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*Acta Cryst.* (1999). C55, 921–923

## (C<sub>2</sub>H<sub>10</sub>N<sub>2</sub>)[Co(H<sub>2</sub>O)<sub>6</sub>](HPO<sub>4</sub>)<sub>2</sub>: a supramolecular three-dimensional hydrogen-bonding network

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(Received 15 June 1998; accepted 27 January 1999)

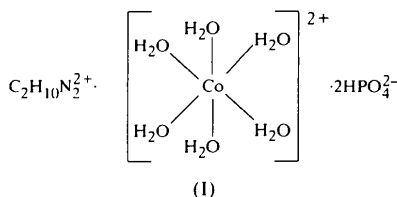
### Abstract

The title compound, ethylenediammonium hexaaquacobalt bis(hydrogenphosphate), consists of [Co(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> and [enH<sub>2</sub>]<sup>2+</sup> cations (en is ethylenediamine), and [HPO<sub>4</sub>]<sup>2-</sup> anions interconnected by an extensive intermolecular three-dimensional hydrogen-bonding network. The [enH<sub>2</sub>]<sup>2+</sup> cations play an important role in the templating effect. Both [Co(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> cations are situated on inversion centers. The average Co—O and P—O bond distances are 2.075 (6) and 1.54 (2) Å, respectively.

### Comment

Most crystal-engineering studies have thus far focused on the use of hydrogen bonding between suitable organic molecules for generating multi-dimensional networks (Desiraju, 1995). To a lesser extent, inorganic synthons or a combination of inorganic and organic building blocks capable of intermolecular hydrogen bonding have been explored for their use in solid-state supramolecular chemistry.

The crystal structure of the title compound, ethylenediammonium hexaaquacobalt bis(hydrogenphosphate), (I), is composed of two crystallographically independent exactly centrosymmetric octahedral [Co(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup>



complex cations, both situated on inversion centers, two [HPO<sub>4</sub>]<sup>2-</sup> anions and an [enH<sub>2</sub>]<sup>2+</sup> cation. First of all, the [Co(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> cations and [HPO<sub>4</sub>]<sup>2-</sup> anions are linked by hydrogen bonds to form an infinite three-dimensional framework with the [enH<sub>2</sub>]<sup>2+</sup> cation located in the tunnel along the *a* axis. Fig. 1 shows two different views of this supramolecular three-dimensional network with and without the [enH<sub>2</sub>]<sup>2+</sup> cation in the void space. The asymmetric unit that gives rise to the network structure under symmetry expansion is shown in Fig. 2. The N

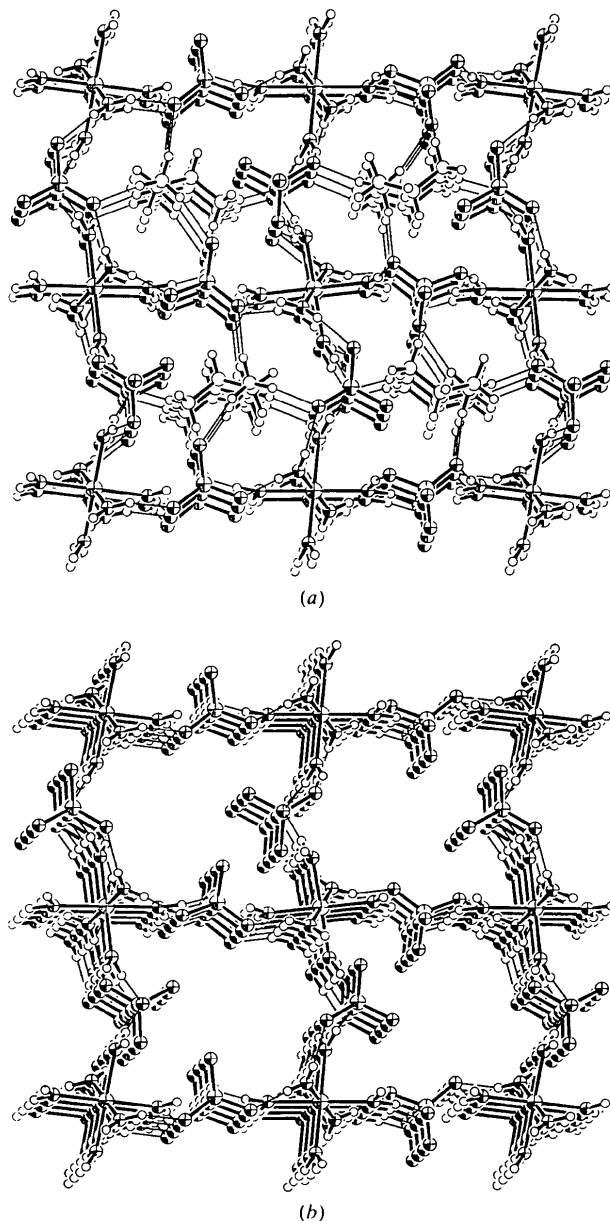


Fig. 1. Projections along the *a* axis of the three-dimensional network formed by the title compound with (a) the [enH<sub>2</sub>]<sup>2+</sup> cations in the void space and (b) the [enH<sub>2</sub>]<sup>2+</sup> cations removed.

