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Bis[tris(ethylenediamine)cobalt(III)] dichlorobis[μ-(1-hydroxyethylidene)diphosphonato(4−)]diruthenium(II,III)(*Ru–Ru*) chloride trihydrate

Yang Peng, Yi-Zhi Li, Song-Song Bao and Li-Min Zheng*

Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, People's Republic of China
Correspondence e-mail: lmzheng@nju.edu.cn

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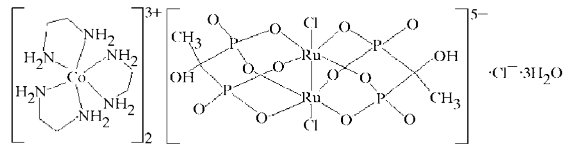
In the title compound, $[Co(C_2H_8N_2)_3]_2[Ru_2(C_2H_4O_7P_2)_2Cl_2]$-$Cl\cdot3H_2O$, the building unit contains two crystallographically independent dinuclear $[Ru_2(hedp)_2Cl_2]^{5-}$ anions, where hedp [*viz.* (1-hydroxyethylidene)diphosphonate] serves as a bis-chelating bridging ligand, two types of $[Co(en)_3]^{3+}$ cations, one uncoordinated Cl^- anion and five water molecules of crystallization. The $[Ru_2(hedp)_2Cl_2]^{5-}$ anions are connected to one another, forming one-dimensional chains along the *a* axis. The $[Co(en)_3]^{3+}$ cations are located between these chains and lie across inversion centres. An extensive series of hydrogen bonds lead to the formation of a three-dimensional supramolecular network structure, with channels generated along the [100] direction. The uncoordinated water molecules and Cl^- anions reside in these channels.

Comment

Metal phosphonates are organic–inorganic hybrid materials that are important because of their potential applications in ion exchange, sensors, catalysis and molecular recognition (Clearfield, 1998; Cao *et al.*, 1992; Zheng *et al.*, 2000; Katz *et al.*, 1991; Alberti, 1996). Although a number of new compounds have been reported, examples of ruthenium phosphonate compounds are extremely limited (Yi *et al.*, 2003; McCann *et al.*, 1993). In a previous paper (Yi *et al.*, 2003), we described the synthesis of the ruthenium–hedp compound $(NH_4)_3$-$Ru_2(hedp)_2\cdot2H_2O$ [hedp is (1-hydroxyethylidene)diphosphonate, $CH_3C(OH)(PO_3)_2$], which exhibits a novel two-dimensional structure. We present here the synthesis and structure of a new ruthenium phosphonate compound, namely $[Co(en)_3]_2$-$[Ru_2(hedp)_2Cl_2]Cl\cdot3H_2O$, (I) (en is ethylenediamine).

Compound (I) has a three-dimensional open-network structure, composed of $[Ru_2(hedp)_2Cl_2]^{5-}$ anions and $[Co(en)_3]^{3+}$ cations. As shown in Fig. 1, there are two crystallographically independent Ru atoms, each having a distorted octahedral environment, with the four basal positions occupied by phosphonate O atoms from two equivalent hedp ligands (O3, O6, O2*A* and O4*A* for atom Ru1, and O9, O12, O8*B* and O13*B* for atom Ru2; see Fig. 1 for symmetry codes). The Ru—O bond distances range from 1.997 (3) to 2.051 (3) Å and the O—Ru—O bond angles range from 88.34 (13) to 92.24 (13)° for *cis* angles and from 174.93 (13) to 176.82 (12)° for *trans* angles. One of the axial positions in each Ru octahedron is occupied by a Cl^- anion and the other site is filled by the equivalent Ru atom. The Ru1—Cl1 and Ru2—Cl2 bond distances are 2.5997 (13) and 2.5525 (13) Å, respectively. Each hedp group serves as a bis-chelating bridging ligand, linking the two equivalent Ru atoms *via* four phosphonate O atoms, thus forming $[Ru_2(hedp)_2Cl_2]^{5-}$ dimers. The remaining two phosphonate O atoms are pendent. The Ru1—Ru1*A* and Ru2—Ru2*B* bond distances are 2.3587 (8) and 2.3786 (8) Å, respectively. These values are in agreement with those reported for $(NH_4)_3Ru_2(hedp)_2\cdot2H_2O$. Inversion centers are located at the mid-points of the Ru1—Ru1*A* and Ru2—Ru2*A* bonds.



