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# Bis(1-ammonioethane-1,1-diyldiphosphonato-$\kappa^2O,O'$)diaquacobalt(II) nonahydrate

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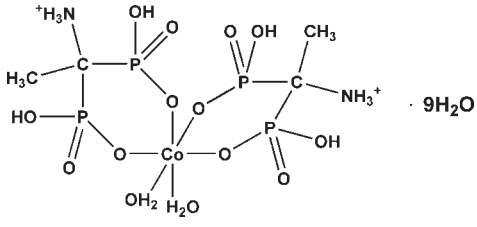
Key indicators: single-crystal X-ray study; $T$ = 173 K; mean $\sigma$(C–C) = 0.003 Å; H-atom completeness 79%; disorder in solvent or counterion; $R$ factor = 0.032; $wR$ factor = 0.090; data-to-parameter ratio = 15.6.

In the title compound, $[Co(C_2H_8NO_6P_2)_2(H_2O)_2]\cdot 9H_2O$, the $Co^{II}$ atom has a slightly distorted octahedral coordination environment consisting of four deprotonated phosphonate O atoms of two independent 1-aminoethylidendiphosphonate anions and complemented by the O atoms of two water molecules in *cis* positions. The anions exists in the zwitterionic form (protonated amino group and two deprotonated phosphonate O atoms) and constitute two six-membered chelate rings. The crystal structure also contains nine partly disordered uncoordinated water molecules, which create an extensive three-dimensional network of strong O—H···O and N—H···O hydrogen bonds.

## Related literature

For general background to organic diphosphonic acids, see: Matczak-Jon & Videnova-Adrabinska (2005). For applications of transition metal bisphosphonates, see: Eberhardt *et al.* (2005). For related structures, see: Xiang *et al.* (2007); Yin *et al.* (2005); Dudko *et al.* (2009).




## Experimental

### Crystal data

$[Co(C_2H_8NO_6P_2)_2(H_2O)_2]\cdot 9H_2O$
$M_r$ = 665.17
Monoclinic, $P2_1/c$
$a$ = 15.1925 (3) Å
$b$ = 13.2046 (2) Å
$c$ = 12.9688 (2) Å
$\beta$ = 106.0866 (11)°
$V$ = 2499.81 (7) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 1.04 mm$^{-1}$
$T$ = 173 K
0.30 × 0.24 × 0.20 mm

### Data collection

Bruker APEX-II CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
$T_{min}$ = 0.749, $T_{max}$ = 0.820
51914 measured reflections
6273 independent reflections
5626 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.030

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.090
$S$ = 1.12
6273 reflections
401 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.73 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.29 e Å$^{-3}$

**Table 1**
Selected bond lengths (Å).

| | | | |
|---|---|---|---|
| Co1—O7 | 2.0697 (14) | Co1—O14 | 2.0837 (16) |
| Co1—O13 | 2.0747 (17) | Co1—O1 | 2.1007 (15) |
| Co1—O10 | 2.0771 (15) | Co1—O4 | 2.1201 (15) |

**Table 2**
Hydrogen-bond geometry (Å, °).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N1—H11*N*···O17 | 0.86 (3) | 2.00 (3) | 2.836 (3) | 165 (3) |
| N1—H12*N*···O7 | 0.81 (3) | 1.98 (3) | 2.785 (2) | 175 (3) |
| N1—H13*N*···O15$^{i}$ | 0.85 (3) | 1.98 (3) | 2.810 (2) | 165 (3) |
| N2—H21*N*···O23*A* | 0.91 (3) | 1.94 (3) | 2.808 (4) | 159 (3) |
| N2—H22*N*···O4 | 0.90 (3) | 2.05 (3) | 2.944 (2) | 173 (3) |
| N2—H23*N*···O16 | 0.90 (3) | 1.90 (3) | 2.783 (3) | 164 (3) |
| O3—H3*O*···O6$^{ii}$ | 0.66 (3) | 1.92 (3) | 2.570 (2) | 169 (4) |
| O5—H5*O*···O2$^{i}$ | 0.76 (3) | 1.84 (3) | 2.592 (2) | 170 (3) |
| O8—H8*O*···O11$^{iii}$ | 0.70 (3) | 1.81 (3) | 2.508 (2) | 169 (3) |
| O12—H12*O*···O9$^{iv}$ | 0.83 (3) | 1.71 (3) | 2.517 (2) | 165 (3) |
| O13—H131···O6$^{ii}$ | 0.79 (3) | 1.92 (3) | 2.691 (2) | 166 (3) |
| O13—H132···O20*A* | 0.77 (3) | 1.92 (3) | 2.671 (3) | 165 (3) |
| O14—H141···O18*A*$^{v}$ | 0.82 (3) | 1.91 (3) | 2.697 (3) | 163 (3) |
| O14—H142···O9$^{iv}$ | 0.74 (3) | 1.95 (3) | 2.688 (2) | 172 (3) |
| O15—H151···O1 | 0.80 (3) | 2.01 (3) | 2.803 (2) | 177 (3) |
| O15—H152···O14 | 0.66 (3) | 2.50 (3) | 2.946 (2) | 127 (3) |
| O15—H152···O12$^{iv}$ | 0.66 (3) | 2.54 (3) | 3.049 (2) | 136 (3) |
| O16—H161···O15$^{i}$ | 0.85 (4) | 1.94 (4) | 2.788 (3) | 176 (3) |
| O16—H162···O17$^{i}$ | 0.89 (4) | 1.97 (4) | 2.844 (3) | 170 (3) |
| O17—H171···O21$^{vi}$ | 0.75 (3) | 2.14 (4) | 2.795 (3) | 147 (3) |
| O17—H172···O18*A*$^{vii}$ | 0.73 (4) | 2.13 (4) | 2.845 (3) | 167 (4) |
| O19—H191···O13 | 0.84 (4) | 2.27 (4) | 3.063 (3) | 158 (3) |
| O19—H192···O2$^{v}$ | 0.75 (4) | 2.04 (4) | 2.773 (3) | 166 (4) |
| O21—H211···O19 | 0.80 (4) | 2.05 (4) | 2.815 (3) | 162 (4) |
| O21—H212···O19$^{viii}$ | 1.00 (4) | 1.93 (4) | 2.914 (3) | 169 (3) |

