.7690 (2)	−0.1894 (5)	0.4183 (2)	0.0282 (7)
N1	0.8629 (2)	0.0538 (4)	0.5875 (2)	0.0193 (5)
N2	0.7449 (2)	0.0130 (4)	0.3857 (2)	0.0230 (5)
C4	0.9226 (2)	0.2112 (5)	0.6487 (2)	0.0248 (6)
C5	0.8622 (2)	0.3766 (5)	0.6480 (2)	0.0222 (6)
O2	0.7795 (1)	0.3745 (3)	0.5787 (1)	0.0246 (4)
O3	0.8918 (2)	0.5017 (3)	0.7070 (2)	0.0332 (5)
C6	0.8227 (2)	−0.0587 (5)	0.6386 (2)	0.0259 (6)
C7	0.7189 (2)	−0.0404 (5)	0.5933 (2)	0.0262 (6)
O4	0.68039 (14)	0.0563 (4)	0.5173 (2)	0.0273 (5)
O5	0.6760 (2)	−0.1180 (4)	0.6298 (2)	0.0392 (6)
C8	0.6434 (2)	0.0264 (5)	0.3201 (2)	0.0306 (7)
C9	0.6133 (2)	0.2314 (5)	0.3157 (2)	0.0280 (7)
O6	0.6620 (2)	0.3283 (3)	0.3910 (2)	0.0272 (5)
O7	0.5472 (2)	0.2977 (4)	0.2475 (2)	0.0440 (7)
C10	0.7982 (2)	0.0886 (5)	0.3386 (2)	0.0267 (6)
C11	0.8453 (2)	0.2756 (5)	0.3804 (2)	0.0254 (6)
O8	0.8431 (2)	0.3265 (3)	0.4564 (2)	0.0245 (5)
O9	0.8841 (2)	0.3699 (4)	0.3457 (2)	0.0391 (6)
O1*W*	0.6385 (2)	0.0045 (4)	0.1073 (2)	0.0305 (5)
O2*W*	0.4487 (2)	0.1020 (4)	0.0871 (2)	0.0313 (5)
O3*W*	0.4909 (2)	−0.2809 (4)	0.0378 (2)	0.0446 (7)

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

Co1—O8	1.869 (2)	N1—C4	1.500 (4)
Co1—O4	1.894 (2)	N2—C10	1.502 (4)
Co1—O2	1.904 (2)	N2—C8	1.505 (4)
Co1—O6	1.914 (2)	C4—C5	1.520 (4)
Co1—N2	1.948 (3)	C5—O3	1.217 (4)
Co1—N1	1.948 (2)	C5—O2	1.297 (4)
Co2—O2*W*	2.078 (2)	C6—C7	1.514 (4)
Co2—O3*W*	2.083 (3)	C7—O5	1.238 (4)
Co2—O1*W*	2.124 (2)	C7—O4	1.284 (4)
O1—C2	1.427 (4)	C8—C9	1.507 (5)
C1—N1	1.494 (4)	C9—O7	1.224 (4)
C1—C2	1.528 (5)	C9—O6	1.294 (4)
C2—C3	1.519 (5)	C10—C11	1.509 (5)
C3—N2	1.497 (4)	C11—O9	1.223 (4)
N1—C6	1.500 (4)	C11—O8	1.298 (4)
O8—Co1—O4	178.4 (1)	C6—N1—Co1	107.7 (2)
O8—Co1—O2	89.6 (1)	C4—N1—Co1	103.7 (2)
O4—Co1—O2	88.9 (1)	C3—N2—C10	112.9 (2)
O8—Co1—O6	89.1 (1)	C3—N2—C8	109.4 (2)
O4—Co1—O6	90.5 (1)	C10—N2—C8	109.6 (2)
O2—Co1—O6	92.46 (9)	C3—N2—Co1	113.1 (2)
O8—Co1—N2	87.7 (1)	C10—N2—Co1	107.8 (2)
O4—Co1—N2	93.8 (1)	C8—N2—Co1	103.5 (2)
O2—Co1—N2	176.4 (1)	N1—C4—C5	109.3 (2)
O6—Co1—N2	85.2 (1)	O3—C5—O2	124.2 (3)
O8—Co1—N1	92.5 (1)	O3—C5—C4	121.3 (3)
O4—Co1—N1	87.8 (1)	O2—C5—C4	114.4 (3)
O2—Co1—N1	84.7 (1)	C5—O2—Co1	113.6 (2)
O6—Co1—N1	176.7 (1)	N1—C6—C7	112.0 (2)
N2—Co1—N1	97.7 (1)	O5—C7—O4	123.6 (3)
O2*W*—Co2—O3*W*	90.9 (1)	O5—C7—C6	119.7 (3)
O2*W*—Co2—O3*W*$^{\rm i}$	89.1 (1)	O4—C7—C6	116.7 (3)
O2*W*—Co2—O1*W*	93.34 (9)	C7—O4—Co1	115.0 (2)
O3*W*—Co2—O1*W*	88.3 (1)	N2—C8—C9	108.9 (3)
N1—C1—C2	115.9 (2)	O7—C9—O6	123.5 (3)
O1—C2—C3	112.0 (3)	O7—C9—C8	122.4 (3)
O1—C2—C1	104.0 (2)	O6—C9—C8	114.1 (3)
C3—C2—C1	116.8 (3)	C9—O6—Co1	114.4 (2)
N2—C3—C2	116.3 (3)	N2—C10—C11	112.0 (2)
C1—N1—C6	113.2 (2)	O9—C11—O8	122.7 (3)
C1—N1—C4	108.1 (2)	O9—C11—C10	121.9 (3)
C6—N1—C4	109.9 (2)	O8—C11—C10	115.4 (3)
C1—N1—Co1	113.7 (2)	C11—O8—Co1	116.0 (2)

Symmetry code: (i) $1 - x, -y, -z$.

Data were collected by established procedures. Dispersion corrections and absorption coefficients were taken from *International Tables for Crystallography* (1992, Vol. C, Tables 6.1.1.4 and 4.2.6.8).

Data collection: *SHELXTL/PC* (Sheldrick, 1990). Cell refinement: *SHELXTL/PC*. Data reduction: *SHELXTL/PC*. Program(s) used to solve structure: *SHELXTL/PC*. Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL*93.

This work was supported by a Zhongshan University Research Grant and a Hong Kong Research Grants Council Earmarked Grant CUHK 89/93E.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KH1107). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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