

Bis(2,3-dimethylanilinium) diaquabis-[dihydrogendiphosphato(2-)]cobaltate(II)

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Key indicators

Single-crystal X-ray study
 T = 296 K
 Mean $\sigma(C-C)$ = 0.003 Å
 R factor = 0.027
 wR factor = 0.076
 Data-to-parameter ratio = 26.3

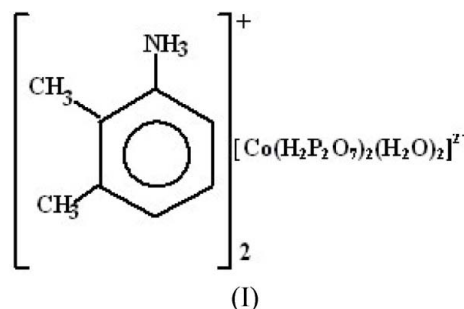
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the title compound, $(C_8H_{12}N)_2[Co(H_2P_2O_7)_2(H_2O)_2]$, the Co atom is located on an inversion center and is surrounded by two dihydrogendiphosphate ligands and two water molecules in an octahedral coordination. The packing is organized in layers containing the cobaltate anions with organic cations arranged in the interlayer spaces and connected through hydrogen bonds to the anions.

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Comment

Hybrid materials with organic and inorganic components are an attractive field of research due to their potential applications in catalysis, ion exchange, *etc.* (Cheetham *et al.*, 1999; Clearfield, 1998). Incorporation of transition elements into the organic–phosphate framework is particularly interesting, not only because of their fascinating structural features, but also due to the possibility of observing interesting magnetic properties. In recent years, a limited number of transition metal-organic diphosphates has been synthesized (Gharbi *et al.*, 1994; Gharbi & Jouini, 2004; Essehli *et al.*, 2006).



The title compound, (I), was prepared as part of our ongoing structural studies on M^{II} -organic diphosphate systems. It is built up from a diaquabis[dihydrogendiphosphato(2-)]cobaltate(II) anion and two organic 2,3-dimethylanilinium cations (Fig. 1). The Co atom is located on an inversion center and is surrounded by two symmetry-related dihydrogendiphosphate anions and two water molecules to give a slightly distorted CoO_6 octahedron. The diphosphate group acts as a bidentate ligand to the central Co^{II} atom, thus producing a bent P_2O_7 group, with a P1–O4–P2 angle of 129.05 (6)°. Four external O atoms, O_E , of the diphosphate anions build an almost regular square around the cobalt, with $Co-O_E$ distances ranging from 2.0524 (15) to 2.0710 (12) Å. The two water molecules are in the axial positions, with a $Co-OW$ distance of 2.1506 (18) Å, significantly longer than the $Co-O_E$ contacts. A similar coordination geometry around the central atom has also been observed

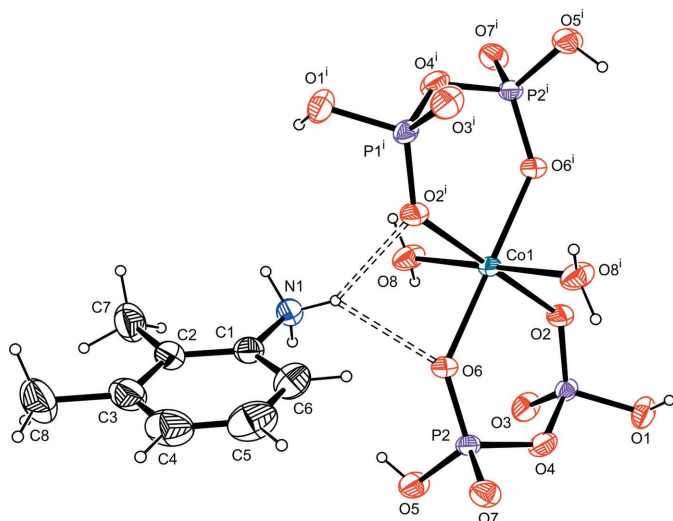


Figure 1

A view of the complex anion and one organic cation with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented as spheres of arbitrary radii. Hydrogen bonds are drawn as dashed lines. [Symmetry code: (i) $1 - x, 1 - y, 1 - z$.]

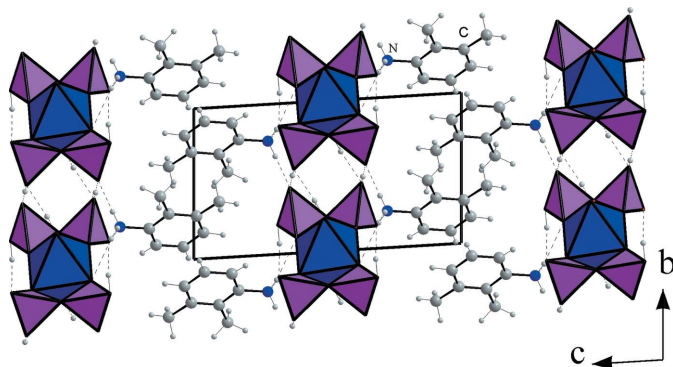


Figure 2

A projection of the structure along the [100] direction. Hydrogen bonds are shown as dashed lines.

in other $M^{\text{II}}\text{O}_6$ octahedra, $M^{\text{II}} = \text{Co}$ or Ni , in organic diphosphate compounds (Essehli *et al.*, 2006; Gharbi *et al.*, 1994; Gharbi & Jouini, 2004).