Symmetry codes: (i) $x, -y+\frac{3}{2}, z-\frac{1}{2}$; (ii) $-x+1, -y+1, -z+1$; (iii) $-x, y+\frac{1}{2}, -z+\frac{1}{2}$; (iv) $-x, -y+1, -z+1$; (v) $-x+1, y-\frac{1}{2}, -z+\frac{3}{2}$; (vi) $-x+1, y+\frac{1}{2}, -z+\frac{3}{2}$; (vii) $-x+1, -y+2, -z+1$; (viii) $-x+1, -y+1, -z+2$.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *publCIF* (Westrip, 2009).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2322).

## References


Bruker (2005). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

Dudko, A., Bon, V., Kozachkova, A. & Pekhnyo, V. (2009). *Acta Cryst.* E**65**, m459.

Eberhardt, C., Schwarz, M. & Kurth, A. H. (2005). *J. Orthop. Sci.* **10**, 622–626.

Matczak-Jon, E. & Videnova-Adrabinska, V. (2005). *Coord. Chem. Rev.* **249**, 2458–2488.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Westrip, S. P. (2009). *publCIF*. In preparation.

Xiang, J., Li, M., Wu, S., Yuan, L.-J. & Sun, J. (2007). *J. Mol. Struct.* **826**, 143–149.

Yin, P., Wang, X.-C., Gao, S. & Zheng, L.-M. (2005). *J. Solid State Chem.* **178**, 1049–1053.

# supporting information

*Acta Cryst.* (2010). E**66**, m537–m538 [https://doi.org/10.1107/S1600536810013681]

## Bis(1-ammonioethane-1,1-diyldiphosphonato-$\kappa^2O,O'$)diaquacobalt(II) nonahydrate

**Vladimir V. Bon, Anatolij V. Dudko, Alexandra N. Kozachkova, Vasily I. Pekhnyo and Natalia V. Tsaryk**

### S1. Comment

Organic diphosphonic acids are potentially very powerful chelating agents used in metal extractions and are tested by the pharmaceutical industry for use as efficient drugs preventing calcification and inhibiting bone resorption (Matczak-Jon *et al.*, 2005). There is evidence that application of transition metal bisphosphonates can improve fixation of cementless metal implants by enhancing the extent of osseointegration (Eberhardt *et al.*, 2005). In this respect, a detailed structure-correlated study of the individual properties and the complex-forming driving factors is desired in order to sufficiently understand bisphosphonate physiological activities.

Several structures of $Co^{II}$ aminoethylidenediphosphonates have been reported previously (Xiang *et al.* 2007; Yin *et al.* 2005). The main difference between these structures and the title compound is the presence of two water molecules instead of a 1,10-phenanthroline ligand in the coordination environment of the transition metal ion (Xiang *et al.* 2007), leading also to a different symmetry.

The asymmetric unit of the title compound contains one molecule of the complex (Fig.1). Two 1-aminoethylidendiphosphonate anions chelate the central metal ion via two oxygen atoms from phosphonate groups forming six-membered non-planar metalla rings. Two water molecules complement the slightly distorted octahedral coordination environment of Co in *cis*-position. The Co—O bond lengths have expected values and conform with the previously reported related structures (Xiang *et al.*, 2007). The values of the O—Co—O angles are in the range from 89.23 (7)° to 91.54 (5)°. The Co1—O1—P1—C1—P2—O4 and Co1—O7—P3—C3—P4—O10 metalla cycles have an envelope conformation with the C1 and C3 atoms out of plane by 0.850 (2) Å and 0.795 (2) Å, respectively. The dihedral angle between the planar fragments Co1—O1—P1—P2—O4 and Co1—O7—P3—P4—O10 is 84.20 (3)°. The coordinated ligand molecules exists in the zwitterionic form with a proton transfer from one of the phosphonic groups to the amino group which is representative for all 1-aminodiphosphonic acids. In addition, the amino group does also not participate in coordination (Dudko *et al.* 2009).

In the crystal structure of the title compound, nine solvent water molecules are present. Such an amount of solvent molecules could be explained by the presence of two coordinated water molecules in addition to the more hydrophilic phosphonate groups. As a result, a 3-D network of mostly strong O—H···O and N—H···O hydrogen bonds is observed in the structure (Fig. 2; Table 1). Several H-bonds can not be unambiguously derived from the model because some of the crystal lattice water molecules are disordered.

## S2. Experimental

Light pink crystals of the title compound were obtained from the mixture of 10 ml ($10^{-2}$ mol/l) water solution of $Co(NO_3)_2$ with 20 ml ($10^{-2}$ mol/l) solution of 1-aminoethylidendiphosphonic acid. The combined solution was stored in a dark place for slow evaporation. After 20 days of staying, suitable crystals for X-ray data collection were obtained.

## S3. Refinement

In the crystal structure of the title compound, O atoms O18 and O20 are disordered over two sites with occupancies 0.87/0.13. Disordered O atoms O22 and O23 were treated with occupancies 0.88/0.12 and 0.71/0.29, respectively. The major component of the disordered site was refined anisotropically, the corresponding minor occupied sites were refined isotropically. Hydrogen atoms bonded to the disordered oxygen atoms could not be located from difference Fourier maps and were eventually omitted from refinement. Other H atoms bonded to N and O atoms were located in a difference map and refined freely with Uiso(H) = 1.5Ueq(N) and Uiso(H) = 1.2Ueq(O), respectively. Methyl hydrogens atoms were positioned geometrically and were refined using a riding model with C—H = 0.98 Å for $CH_3$ [Uiso(H) = 1.5Ueq(C)].