(I)

The diruthenium units, $Ru1_2$ and $Ru2_2$, are each linked to their equivalents *via* O···O hydrogen bonds [O7—H7*E*···O5^{vii} = 2.717 (5) Å for $Ru1_2$ and O14—H14*D*···O11^{viii} = 2.679 (5) Å for $Ru2_2$; symmetry codes: (vii) $-x, 1-y, 2-z$; (viii) $1-x, -y, 1-z$; Table 1], forming two types of chains along the *a* axis (Fig. 2). These chains are separated by $[Co(en)_3]^{3+}$ cations. An extensive series of intermolecular hydrogen bonds [N3—H3*C*···O2^{i} = 3.006 (5) Å, N6—H6*C*···O6^{ii} = 3.040 (5) Å, N6—H6*C*···O2^{i} = 2.872 (5) Å, N8—H8*C*···O3^{iv} = 2.906 (5) Å, N9—H9*C*···O7^{iv} = 2.978 (5) Å,

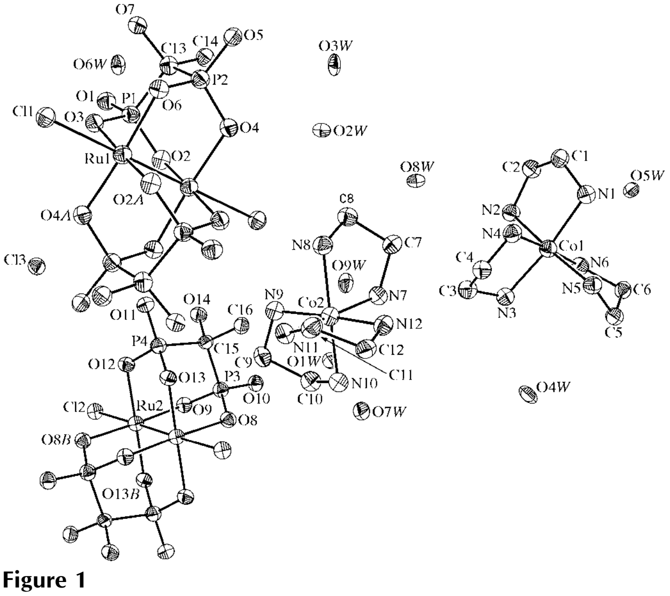


Figure 1
The molecular structure of (I), with the atomic labeling scheme. H atoms have been omitted for clarity. Atoms labeled with the suffixes *A* and *B* are at the symmetry positions $(1-x, 1-y, 2-z)$ and $(2-x, -y, 1-z)$, respectively.

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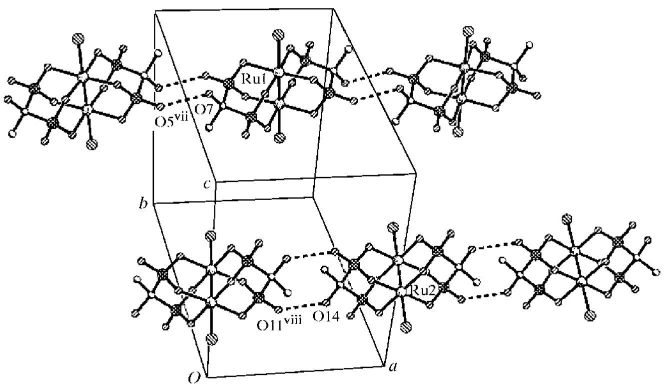

Figure 2
Two types of diruthenium phosphonate chains in (I), viewed along the [100] direction. All H atoms, water molecules and hydrogen bonds, except for the N—H···O and O—H···O bonds, have been omitted for clarity. [Symmetry codes: (vii) $-x, 1-y, 2-z$; (viii) $1-x, -y, 1-z$.]

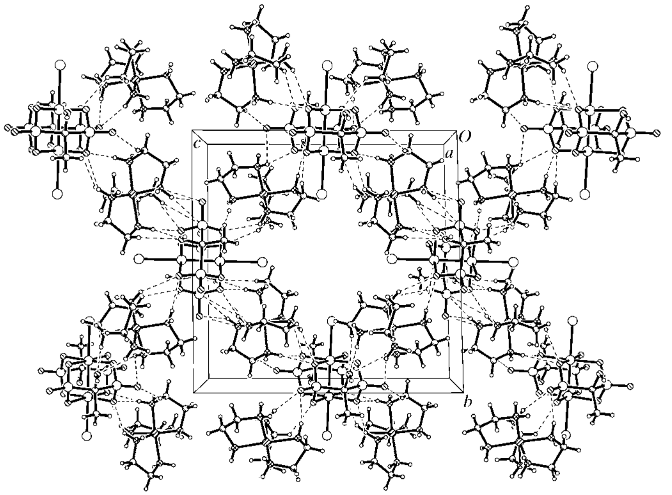

Figure 3
Packing diagram of (I). All H atoms, water molecules and hydrogen bonds, except for the N—H···O bonds, have been omitted for clarity.