atoms of the  $[enH_2]^{2+}$  cation also participate in the extensive hydrogen bonding through interactions with the O atoms of the  $[HPO_4]^{2-}$  anions in the framework. It is tempting to conclude that such a supramolecular architecture is formed by self-assembly, with the  $[enH_2]^{2+}$  cation acting as a structure-directing template.

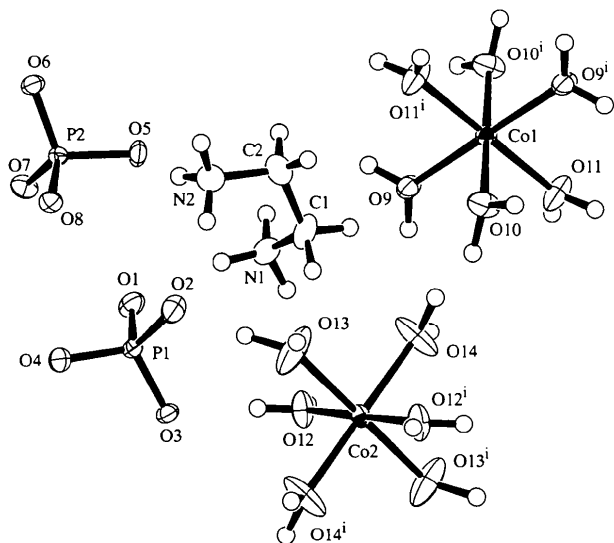


Fig. 2. The asymmetric unit of the title compound with the atom-labeling scheme and ellipsoids plotted at the 50% probability level. Symmetry code as in Table 2.

There are two distinct types of O atoms in the slightly distorted tetrahedral  $[HPO_4]^{2-}$  anion. One type acts as a hydrogen-bond acceptor and forms three hydrogen bonds (*i.e.* O2, O3, O4, O6, O7 and O8). Another type acts as both an acceptor and a donor, and forms two hydrogen bonds (*i.e.* O1 and O5). The formation of hydrogen bonds between the two different phosphate groups is a good indication of protonation of the O atoms in the  $PO_4$  units, and confirms the existence of the  $[HPO_4]^{2-}$  anions in the compound. It should be noted that the H atoms in the  $[HPO_4]^{2-}$  anions could not be located directly from the electron-density maps. However, the longer P1—O1 and P2—O5 bond distances of 1.605 (3) and 1.591 (3) Å, respectively, in the two tetrahedral fragments provide further evidence for the protonation of these two O atoms. The Co—O and P—O bond lengths are unexceptional and are comparable with those found in  $[Co(H_2O)_6](BrO_4)_2$  [average Co—O 2.084 (4) Å; Blackburn & Gerkin, 1993] and  $Co_3(OH)_2(PO_3OH)$  [average P—O 1.54 (4) Å; Effenberger, 1992].

## Experimental

The title compound was synthesized hydrothermally by heating a mixture of  $CoCl_2 \cdot 6H_2O$  (0.08 mmol, 30 mg), *en* (1.00 mmol, 60 mg),  $H_3PO_4$  (85%, 1.5 mmol, 175 mg) and water (0.5 ml) in a sealed thick-walled Pyrex tube at 383 K for 5 d to give pink single crystals in *ca* 60% yield.

## Crystal data

$(C_2H_{10}N_2)[Co(H_2O)_6](HPO_4)_2$   
 $M_r = 421.10$   
 Monoclinic  
 $P2_1/c$   
 $a = 6.2578 (5) \text{ \AA}$   
 $b = 16.352 (1) \text{ \AA}$   
 $c = 14.819 (1) \text{ \AA}$   
 $\beta = 91.255 (1)^\circ$   
 $V = 1516.1 (2) \text{ \AA}^3$   
 $Z = 4$   
 $D_x = 1.85 \text{ Mg m}^{-3}$   
 $D_m$  not measured