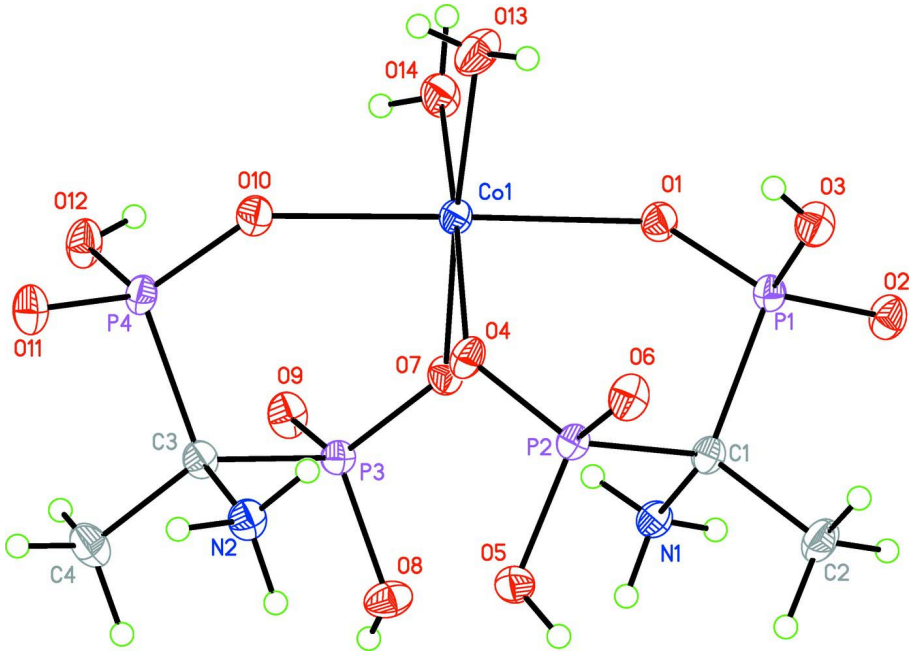



**Figure 1**

The molecular structure of title compound showing 50% probability displacement ellipsoids for the non-hydrogen atoms. Solvent water molecules are omitted for clarity.

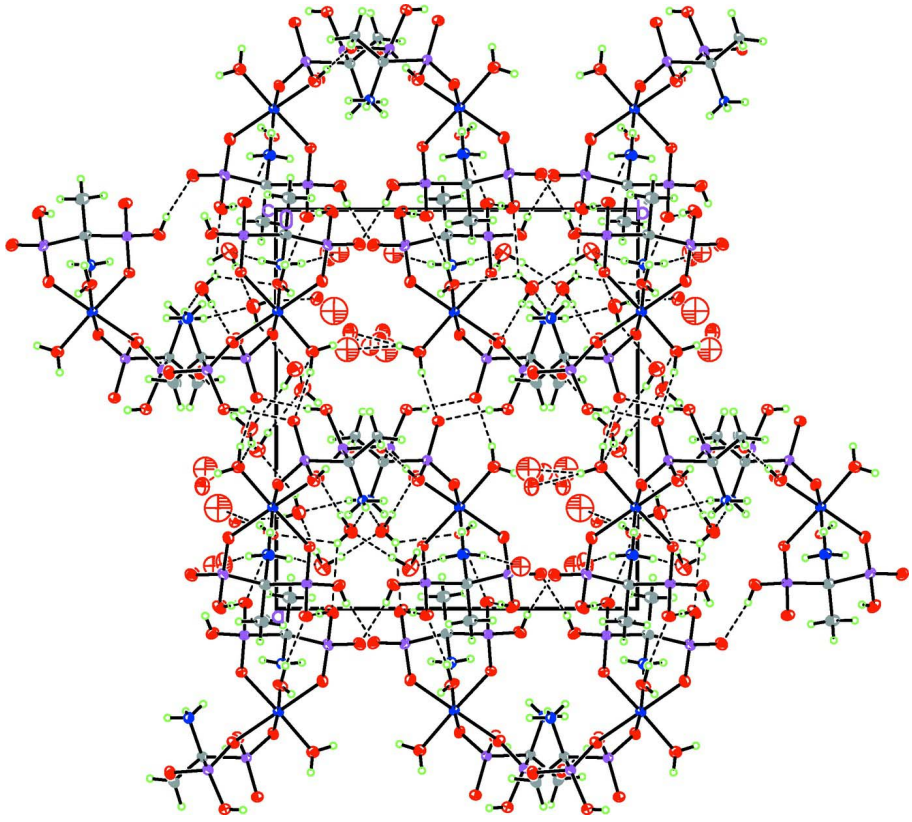


**Figure 2**

Crystal packing of title compound, in a projection along the *c* axis. Dashed lines indicate hydrogen bonds.

