

Diammonium diaquabis(methylene-diphosphonato- κ^2O,O')cobaltate(II)

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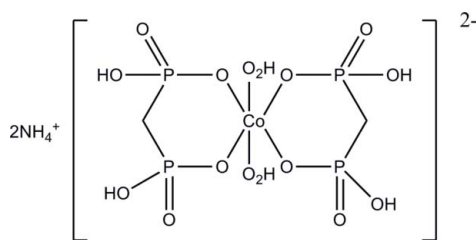
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 Key indicators: single-crystal X-ray study; $T = 103$ K; mean $\sigma(P-C) = 0.003$ Å; R factor = 0.026; wR factor = 0.097; data-to-parameter ratio = 14.0.

In the salt, $(\text{NH}_4)_2[\text{Co}(\text{CH}_4\text{O}_6\text{P}_2)_2(\text{H}_2\text{O})_2]$, the methylene-diphosphonate acts as a bidentate ligand and the Co^{II} ion (site symmetry $\bar{1}$) assumes an octahedral CoO_6 coordination geometry. The acid H atom of the ligand is distributed over two O atoms. In the crystal, a three-dimensional network is formed through $\text{O}-\text{H}\cdots\text{O}$ and $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds between the cations and anions.

Related literature

For related structures, see: DeLaMatter *et al.* (1973); Jurisson *et al.* (1983); Barthelet *et al.* (2002); Stahl *et al.* (2006).



Experimental

Crystal data

 $(\text{NH}_4)_2[\text{Co}(\text{CH}_4\text{O}_6\text{P}_2)_2(\text{H}_2\text{O})_2]$
 $M_r = 479.01$

 Triclinic, $P\bar{1}$
 $a = 7.455$ (5) Å

 $b = 7.560$ (5) Å

 $c = 8.035$ (5) Å

 $\alpha = 88.282$ (5)°

 $\beta = 62.450$ (5)°

 $\gamma = 71.834$ (5)°

 $V = 378.0$ (4) Å³
 $Z = 1$

 Mo $K\alpha$ radiation

 $\mu = 1.63$ mm⁻¹
 $T = 103$ K

 $0.28 \times 0.16 \times 0.11$ mm

Data collection

 Bruker SMART diffractometer
 Absorption correction: multi-scan
 (*SADABS*; Sheldrick, 1996)
 $T_{\text{min}} = 0.739$, $T_{\text{max}} = 0.830$

 8419 measured reflections
 1875 independent reflections
 1735 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.029$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.026$
 $wR(F^2) = 0.097$
 $S = 1.23$

1875 reflections

134 parameters

6 restraints

H atoms treated by a mixture of independent and constrained refinement

 $\Delta\rho_{\text{max}} = 0.58$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.48$ e Å⁻³
Table 1

Hydrogen-bond geometry (Å, °).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|-----------------------------------|------------|-------------|-------------|---------------|
| O1—H1A \cdots O5 ⁱ | 0.819 (18) | 1.99 (2) | 2.795 (3) | 166 (4) |
| O1—H1B \cdots O4 ⁱⁱ | 0.835 (19) | 1.994 (19) | 2.827 (3) | 175 (4) |
| N1—H1N \cdots O7 ⁱⁱⁱ | 0.825 (18) | 2.09 (2) | 2.892 (3) | 166 (3) |
| N1—H2N \cdots O6 | 0.825 (18) | 1.98 (2) | 2.796 (3) | 171 (4) |
| N1—H3N \cdots O3 ^{iv} | 0.821 (18) | 2.17 (2) | 2.959 (3) | 161 (3) |
| N1—H4N \cdots O3 ^v | 0.821 (18) | 2.146 (19) | 2.966 (3) | 177 (3) |
| O6—H6A \cdots O6 ^{vi} | 0.82 | 1.66 | 2.463 (4) | 165 |
| O7—H7 \cdots O4 ^{vii} | 0.82 | 1.66 | 2.435 (3) | 156 |

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

Data collection: *SMART* (Bruker, 2004); cell refinement: *SAINTE* (Bruker, 2004); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2005); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NG2665).