Mo  $K\alpha$  radiation

$\lambda = 0.7107 \text{ \AA}$

Cell parameters from 4453 reflections

$\theta = 1.25\text{--}27.10^\circ$

$\mu = 1.415 \text{ mm}^{-1}$

$T = 296 (1) \text{ K}$

Plate

$0.20 \times 0.20 \times 0.04 \text{ mm}$

Pink

## Data collection

Quantum CCD diffractometer

$\omega$  scans

Absorption correction:

empirical *via* simulated

$\psi$  scans (Sheldrick, 1996)

$T_{\min} = 0.848$ ,  $T_{\max} = 0.945$

7917 measured reflections

3127 independent reflections

2014 reflections with

$I > 2\sigma(I)$

$R_{\text{int}} = 0.028$

$\theta_{\max} = 27.10^\circ$

$h = -7 \rightarrow 7$

$k = -20 \rightarrow 20$

$l = -18 \rightarrow 18$

## Refinement

Refinement on  $F$

$R = 0.034$

$wR = 0.044$

$S = 1.090$

2014 reflections

194 parameters

H atoms not refined

$w = 1/[\sigma^2(F_o) + 0.00073|F_o|^2]$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.54 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -0.39 \text{ e \AA}^{-3}$

Extinction correction:

Zachariasen (1967)

Extinction coefficient:

$6 (1) \times 10^{-7}$

Scattering factors from

*International Tables for Crystallography* (Vol. C)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

$$U_{\text{eq}} = (1/3) \sum_i \sum_j U^{ij} a^i a^j \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$
Co1	1/2	1/2	1/2	0.0186 (2)
Co2	1/2	1/2	0	0.0179 (2)
P1	0.0879 (2)	0.24717 (7)	0.00550 (6)	0.0166 (2)
P2	-0.0857 (2)	0.08181 (6)	0.25161 (6)	0.0146 (2)
O1	-0.0301 (5)	0.2365 (2)	0.0999 (2)	0.0263 (8)
O2	0.3269 (4)	0.2464 (2)	0.0268 (2)	0.0290 (8)
O3	0.0113 (4)	0.3301 (2)	-0.0299 (2)	0.0196 (7)
O4	0.0171 (5)	0.1774 (2)	-0.0558 (2)	0.0250 (8)
O5	0.0083 (5)	0.1617 (2)	0.2993 (2)	0.0258 (8)
O6	-0.0040 (4)	0.0067 (2)	0.3018 (2)	0.0215 (8)
O7	-0.3278 (4)	0.0867 (2)	0.2507 (2)	0.0239 (8)
O8	0.0026 (4)	0.0870 (2)	0.1562 (2)	0.0191 (7)
O9	0.2026 (4)	0.4710 (2)	0.4458 (2)	0.0307 (9)
O10	0.6084 (5)	0.5208 (2)	0.3712 (2)	0.0344 (9)
O11	0.4047 (5)	0.6225 (2)	0.5140 (2)	0.039 (1)
O12	0.2043 (5)	0.4628 (2)	0.0428 (2)	0.0318 (9)
O13	0.5964 (6)	0.3769 (2)	0.0004 (3)	0.061 (1)
O14	0.5969 (5)	0.5122 (3)	0.1328 (2)	0.053 (1)
N1	0.1001 (7)	0.3505 (2)	0.2578 (3)	0.032 (1)
N2	0.4074 (6)	0.2129 (2)	0.2144 (3)	0.034 (1)
C1	0.3363 (8)	0.3584 (3)	0.2501 (3)	0.035 (1)
C2	0.4582 (8)	0.2823 (3)	0.2740 (3)	0.038 (1)

Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Co1—O9	2.066 (3)	P1—O2	1.522 (3)
Co1—O10	2.068 (3)	P1—O3	1.528 (3)
Co1—O11	2.102 (3)	P1—O4	1.519 (3)
Co2—O12	2.061 (3)	N1—C1	1.491 (6)
Co2—O13	2.101 (3)	N2—C2	1.469 (6)
Co2—O14	2.056 (3)	C1—C2	1.499 (7)
P1—O1	1.605 (3)		
O9—Co1—O9 <sup>i</sup>	180	O1—P1—O3	104.4 (2)
O9—Co1—O10	89.4 (1)	O1—P1—O4	107.8 (2)
O9—Co1—O10 <sup>i</sup>	90.6 (1)	O2—P1—O3	112.2 (2)
O10—Co1—O11	91.9 (1)	O2—P1—O4	113.0 (2)
O10—Co1—O11 <sup>i</sup>	88.1 (1)	O3—P1—O4	112.1 (2)
O1—P1—O2	106.7 (2)		