**Bis(1-ammonioethane-1,1-diyldiphosphonato-$\kappa^2O,O'$)diaquacobalt(II) nonahydrate**

*Crystal data*

$[Co(C_2H_8NO_6P_2)_2(H_2O)_2]\cdot 9H_2O$
$M_r = 665.17$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 15.1925\ (3)$ Å
$b = 13.2046\ (2)$ Å
$c = 12.9688\ (2)$ Å
$\beta = 106.0866\ (11)°$
$V = 2499.81\ (7)$ Å$^3$
$Z = 4$
$F(000) = 1388$
$D_x = 1.767$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 9983 reflections
$\theta = 2.3–28.4°$
$\mu = 1.04$ mm$^{-1}$
$T = 173$ K
Block, light pink
0.30 × 0.24 × 0.20 mm

*Data collection*

Bruker APEX-II CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 8.33 pixels mm$^{-1}$
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
$T_{min} = 0.749$, $T_{max} = 0.820$
51914 measured reflections
6273 independent reflections
5626 reflections with $I > 2\sigma(I)$
$R_{int} = 0.030$
$\theta_{max} = 28.4°$, $\theta_{min} = 1.4°$
$h = -19\rightarrow20$
$k = -17\rightarrow17$
$l = -17\rightarrow17$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.090$
$S = 1.12$
6273 reflections
401 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0396P)^2 + 3.3375P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.73$ e Å$^{-3}$
$\Delta\rho_{min} = -0.29$ e Å$^{-3}$

*Special details*

**Geometry**. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

**Refinement**. Refinement of $F^2$ against ALL reflections. The weighted *R*-factor wR and goodness of fit *S* are based on $F^2$, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative $F^2$. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) etc. and is not relevant to the choice of reflections for refinement. *R*-factors based on $F^2$ are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ | Occ. (<1) |
|---|---|---|---|---|---|
| Co1 | 0.255576 (18) | 0.49258 (2) | 0.52538 (2) | 0.01238 (8) | |
| P1 | 0.40125 (3) | 0.68696 (4) | 0.57579 (4) | 0.01281 (11) | |
| P2 | 0.37271 (3) | 0.58209 (4) | 0.35868 (4) | 0.01196 (11) | |
| P3 | 0.06525 (3) | 0.58713 (4) | 0.36181 (4) | 0.01226 (11) | |
| P4 | 0.08900 (3) | 0.35638 (4) | 0.36325 (4) | 0.01415 (11) | |
| C1 | 0.36957 (13) | 0.70306 (15) | 0.42887 (16) | 0.0131 (4) | |
| C2 | 0.43053 (15) | 0.78295 (17) | 0.39660 (17) | 0.0188 (4) | |
| H21C | 0.4116 | 0.7914 | 0.3185 | 0.028* | |
| H22C | 0.4946 | 0.7608 | 0.4198 | 0.028* | |
| H23C | 0.4243 | 0.8477 | 0.4309 | 0.028* | |
| C3 | 0.06352 (13) | 0.47197 (16) | 0.28100 (16) | 0.0141 (4) | |
| C4 | −0.02844 (14) | 0.46254 (19) | 0.19417 (17) | 0.0204 (4) | |
| H41C | −0.0374 | 0.5219 | 0.1470 | 0.031* | |
| H42C | −0.0784 | 0.4586 | 0.2283 | 0.031* | |
| H43C | −0.0282 | 0.4011 | 0.1518 | 0.031* | |
| N1 | 0.27212 (12) | 0.74065 (14) | 0.39596 (15) | 0.0142 (3) | |
| H11N | 0.2720 (19) | 0.799 (2) | 0.426 (2) | 0.021* | |
| H12N | 0.237 (2) | 0.701 (2) | 0.412 (2) | 0.021* | |
| H13N | 0.2560 (19) | 0.749 (2) | 0.328 (2) | 0.021* | |
| N2 | 0.13796 (12) | 0.48190 (15) | 0.22493 (15) | 0.0165 (3) | |
| H21N | 0.1347 (19) | 0.429 (2) | 0.179 (2) | 0.025* | |
| H22N | 0.193 (2) | 0.486 (2) | 0.273 (2) | 0.025* | |
| H23N | 0.128 (2) | 0.538 (2) | 0.183 (2) | 0.025* | |
| O1 | 0.33239 (10) | 0.61709 (12) | 0.60220 (11) | 0.0160 (3) | |