The packing consists of layers built up from the monomeric complex connected *via* hydrogen bonds and stacked perpendicular to the c axis. The protonated organic 2,3-dimethylanilinium cations occupy the interlayer spaces and interact with the anionic framework through $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds, as shown in the projection of the structure along the a -axis direction (Fig. 2 and Table 1).

The main geometric features of the hydrogen bonds (Table 1) shows two kinds of hydrogen bonds: (i) $\text{O}-\text{H}\cdots\text{O}$ contacts, with $\text{O}\cdots\text{O}$ distances ranging from 2.521 (2) to 3.028 (2) Å, link the complex anions, giving rise to a two-dimensional anionic framework with the formula $[\text{Co}(\text{H}_2\text{P}_2\text{O}_7)_2(\text{H}_2\text{O})_2]^{2n-}$, as shown in Fig. 3, and (ii) $\text{N}-\text{H}\cdots\text{O}$ contacts, involving weak contacts since the $\text{N}\cdots\text{O}$

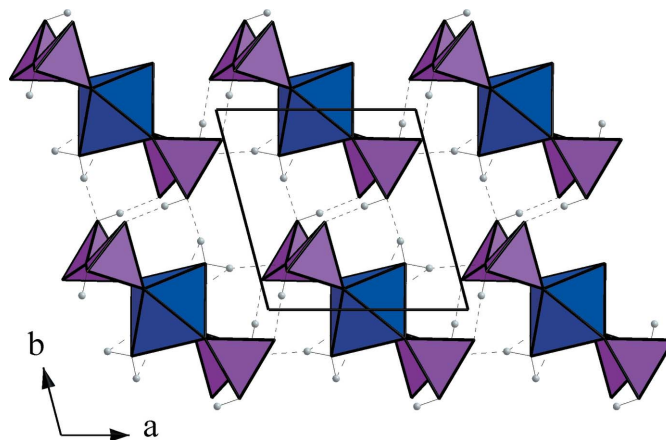


Figure 3

A projection of the $[\text{Co}(\text{H}_2\text{P}_2\text{O}_7)_2(\text{H}_2\text{O})_2]^{2n-}$ anionic framework along the c axis

distances are longer, ranging from 2.776 (2) to 2.971 (2) Å, assuring the cohesion of the network.

Experimental

Crystals of the title compound were prepared by adding an ethanol solution (10 ml) of 2,3-dimethylaniline (7.52 mmol, density = 0.9930) dropwise to a mixture of $\text{H}_4\text{P}_2\text{O}_7$ (3.75 mmol) and CoCl_2 (1.88 mmol) in a 4:2:1 molar ratio in aqueous solution (20 ml). Good quality pink prisms were obtained after a few days at ambient temperature. The diphosphoric acid, $\text{H}_4\text{P}_2\text{O}_7$, was produced from $\text{Na}_4\text{P}_2\text{O}_7$ by using an ion-exchange resin (Amberlite IR 120).

Crystal data

$2\text{C}_8\text{H}_{12}\text{N}^+ \cdot \text{CoH}_8\text{O}_{16}\text{P}_4^{2-}$
 $M_r = 691.25$
 Triclinic, $P\bar{1}$
 $a = 7.420$ (4) Å
 $b = 7.502$ (5) Å
 $c = 13.265$ (4) Å
 $\alpha = 90.14$ (6)°
 $\beta = 102.73$ (4)°
 $\gamma = 104.27$ (5)°

$V = 696.8$ (7) Å³
 $Z = 1$
 $D_x = 1.648$ Mg m⁻³
 Ag $K\alpha$ radiation
 $\mu = 0.48$ mm⁻¹
 $T = 296$ K
 Prism, pink
 $0.19 \times 0.15 \times 0.12$ mm

Data collection

Enraf-Nonius CAD-4
 diffractometer
 Non-profiled ω scans
 Absorption correction: none
 5154 measured reflections
 4968 independent reflections

4360 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.008$
 $\theta_{\text{max}} = 25.0^\circ$
 2 standard reflections
 every 120 reflections
 intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.027$
 $wR(F^2) = 0.076$
 $S = 1.05$
 4968 reflections
 189 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0422P)^2 + 0.1924P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.45$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.27$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N1-H1A\cdots O2^i$	0.89	2.17	2.962 (2)	148
$N1-H1A\cdots O6$	0.89	2.32	2.971 (2)	130
$N1-H1B\cdots O7^{ii}$	0.89	1.94	2.799 (2)	161
$N1-H1C\cdots O3^{iii}$	0.89	1.90	2.776 (2)	168
$O5-H51\cdots O3^{iii}$	0.82	1.71	2.521 (2)	171
$O8-H82\cdots O5^{iii}$	0.85 (1)	2.02 (1)	2.867 (2)	177 (2)
$O8-H81\cdots O4^{ii}$	0.84 (1)	2.24 (1)	3.028 (2)	157 (2)
$O1-H1\cdots O7^{iv}$	0.82	1.74	2.549 (2)	170

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

All H atoms attached to C, N and O(hydroxyl) were treated as riding on their parent atoms, with $C-H = 0.93$ (CH), 0.96 (CH₃), 0.89 (NH₃) and 0.82 Å (OH), with $U_{iso}(H) = 1.2U_{eq}(CH)$ or $1.5U_{eq}(CH_3, NH_3 \text{ and } OH)$. The water H atoms were refined using restraints [$O-H = 0.84$ (1) Å, $H\cdots H = 1.44$ (2) Å and $U_{iso}(H) = 1.5U_{eq}(O)$].

Data collection: *CAD-4 EXPRESS* (Enraf-Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97*

(Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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