Symmetry code: (i)  $1 - x, 1 - y, 1 - z$ .Table 3. Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ )

D—H...A	D—H	H...A	D...A	D—H...A
O9—H11...O4 <sup>i</sup>	0.94	1.78	2.690 (4)	162.2
O9—H12...O8 <sup>ii</sup>	0.92	1.86	2.728 (4)	155.9
O10—H13...O7 <sup>iii</sup>	1.01	1.70	2.714 (4)	177.2
O10—H14...O8 <sup>iii</sup>	0.96	1.75	2.702 (4)	172.5
O11—H15...O2 <sup>iii</sup>	0.89	1.82	2.708 (4)	176.1
O11—H16...O4 <sup>ii</sup>	0.95	1.92	2.868 (4)	173.2
O12—H17...O6 <sup>i</sup>	0.87	1.92	2.742 (4)	157.4
O12—H18...O3	0.90	1.80	2.697 (4)	175.1
O13—H19...O2	1.08	1.68	2.754 (4)	173.1
O13—H20...O3 <sup>iv</sup>	0.89	1.89	2.753 (4)	161.0
O14—H21...O6 <sup>iii</sup>	0.97	1.79	2.707 (4)	157.7
O14—H22...O7 <sup>iii</sup>	0.99	1.74	2.725 (4)	172.0
N1—H2...O4 <sup>i</sup>	0.95	1.92	2.859 (4)	170.0
N1—H3...O6 <sup>i</sup>	0.95	1.86	2.764 (5)	158.8
N2—H8...O7 <sup>iv</sup>	0.95	1.76	2.694 (5)	168.9
N2—H9...O2	0.95	1.94	2.867 (5)	163.0
N2—H10...O5	0.95	2.03	2.943 (5)	161.2

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

The H atoms in the  $[\text{enH}_2]^{2+}$  cation were calculated and included in the structural model and those in the  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  cation were found in difference Fourier maps. All H atoms were fixed.

Data collection: *SMART* (Siemens, 1996). Cell refinement: *SAINT* (Siemens, 1996). Data reduction: *SAINT*. Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993). Program(s) used to refine structure: *TEXSAN* (Molecular Structure Corporation, 1997). Software used to prepare material for publication: *TEXSAN*.

This work was supported by the NSF-EPSCoR (grant No. OSR-9452893) and the DOE-EPSCoR (DE-FC02-91ER75674). We thank the National Institutes of Health for a grant in support of the purchase of a Bruker CCD SMART diffractometer (3S06GM08102-25S1/M1HREV). SDH is a recipient of the NSF CAREER award from 1998 to 2002 (DMR-9733275).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1152). Services for accessing these data are described at the back of the journal.

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*Acta Cryst.* (1999). **C55**, 923–925

## { $[\mu$ -Bis(salicylidene)-1,3-propanediaminato]-copper(II)}dichlorozinc(II)†

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(Received 8 February 1999; accepted 22 February 1999)

## Abstract

The title compound,  $[\text{CuZnCl}_2(\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_2)]$ , is a double oxygen-bridged hetero-dinuclear complex. The  $\text{Cu}^{2+}$  atom has a distorted square-planar environment involving the two O and two N atoms from the bis(salicylidene)-1,3-propanediaminate ( $\text{SALPD}^{2-}$ ) ligand. The average Cu—O distance is 1.940 (3)  $\text{\AA}$  and the average Cu—N distance is 1.966 (3)  $\text{\AA}$ . The coordination around the  $\text{Zn}^{2+}$  atom is distorted tetrahedral, with average Zn—O and Zn—Cl distances of 2.007 (3) and 2.208 (1)  $\text{\AA}$ , respectively. In the bridging plane, the Zn—O1—Cu, Zn—O2—Cu, O1—Zn—O2 and O1—Cu—O2 angles are 102.4 (1), 102.3 (1), 75.0 (1) and 78.1 (1)  $^\circ$ , respectively.

## Comment

Zinc is an essential trace element for all living organisms, especially during development and growth. Therefore, new zinc compounds are the subject of interest in bioinorganic chemistry research (Bertini *et al.*, 1994; Lippard & Berg, 1994).

In the present work, a complex, (I), containing  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$  ions was prepared, and the crystal structure of this new hetero-dinuclear complex determined. Similar hetero-dinuclear complexes have been reported in the

† Systematic name: dichloro- $2\kappa^2\text{Cl}$ - $\mu$ -{2,2'-[1,3-propanediylbis(nitrilomethylidene)]diphenolato}- $1\kappa^4\text{O,N,N',O'}$ : $2\kappa^2\text{O,O'}$ -copper(II)zinc(II).