| | | | | | |
|---|---|---|---|---|---|
| O2 | 0.40782 (10) | 0.79109 (11) | 0.62352 (12) | 0.0181 (3) | |
| O3 | 0.49936 (10) | 0.64009 (13) | 0.60579 (13) | 0.0188 (3) | |
| H3O | 0.502 (2) | 0.590 (2) | 0.605 (2) | 0.023* | |
| O4 | 0.31168 (10) | 0.50763 (11) | 0.39358 (12) | 0.0154 (3) | |
| O5 | 0.32357 (10) | 0.60670 (12) | 0.23804 (12) | 0.0171 (3) | |
| H5O | 0.3517 (19) | 0.640 (2) | 0.211 (2) | 0.020* | |
| O6 | 0.47085 (10) | 0.55160 (12) | 0.37641 (12) | 0.0178 (3) | |
| O7 | 0.15729 (9) | 0.59446 (11) | 0.44381 (11) | 0.0151 (3) | |
| O8 | 0.06089 (11) | 0.67523 (12) | 0.28140 (13) | 0.0191 (3) | |
| H8O | 0.017 (2) | 0.695 (2) | 0.258 (2) | 0.023* | |
| O9 | −0.01614 (10) | 0.58374 (12) | 0.40569 (12) | 0.0179 (3) | |
| O10 | 0.17939 (10) | 0.37086 (11) | 0.44643 (12) | 0.0179 (3) | |
| O11 | 0.08724 (10) | 0.26901 (12) | 0.28832 (12) | 0.0195 (3) | |
| O12 | 0.00608 (11) | 0.34512 (13) | 0.41132 (13) | 0.0199 (3) | |
| H12O | 0.0100 (19) | 0.378 (2) | 0.467 (2) | 0.024* | |
| O13 | 0.35601 (12) | 0.39698 (14) | 0.61576 (15) | 0.0238 (4) | |
| H131 | 0.407 (2) | 0.403 (2) | 0.614 (2) | 0.029* | |
| H132 | 0.340 (2) | 0.341 (3) | 0.611 (2) | 0.029* | |
| O14 | 0.18902 (11) | 0.48630 (13) | 0.64577 (13) | 0.0198 (3) | |
| H141 | 0.210 (2) | 0.456 (2) | 0.702 (3) | 0.024* | |
| H142 | 0.140 (2) | 0.472 (2) | 0.630 (2) | 0.024* | |
| O15 | 0.19611 (13) | 0.70714 (14) | 0.67947 (14) | 0.0234 (4) | |
| H151 | 0.235 (2) | 0.680 (2) | 0.660 (2) | 0.028* | |
| H152 | 0.165 (2) | 0.671 (3) | 0.674 (3) | 0.028* | |
| O16 | 0.10482 (14) | 0.62776 (16) | 0.06388 (15) | 0.0310 (4) | |
| H161 | 0.130 (2) | 0.679 (3) | 0.099 (3) | 0.037* | |
| H162 | 0.143 (2) | 0.610 (3) | 0.026 (3) | 0.037* | |
| O17 | 0.24161 (13) | 0.93732 (14) | 0.46692 (16) | 0.0265 (4) | |
| H171 | 0.287 (2) | 0.949 (3) | 0.506 (3) | 0.032* | |
| H172 | 0.229 (2) | 0.979 (3) | 0.429 (3) | 0.032* | |
| O19 | 0.44927 (14) | 0.42724 (16) | 0.85539 (17) | 0.0329 (4) | |
| H191 | 0.415 (2) | 0.433 (3) | 0.793 (3) | 0.039* | |
| H192 | 0.483 (3) | 0.385 (3) | 0.866 (3) | 0.039* | |
| O21 | 0.60125 (14) | 0.55256 (16) | 0.94457 (19) | 0.0359 (4) | |
| H211 | 0.559 (3) | 0.523 (3) | 0.907 (3) | 0.043* | |
| H212 | 0.590 (2) | 0.567 (3) | 1.015 (3) | 0.043* | |
| O18A | 0.77849 (14) | 0.88751 (17) | 0.66533 (16) | 0.0234 (8) | 0.873 (11) |
| O20A | 0.3072 (2) | 0.20567 (19) | 0.6380 (3) | 0.0415 (11) | 0.869 (14) |
| O22A | 0.67469 (18) | 0.7176 (2) | 0.6366 (4) | 0.0409 (12) | 0.876 (13) |
| O23A | 0.1129 (3) | 0.3552 (6) | 0.0452 (6) | 0.0420 (16) | 0.71 (3) |
| O18B | 0.747 (3) | 0.840 (3) | 0.668 (3) | 0.101 (12)* | 0.127 (11) |
| O20B | 0.350 (3) | 0.197 (2) | 0.684 (3) | 0.076 (10)* | 0.131 (14) |
| O22B | 0.6582 (15) | 0.7397 (17) | 0.579 (3) | 0.042 (6)* | 0.124 (13) |
| O23B | 0.1074 (8) | 0.3242 (16) | 0.0717 (14) | 0.048 (3)* | 0.29 (3) |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Co1 | 0.01106 (13) | 0.01304 (14) | 0.01351 (13) | −0.00105 (9) | 0.00416 (10) | 0.00019 (10) |
| P1 | 0.0123 (2) | 0.0130 (2) | 0.0135 (2) | −0.00120 (18) | 0.00427 (18) | −0.00135 (18) |
| P2 | 0.0114 (2) | 0.0119 (2) | 0.0137 (2) | −0.00023 (17) | 0.00541 (17) | −0.00051 (18) |
| P3 | 0.0101 (2) | 0.0140 (2) | 0.0133 (2) | 0.00027 (17) | 0.00432 (17) | 0.00080 (18) |
| P4 | 0.0142 (2) | 0.0133 (2) | 0.0157 (2) | −0.00344 (18) | 0.00540 (18) | −0.00208 (19) |
| C1 | 0.0119 (8) | 0.0131 (9) | 0.0154 (9) | −0.0009 (7) | 0.0056 (7) | −0.0006 (7) |
| C2 | 0.0221 (10) | 0.0161 (10) | 0.0206 (10) | −0.0057 (8) | 0.0102 (8) | −0.0005 (8) |
| C3 | 0.0121 (8) | 0.0177 (10) | 0.0135 (8) | −0.0022 (7) | 0.0053 (7) | −0.0013 (7) |
| C4 | 0.0162 (9) | 0.0272 (12) | 0.0164 (9) | −0.0025 (8) | 0.0020 (8) | −0.0024 (9) |
| N1 | 0.0146 (8) | 0.0126 (9) | 0.0157 (8) | 0.0005 (6) | 0.0049 (6) | 0.0004 (7) |
| N2 | 0.0154 (8) | 0.0186 (9) | 0.0169 (8) | −0.0017 (7) | 0.0064 (7) | −0.0012 (7) |
| O1 | 0.0161 (7) | 0.0180 (7) | 0.0150 (7) | −0.0036 (6) | 0.0062 (5) | −0.0009 (6) |
| O2 | 0.0222 (7) | 0.0143 (7) | 0.0193 (7) | −0.0018 (6) | 0.0083 (6) | −0.0045 (6) |
| O3 | 0.0143 (7) | 0.0166 (7) | 0.0246 (8) | 0.0010 (6) | 0.0038 (6) | −0.0001 (7) |
| O4 | 0.0170 (7) | 0.0132 (7) | 0.0189 (7) | −0.0030 (5) | 0.0095 (6) | −0.0016 (5) |
| O5 | 0.0183 (7) | 0.0189 (8) | 0.0143 (7) | −0.0020 (6) | 0.0050 (5) | 0.0013 (6) |
| O6 | 0.0125 (6) | 0.0175 (7) | 0.0249 (7) | 0.0006 (6) | 0.0078 (6) | −0.0010 (6) |
| O7 | 0.0119 (6) | 0.0145 (7) | 0.0177 (7) | 0.0005 (5) | 0.0020 (5) | −0.0005 (6) |
| O8 | 0.0159 (7) | 0.0200 (8) | 0.0223 (8) | 0.0043 (6) | 0.0068 (6) | 0.0073 (6) |
| O9 | 0.0135 (7) | 0.0236 (8) | 0.0192 (7) | −0.0022 (6) | 0.0088 (6) | −0.0036 (6) |
| O10 | 0.0184 (7) | 0.0147 (7) | 0.0188 (7) | −0.0015 (6) | 0.0024 (6) | −0.0002 (6) |
| O11 | 0.0185 (7) | 0.0187 (8) | 0.0221 (7) | −0.0035 (6) | 0.0070 (6) | −0.0068 (6) |
| O12 | 0.0206 (7) | 0.0221 (8) | 0.0204 (7) | −0.0081 (6) | 0.0112 (6) | −0.0056 (6) |
| O13 | 0.0156 (7) | 0.0193 (8) | 0.0364 (9) | −0.0003 (6) | 0.0071 (7) | 0.0082 (7) |
| O14 | 0.0145 (7) | 0.0269 (9) | 0.0186 (8) | −0.0058 (6) | 0.0054 (6) | 0.0001 (6) |
| O15 | 0.0258 (9) | 0.0214 (9) | 0.0252 (8) | −0.0049 (7) | 0.0108 (7) | −0.0066 (7) |
| O16 | 0.0389 (10) | 0.0333 (10) | 0.0234 (8) | −0.0088 (8) | 0.0127 (8) | −0.0040 (8) |
| O17 | 0.0268 (9) | 0.0222 (9) | 0.0283 (9) | 0.0019 (7) | 0.0036 (7) | −0.0002 (7) |
| O19 | 0.0286 (9) | 0.0351 (11) | 0.0330 (10) | 0.0094 (8) | 0.0052 (8) | −0.0034 (8) |
| O21 | 0.0277 (10) | 0.0321 (11) | 0.0470 (12) | 0.0015 (8) | 0.0086 (9) | −0.0061 (9) |
| O18A | 0.0236 (11) | 0.0192 (12) | 0.0270 (11) | −0.0037 (8) | 0.0064 (8) | −0.0031 (8) |
| O20A | 0.0413 (19) | 0.0277 (14) | 0.055 (2) | −0.0005 (10) | 0.0119 (15) | 0.0096 (11) |
| O22A | 0.0299 (13) | 0.0307 (14) | 0.064 (3) | −0.0050 (10) | 0.0168 (13) | −0.0156 (15) |
| O23A | 0.063 (2) | 0.034 (3) | 0.032 (2) | −0.0083 (17) | 0.0194 (16) | −0.0152 (19) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Co1—O7 | 2.0697 (14) | C3—C4 | 1.537 (3) |
| Co1—O13 | 2.0747 (17) | C4—H41C | 0.9800 |
| Co1—O10 | 2.0771 (15) | C4—H42C | 0.9800 |
| Co1—O14 | 2.0837 (16) | C4—H43C | 0.9800 |
| Co1—O1 | 2.1007 (15) | N1—H11N | 0.86 (3) |
| Co1—O4 | 2.1201 (15) | N1—H12N | 0.81 (3) |
| P1—O2 | 1.4999 (15) | N1—H13N | 0.85 (3) |
| P1—O1 | 1.5039 (15) | N2—H21N | 0.91 (3) |