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supplementary materials

Acta Cryst. (2009). E65, m1394 [doi:10.1107/S1600536809042159]

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Comment

Diphosphonic acids are useful for the synthesis of metalorganic frameworks exhibiting microporous properties (Barthelet *et al.*, 2002).

The Co^{II} ion in the title complex, (NH₄)₂[Co(C₂H₈O₁₂)₂(H₂O)₂], is in a slightly distorted octahedral environment with O—Co—O bonding angles ranging from 84.72 (8) to 95.28 (8)°. All the bonding distances and angles fall within the normal range observed for complexes of this nature (DeLaMatter *et al.*, 1973; Jurisson *et al.*, 1983 and Stahl *et al.*, 2006). In the bidentate ligand, the distances of uncoordinated O atoms to their respective P atoms do not vary much with values ranging from 1.5304 (19) and 1.5469 (19) Å. This, together with the fact that the best fits of our data were obtained when a 50% positional disorder was applied to the hydrogen atoms bonded to these O atoms, probably is enough to validate the slight disorder. A three-dimensional network is provided by numerous hydrogen bonds between the oxygen atoms of the anionic species and the ammonium cations.

Experimental

CoCl₂·6H₂O (0,1696 g, 0,00071 mol) was dissolved in water (7 cm³) and heated to 70°C. The pH of the solution was 4,89 and deep pink in colour. Ammonium bicarbonate was added to raise the pH to 5,61 after which methylene diphosphonate (0,25 g, 0,00142 mol), dissolved in water (5 cm³) was added dropwise. The final pH of the solution was adjusted to 1.50 with ammonium bicarbonate. (Yield: 84.1%)

Refinement

The aliphatic H atoms were placed in geometrically idealized positions and constrained to ride on its parent atoms with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The hydroxyl H atoms were placed in geometrically idealized positions and constrained to ride on its parent atoms with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$. A 50% positional disorder was assigned to these hydrogen atoms and provided the best fits of the data. The highest electron density lies within 0.74 Å from O7.

Figures

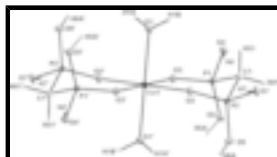


Fig. 1. View of (I) (50% probability displacement ellipsoids). The ammonium cations have been omitted for clarity.

Diammonium diaquabis(methylenediphosphonato- κ^2O,O')cobaltate(II)

Crystal data

| | |
|---|---|
| $(\text{NH}_4)_2[\text{Co}(\text{CH}_4\text{O}_6\text{P}_2)_2(\text{H}_2\text{O})_2]$ | $Z = 1$ |
| $M_r = 479.01$ | $F_{000} = 237$ |
| Triclinic, $P\bar{1}$ | $D_x = 2.069 \text{ Mg m}^{-3}$ |
| Hall symbol: -P 1 | Mo $K\alpha$ radiation, $\lambda = 0.71069 \text{ \AA}$ |
| $a = 7.455 (5) \text{ \AA}$ | Cell parameters from 4649 reflections |
| $b = 7.560 (5) \text{ \AA}$ | $\theta = 3.2\text{--}28.3^\circ$ |
| $c = 8.035 (5) \text{ \AA}$ | $\mu = 1.63 \text{ mm}^{-1}$ |
| $\alpha = 88.282 (5)^\circ$ | $T = 103 \text{ K}$ |
| $\beta = 62.450 (5)^\circ$ | Rod, pink |
| $\gamma = 71.834 (5)^\circ$ | $0.28 \times 0.16 \times 0.11 \text{ mm}$ |
| $V = 378.0 (4) \text{ \AA}^3$ | |