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|---|---|---|---|
| P1—O3 | 1.5604 (16) | N2—H22N | 0.90 (3) |
| P1—C1 | 1.844 (2) | N2—H23N | 0.90 (3) |
| P2—O6 | 1.4993 (15) | O3—H3O | 0.66 (3) |
| P2—O4 | 1.5047 (15) | O5—H5O | 0.76 (3) |
| P2—O5 | 1.5696 (15) | O8—H8O | 0.70 (3) |
| P2—C1 | 1.846 (2) | O12—H12O | 0.83 (3) |
| P3—O9 | 1.4982 (15) | O13—H131 | 0.79 (3) |
| P3—O7 | 1.5071 (14) | O13—H132 | 0.77 (3) |
| P3—O8 | 1.5515 (16) | O14—H141 | 0.82 (3) |
| P3—C3 | 1.843 (2) | O14—H142 | 0.74 (3) |
| P4—O11 | 1.5038 (16) | O15—H151 | 0.80 (3) |
| P4—O10 | 1.5050 (15) | O15—H152 | 0.66 (3) |
| P4—O12 | 1.5599 (16) | O16—H161 | 0.85 (4) |
| P4—C3 | 1.841 (2) | O16—H162 | 0.89 (4) |
| C1—N1 | 1.507 (3) | O17—H171 | 0.75 (3) |
| C1—C2 | 1.536 (3) | O17—H172 | 0.73 (4) |
| C2—H21C | 0.9800 | O19—H191 | 0.84 (4) |
| C2—H22C | 0.9800 | O19—H192 | 0.75 (4) |
| C2—H23C | 0.9800 | O21—H211 | 0.80 (4) |
| C3—N2 | 1.510 (3) | O21—H212 | 1.00 (4) |

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|---|---|---|---|
| O7—Co1—O13 | 176.20 (7) | H21C—C2—H22C | 109.5 |
| O7—Co1—O10 | 91.52 (6) | C1—C2—H23C | 109.5 |
| O13—Co1—O10 | 91.71 (7) | H21C—C2—H23C | 109.5 |
| O7—Co1—O14 | 88.73 (6) | H22C—C2—H23C | 109.5 |
| O13—Co1—O14 | 89.20 (7) | N2—C3—C4 | 107.71 (16) |
| O10—Co1—O14 | 91.08 (6) | N2—C3—P4 | 106.60 (14) |
| O7—Co1—O1 | 87.76 (6) | C4—C3—P4 | 111.09 (15) |
| O13—Co1—O1 | 89.05 (7) | N2—C3—P3 | 107.91 (14) |
| O10—Co1—O1 | 178.83 (6) | C4—C3—P3 | 110.50 (15) |
| O14—Co1—O1 | 89.83 (6) | P4—C3—P3 | 112.77 (10) |
| O7—Co1—O4 | 85.48 (6) | C3—C4—H41C | 109.5 |
| O13—Co1—O4 | 96.63 (7) | C3—C4—H42C | 109.5 |
| O10—Co1—O4 | 88.21 (6) | H41C—C4—H42C | 109.5 |
| O14—Co1—O4 | 174.14 (6) | C3—C4—H43C | 109.5 |
| O1—Co1—O4 | 90.82 (6) | H41C—C4—H43C | 109.5 |
| O2—P1—O1 | 116.06 (9) | H42C—C4—H43C | 109.5 |
| O2—P1—O3 | 108.12 (9) | C1—N1—H11N | 106.9 (18) |
| O1—P1—O3 | 112.13 (9) | C1—N1—H12N | 112 (2) |
| O2—P1—C1 | 106.81 (9) | H11N—N1—H12N | 112 (3) |
| O1—P1—C1 | 107.89 (9) | C1—N1—H13N | 108.4 (19) |
| O3—P1—C1 | 105.14 (9) | H11N—N1—H13N | 108 (3) |
| O6—P2—O4 | 116.61 (9) | H12N—N1—H13N | 109 (3) |
| O6—P2—O5 | 112.75 (9) | C3—N2—H21N | 109.5 (18) |
| O4—P2—O5 | 105.82 (9) | C3—N2—H22N | 110.4 (19) |
| O6—P2—C1 | 108.50 (9) | H21N—N2—H22N | 112 (3) |
| O4—P2—C1 | 108.35 (9) | C3—N2—H23N | 110.0 (18) |
| O5—P2—C1 | 104.02 (9) | H21N—N2—H23N | 106 (3) |

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| O9—P3—O7 | 115.85 (9) | H22N—N2—H23N | 109 (3) |
| O9—P3—O8 | 113.06 (9) | P1—O1—Co1 | 134.61 (9) |
| O7—P3—O8 | 106.53 (9) | P1—O3—H3O | 116 (3) |
| O9—P3—C3 | 107.95 (9) | P2—O4—Co1 | 136.28 (9) |
| O7—P3—C3 | 108.57 (9) | P2—O5—H5O | 114 (2) |
| O8—P3—C3 | 104.19 (9) | P3—O7—Co1 | 135.71 (9) |
| O11—P4—O10 | 114.20 (9) | P3—O8—H8O | 115 (3) |
| O11—P4—O12 | 108.26 (9) | P4—O10—Co1 | 136.45 (10) |
| O10—P4—O12 | 113.78 (9) | P4—O12—H12O | 115 (2) |
| O11—P4—C3 | 107.37 (9) | Co1—O13—H131 | 120 (2) |
| O10—P4—C3 | 108.28 (9) | Co1—O13—H132 | 112 (2) |
| O12—P4—C3 | 104.31 (9) | H131—O13—H132 | 112 (3) |
| N1—C1—C2 | 108.41 (17) | Co1—O14—H141 | 123 (2) |
| N1—C1—P1 | 106.58 (13) | Co1—O14—H142 | 117 (2) |
| C2—C1—P1 | 110.87 (14) | H141—O14—H142 | 104 (3) |
| N1—C1—P2 | 107.64 (13) | H151—O15—H152 | 102 (4) |
| C2—C1—P2 | 111.10 (14) | H161—O16—H162 | 104 (3) |
| P1—C1—P2 | 112.02 (11) | H171—O17—H172 | 109 (4) |
| C1—C2—H21C | 109.5 | H191—O19—H192 | 117 (4) |
| C1—C2—H22C | 109.5 | H211—O21—H212 | 110 (3) |

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| O2—P1—C1—N1 | −69.60 (15) | O8—P3—C3—C4 | −65.37 (16) |
| O1—P1—C1—N1 | 55.84 (15) | O9—P3—C3—P4 | −69.94 (12) |
| O3—P1—C1—N1 | 175.67 (13) | O7—P3—C3—P4 | 56.38 (12) |
| O2—P1—C1—C2 | 48.19 (16) | O8—P3—C3—P4 | 169.62 (10) |
| O1—P1—C1—C2 | 173.63 (14) | O2—P1—O1—Co1 | 152.91 (11) |
| O3—P1—C1—C2 | −66.54 (16) | O3—P1—O1—Co1 | −82.16 (14) |
| O2—P1—C1—P2 | 172.92 (9) | C1—P1—O1—Co1 | 33.15 (15) |
| O1—P1—C1—P2 | −61.64 (12) | O7—Co1—O1—P1 | −86.87 (13) |
| O3—P1—C1—P2 | 58.19 (12) | O13—Co1—O1—P1 | 95.20 (13) |
| O6—P2—C1—N1 | 171.19 (13) | O14—Co1—O1—P1 | −175.60 (13) |
| O4—P2—C1—N1 | −61.33 (15) | O4—Co1—O1—P1 | −1.42 (13) |
| O5—P2—C1—N1 | 50.94 (15) | O6—P2—O4—Co1 | 102.36 (14) |
| O6—P2—C1—C2 | 52.64 (16) | O5—P2—O4—Co1 | −131.38 (13) |
| O4—P2—C1—C2 | −179.87 (14) | C1—P2—O4—Co1 | −20.33 (16) |
| O5—P2—C1—C2 | −67.61 (15) | O7—Co1—O4—P2 | 81.31 (13) |
| O6—P2—C1—P1 | −71.96 (12) | O13—Co1—O4—P2 | −95.52 (14) |
| O4—P2—C1—P1 | 55.52 (12) | O10—Co1—O4—P2 | 172.97 (14) |
| O5—P2—C1—P1 | 167.78 (10) | O1—Co1—O4—P2 | −6.38 (14) |
| O11—P4—C3—N2 | −60.67 (15) | O9—P3—O7—Co1 | 92.63 (14) |
| O10—P4—C3—N2 | 63.09 (15) | O8—P3—O7—Co1 | −140.66 (12) |
| O12—P4—C3—N2 | −175.41 (13) | C3—P3—O7—Co1 | −28.97 (15) |
| O11—P4—C3—C4 | 56.41 (16) | O10—Co1—O7—P3 | 1.53 (13) |
| O10—P4—C3—C4 | −179.83 (14) | O14—Co1—O7—P3 | −89.51 (13) |
| O12—P4—C3—C4 | −58.34 (16) | O1—Co1—O7—P3 | −179.38 (13) |
| O11—P4—C3—P3 | −178.91 (10) | O4—Co1—O7—P3 | 89.61 (13) |
| O10—P4—C3—P3 | −55.15 (12) | O11—P4—O10—Co1 | 146.29 (12) |
| O12—P4—C3—P3 | 66.35 (12) | O12—P4—O10—Co1 | −88.72 (15) |