Data collection

| | |
|---|--|
| Bruker SMART diffractometer | 1875 independent reflections |
| Radiation source: sealed tube | 1735 reflections with $I > 2\sigma(I)$ |
| Monochromator: graphite | $R_{\text{int}} = 0.029$ |
| $T = 103 \text{ K}$ | $\theta_{\text{max}} = 28.4^\circ$ |
| φ and ω scans | $\theta_{\text{min}} = 3.2^\circ$ |
| Absorption correction: multi-scan (SADABS; Sheldrick, 1996) | $h = -9 \rightarrow 9$ |
| $T_{\text{min}} = 0.739$, $T_{\text{max}} = 0.830$ | $k = -9 \rightarrow 10$ |
| 8419 measured reflections | $l = -10 \rightarrow 9$ |

Refinement

| | |
|---------------------------------|--|
| Refinement on F^2 | 6 restraints |
| Least-squares matrix: full | H atoms treated by a mixture of independent and constrained refinement |
| $R[F^2 > 2\sigma(F^2)] = 0.026$ | $w = 1/[\sigma^2(F_o^2) + (0.0501P)^2 + 0.4031P]$ |
| $wR(F^2) = 0.097$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.23$ | $(\Delta/\sigma)_{\text{max}} < 0.001$ |
| 1875 reflections | $\Delta\rho_{\text{max}} = 0.58 \text{ e \AA}^{-3}$ |
| 134 parameters | $\Delta\rho_{\text{min}} = -0.48 \text{ e \AA}^{-3}$ |
| | Extinction correction: none |

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations

between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ | Occ. (<1) |
|-----|-------------|-------------|-------------|----------------------------------|-----------|
| Co1 | 0.5 | 0 | 1 | 0.00601 (14) | |
| P1 | 0.79673 (9) | 0.26243 (8) | 0.74506 (8) | 0.00547 (16) | |
| P2 | 0.40236 (9) | 0.26654 (8) | 0.71287 (8) | 0.00548 (15) | |
| C1 | 0.5577 (4) | 0.3956 (3) | 0.7338 (3) | 0.0069 (4) | |
| H51 | 0.4658 | 0.487 | 0.847 | 0.008* | |
| H61 | 0.5984 | 0.465 | 0.6264 | 0.008* | |
| O2 | 0.3230 (3) | 0.1616 (2) | 0.8790 (2) | 0.0082 (3) | |
| O3 | 0.7476 (3) | 0.1227 (2) | 0.8847 (2) | 0.0079 (3) | |
| O6 | 0.5476 (3) | 0.1357 (2) | 0.5238 (2) | 0.0103 (4) | |
| H6A | 0.4935 | 0.058 | 0.5191 | 0.016* | 0.5 |