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| O9—P3—C3—N2 | 172.59 (13) | C3—P4—O10—Co1 | 26.74 (16) |
| O7—P3—C3—N2 | −61.09 (15) | O7—Co1—O10—P4 | −0.20 (14) |
| O8—P3—C3—N2 | 52.15 (15) | O13—Co1—O10—P4 | 177.79 (14) |
| O9—P3—C3—C4 | 55.06 (16) | O14—Co1—O10—P4 | 88.55 (14) |
| O7—P3—C3—C4 | −178.61 (14) | O4—Co1—O10—P4 | −85.63 (14) |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1—H11*N*···O17 | 0.86 (3) | 2.00 (3) | 2.836 (3) | 165 (3) |
| N1—H12*N*···O7 | 0.81 (3) | 1.98 (3) | 2.785 (2) | 175 (3) |
| N1—H13*N*···O15$^{i}$ | 0.85 (3) | 1.98 (3) | 2.810 (2) | 165 (3) |
| N2—H21*N*···O23*A* | 0.91 (3) | 1.94 (3) | 2.808 (4) | 159 (3) |
| N2—H22*N*···O4 | 0.90 (3) | 2.05 (3) | 2.944 (2) | 173 (3) |
| N2—H23*N*···O16 | 0.90 (3) | 1.90 (3) | 2.783 (3) | 164 (3) |
| O3—H3*O*···O6$^{ii}$ | 0.66 (3) | 1.92 (3) | 2.570 (2) | 169 (4) |
| O5—H5*O*···O2$^{i}$ | 0.76 (3) | 1.84 (3) | 2.592 (2) | 170 (3) |
| O8—H8*O*···O11$^{iii}$ | 0.70 (3) | 1.81 (3) | 2.508 (2) | 169 (3) |
| O12—H12*O*···O9$^{iv}$ | 0.83 (3) | 1.71 (3) | 2.517 (2) | 165 (3) |
| O13—H131···O6$^{ii}$ | 0.79 (3) | 1.92 (3) | 2.691 (2) | 166 (3) |
| O13—H132···O20*A* | 0.77 (3) | 1.92 (3) | 2.671 (3) | 165 (3) |
| O14—H141···O18*A*$^{v}$ | 0.82 (3) | 1.91 (3) | 2.697 (3) | 163 (3) |
| O14—H142···O9$^{iv}$ | 0.74 (3) | 1.95 (3) | 2.688 (2) | 172 (3) |
| O15—H151···O1 | 0.80 (3) | 2.01 (3) | 2.803 (2) | 177 (3) |
| O15—H152···O14 | 0.66 (3) | 2.50 (3) | 2.946 (2) | 127 (3) |
| O15—H152···O12$^{iv}$ | 0.66 (3) | 2.54 (3) | 3.049 (2) | 136 (3) |
| O16—H161···O15$^{i}$ | 0.85 (4) | 1.94 (4) | 2.788 (3) | 176 (3) |
| O16—H162···O17$^{i}$ | 0.89 (4) | 1.97 (4) | 2.844 (3) | 170 (3) |
| O17—H171···O21$^{vi}$ | 0.75 (3) | 2.14 (4) | 2.795 (3) | 147 (3) |
| O17—H172···O18*A*$^{vii}$ | 0.73 (4) | 2.13 (4) | 2.845 (3) | 167 (4) |
| O19—H191···O13 | 0.84 (4) | 2.27 (4) | 3.063 (3) | 158 (3) |
| O19—H192···O2$^{v}$ | 0.75 (4) | 2.04 (4) | 2.773 (3) | 166 (4) |
| O21—H211···O19 | 0.80 (4) | 2.05 (4) | 2.815 (3) | 162 (4) |
| O21—H212···O19$^{viii}$ | 1.00 (4) | 1.93 (4) | 2.914 (3) | 169 (3) |

Symmetry codes: (i) *x*, −*y*+3/2, *z*−1/2; (ii) −*x*+1, −*y*+1, −*z*+1; (iii) −*x*, *y*+1/2, −*z*+1/2; (iv) −*x*, −*y*+1, −*z*+1; (v) −*x*+1, *y*−1/2, −*z*+3/2; (vi) −*x*+1, *y*+1/2, −*z*+3/2; (vii) −*x*+1, −*y*+2, −*z*+1; (viii) −*x*+1, −*y*+1, −*z*+2.