| O1 | 0.3253 (3) | 0.2144 (3) | 1.2321 (2) | 0.0101 (4) | |
| N1 | 0.8609 (4) | 0.1904 (3) | 0.1800 (3) | 0.0114 (4) | |
| O7 | 0.2170 (3) | 0.4231 (2) | 0.7030 (2) | 0.0092 (3) | |
| H7 | 0.1063 | 0.3971 | 0.7569 | 0.014* | 0.5 |
| O5 | 0.9736 (3) | 0.1640 (2) | 0.5452 (2) | 0.0091 (3) | |
| H5A | 0.9708 | 0.0583 | 0.5301 | 0.014* | 0.5 |
| O4 | 0.8575 (3) | 0.4110 (2) | 0.8125 (2) | 0.0083 (3) | |
| H4 | 0.9866 | 0.3715 | 0.7787 | 0.013* | 0.5 |
| H1N | 0.860 (5) | 0.298 (3) | 0.197 (4) | 0.010 (8)* | |
| H2N | 0.779 (5) | 0.165 (6) | 0.282 (4) | 0.029 (10)* | |
| H3N | 0.984 (3) | 0.121 (4) | 0.149 (5) | 0.020 (9)* | |
| H4N | 0.829 (6) | 0.175 (5) | 0.098 (4) | 0.020 (9)* | |
| H1A | 0.233 (5) | 0.201 (5) | 1.334 (3) | 0.020 (9)* | |
| H1B | 0.274 (6) | 0.323 (3) | 1.212 (5) | 0.027 (10)* | |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|---------------|---------------|--------------|
| Co1 | 0.0060 (2) | 0.0058 (2) | 0.0061 (2) | -0.00256 (17) | -0.00242 (18) | 0.00160 (16) |
| P1 | 0.0050 (3) | 0.0051 (3) | 0.0066 (3) | -0.0025 (2) | -0.0026 (2) | 0.0016 (2) |
| P2 | 0.0056 (3) | 0.0052 (3) | 0.0062 (3) | -0.0025 (2) | -0.0028 (2) | 0.0017 (2) |
| C1 | 0.0074 (11) | 0.0060 (10) | 0.0083 (10) | -0.0026 (8) | -0.0043 (9) | 0.0013 (8) |
| O2 | 0.0077 (8) | 0.0087 (8) | 0.0093 (8) | -0.0042 (6) | -0.0043 (7) | 0.0044 (6) |
| O3 | 0.0071 (8) | 0.0083 (8) | 0.0087 (8) | -0.0038 (6) | -0.0036 (6) | 0.0034 (6) |
| O6 | 0.0115 (9) | 0.0112 (8) | 0.0081 (8) | -0.0071 (7) | -0.0023 (7) | -0.0008 (6) |
| O1 | 0.0107 (9) | 0.0075 (8) | 0.0085 (8) | -0.0032 (7) | -0.0017 (7) | 0.0011 (6) |
| N1 | 0.0107 (11) | 0.0102 (10) | 0.0108 (10) | -0.0006 (8) | -0.0051 (9) | 0.0010 (8) |
| O7 | 0.0077 (8) | 0.0076 (8) | 0.0147 (9) | -0.0033 (6) | -0.0069 (7) | 0.0055 (6) |
| O5 | 0.0086 (8) | 0.0067 (8) | 0.0083 (8) | -0.0033 (6) | -0.0006 (6) | -0.0003 (6) |
| O4 | 0.0056 (8) | 0.0087 (8) | 0.0113 (8) | -0.0026 (6) | -0.0042 (7) | 0.0002 (6) |

supplementary materials

Geometric parameters (\AA , $^\circ$)

| | | | |
|--------------------------------------|---------------|------------|-------------|
| Co1—O2 | 2.0714 (18) | P2—C1 | 1.793 (2) |
| Co1—O2 ⁱ | 2.0714 (18) | C1—H51 | 0.97 |
| Co1—O1 ⁱ | 2.102 (2) | C1—H61 | 0.97 |
| Co1—O1 | 2.102 (2) | O6—H6A | 0.82 |
| Co1—O3 ⁱ | 2.135 (2) | O1—H1A | 0.819 (18) |
| Co1—O3 | 2.135 (2) | O1—H1B | 0.835 (19) |
| P1—O3 | 1.5166 (18) | N1—H1N | 0.825 (18) |
| P1—O4 | 1.5304 (19) | N1—H2N | 0.825 (18) |
| P1—O5 | 1.5403 (19) | N1—H3N | 0.821 (18) |
| P1—C1 | 1.795 (3) | N1—H4N | 0.821 (18) |
| P2—O2 | 1.5032 (18) | O7—H7 | 0.82 |
| P2—O6 | 1.5363 (19) | O5—H5A | 0.82 |
| P2—O7 | 1.5469 (19) | O4—H4 | 0.82 |
| O2—Co1—O2 ⁱ | 180 | O2—P2—C1 | 111.74 (11) |
| O2—Co1—O1 ⁱ | 92.53 (8) | O6—P2—C1 | 106.30 (11) |
| O2 ⁱ —Co1—O1 ⁱ | 87.47 (8) | O7—P2—C1 | 102.44 (12) |
| O2—Co1—O1 | 87.47 (8) | P2—C1—P1 | 116.96 (14) |
| O2 ⁱ —Co1—O1 | 92.53 (8) | P2—C1—H51 | 108.1 |
| O1 ⁱ —Co1—O1 | 180.0000 (10) | P1—C1—H51 | 108.1 |
| O2—Co1—O3 ⁱ | 84.72 (8) | P2—C1—H61 | 108.1 |
| O2 ⁱ —Co1—O3 ⁱ | 95.28 (8) | P1—C1—H61 | 108.1 |
| O1 ⁱ —Co1—O3 ⁱ | 88.91 (8) | H51—C1—H61 | 107.3 |
| O1—Co1—O3 ⁱ | 91.09 (8) | P2—O2—Co1 | 126.71 (11) |
| O2—Co1—O3 | 95.28 (8) | P1—O3—Co1 | 133.61 (10) |
| O2 ⁱ —Co1—O3 | 84.72 (8) | P2—O6—H6A | 109.5 |
| O1 ⁱ —Co1—O3 | 91.09 (8) | Co1—O1—H1A | 121 (2) |
| O1—Co1—O3 | 88.91 (8) | Co1—O1—H1B | 117 (3) |
| O3 ⁱ —Co1—O3 | 180.00 (7) | H1A—O1—H1B | 106 (4) |
| O3—P1—O4 | 111.68 (11) | H1N—N1—H2N | 108 (4) |
| O3—P1—O5 | 111.77 (11) | H1N—N1—H3N | 105 (3) |
| O4—P1—O5 | 110.47 (11) | H2N—N1—H3N | 108 (4) |
| O3—P1—C1 | 109.61 (11) | H1N—N1—H4N | 114 (3) |
| O4—P1—C1 | 103.92 (11) | H2N—N1—H4N | 111 (4) |
| O5—P1—C1 | 109.08 (11) | H3N—N1—H4N | 110 (3) |
| O2—P2—O6 | 112.62 (11) | P2—O7—H7 | 109.5 |
| O2—P2—O7 | 112.39 (10) | P1—O5—H5A | 109.5 |
| O6—P2—O7 | 110.73 (11) | P1—O4—H4 | 109.5 |

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

Hydrogen-bond geometry (\AA , $^\circ$)

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|----------------------------------|------------|-------------|-------------|---------------|
| O1—H1A \cdots O5 ⁱⁱ | 0.819 (18) | 1.99 (2) | 2.795 (3) | 166 (4) |

| | | | | |
|----------------------------|------------|------------|-----------|---------|
| O1—H1B···O4 ⁱⁱⁱ | 0.835 (19) | 1.994 (19) | 2.827 (3) | 175 (4) |
| N1—H1N···O7 ^{iv} | 0.825 (18) | 2.09 (2) | 2.892 (3) | 166 (3) |
| N1—H2N···O6 | 0.825 (18) | 1.98 (2) | 2.796 (3) | 171 (4) |
| N1—H3N···O3 ^v | 0.821 (18) | 2.17 (2) | 2.959 (3) | 161 (3) |
| N1—H4N···O3 ^{vi} | 0.821 (18) | 2.146 (19) | 2.966 (3) | 177 (3) |
| O6—H6A···O6 ^{vii} | 0.82 | 1.66 | 2.463 (4) | 165 |
| O7—H7···O4 ^{viii} | 0.82 | 1.66 | 2.435 (3) | 156 |

Symmetry codes: (ii) $x-1, y, z+1$; (iii) $-x+1, -y+1, -z+2$; (iv) $-x+1, -y+1, -z+1$; (v) $-x+2, -y, -z+1$; (vi) $x, y, z-1$; (vii) $-x+1, -y, -z+1$; (viii) $x-1, y, z$.

Fig. 1