N9—H9*C*···O3^{iv} = 3.052 (5) Å and N11—H11*C*···O1^{iv} = 2.955 (5) Å for Ru1$_2$, and N1—H1*C*···O11^{i} = 3.001 (5) Å and N10—H10*C*···O8^{v} = 2.967 (5) Å for Ru2$_2$; symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $x, y, z-1$; (iv) $1-x, 1-y, 2-z$; (v) $2-x, 1-y, 1-z$] leads to the formation of a three-dimensional supramolecular open-network structure, with channels generated along the [100] direction (Fig. 3). The uncoordinated water molecules and chloride anions reside within these channels. Although each $[Co(en)_3]^{3+}$ ion is chiral, the overall structure of (I) is not chiral because each $[Co(en)_3]^{3+}$ ion is centrosymmetrically related to its equivalent.

Experimental

$(NH_4)_3[Ru_2\{CH_3C(OH)(PO_3)_2\}_2]\cdot 2H_2O$ was synthesized according to the method described by Yi *et al.* (2003). A mixture of $(NH_4)_3[Ru_2(hedp)_2]\cdot 2H_2O$ (0.0634 g, 0.089 mmol), $Co(en)_3Cl_3\cdot 3H_2O$ (2.0231 g, 5.1 mmol) and water (10 ml) was stirred at 343 K for 5 h. The filtrate was kept at room temperature for 30 d, after which time brown column-like single crystals were collected as monophasic material. Analysis calculated for (I): C 15.29, N 13.37%; found: C 14.61, N 12.32%. IR (KBr, cm^{-1}): 3.507 (*s*, *br*), 3440 (*s*, *br*), 3212 (*s*, *br*), 2362 (*w*), 1612 (*m*), 1579 (*s*), 1463 (*s*), 1365 (*m*), 1326 (*m*), 1155 (*s*), 1057 (*s*), 963 (*s*), 903 (*s*), 815 (*m*), 776 (*w*), 583 (*s*), 487 (*s*), 439 (*m*).

Crystal data

$[Co(C_2H_8N_2)_3]_2[Ru_2(C_2H_4O_7P_2)_2Cl_2]Cl\cdot 3H_2O$
$M_r = 1245.01$
Triclinic, $P\bar{1}$
$a = 10.5166\ (16)$ Å
$b = 15.297\ (2)$ Å
$c = 15.497\ (2)$ Å
$\alpha = 90.788\ (3)°$
$\beta = 91.362\ (4)°$
$\gamma = 96.273\ (3)°$
$V = 2477.2\ (6)$ Å^3
$Z = 2$
$D_x = 1.669$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1000 reflections
$\theta = 2.3$–$19.8°$
$\mu = 1.61$ mm^{-1}
$T = 293\ (2)$ K
Prism, brown
0.3 × 0.2 × 0.2 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{min} = 0.69$, $T_{max} = 0.72$
12 440 measured reflections
8573 independent reflections
6430 reflections with $I > 2\sigma(I)$
$R_{int} = 0.047$
$\theta_{max} = 25.0°$
$h = -12 \rightarrow 6$
$k = -18 \rightarrow 18$
$l = -17 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.109$
$S = 1.09$
8573 reflections
559 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.06P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.39$ e Å^{-3}
$\Delta\rho_{min} = -0.37$ e Å^{-3}

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*C*···O11^{i}	0.90	2.13	3.001 (5)	162
N2—H2*C*···O6^{ii}	0.90	2.48	3.282 (5)	148
N3—H3*C*···Cl1^{ii}	0.90	2.40	3.197 (4)	148
N3—H3*C*···O2^{i}	0.90	2.38	3.006 (5)	127
N4—H4*C*···O11^{i}	0.90	2.24	3.079 (5)	154
N5—H5*C*···Cl3^{i}	0.90	2.54	3.320 (4)	146
N6—H6*C*···O2^{i}	0.90	1.99	2.872 (5)	167
N6—H6*C*···O6^{ii}	0.90	2.54	3.040 (5)	116
N6—H6*D*···O5*W*	0.90	2.19	2.999 (14)	150
N7—H7*C*···O12^{iii}	0.90	2.37	3.161 (5)	147
N7—H7*D*···O9*W*	0.90	2.19	3.062 (13)	162
N8—H8*C*···O3^{iv}	0.90	2.03	2.906 (5)	164
N8—H8*D*···Cl3^{iii}	0.90	2.33	3.193 (4)	160
N9—H9*C*···O3^{iv}	0.90	2.33	3.052 (5)	137
N9—H9*C*···O7^{iv}	0.90	2.22	2.978 (5)	141
N9—H9*D*···Cl1^{iv}	0.90	2.52	3.297 (4)	146
N10—H10*C*···Cl2^{iii}	0.90	2.56	3.323 (4)	143
N10—H10*D*···O3*W*^{vi}	0.90	2.24	3.032 (12)	147
N11—H11*C*···O1^{iv}	0.90	2.13	2.955 (5)	151
N11—H11*D*···O3*W*^{vi}	0.90	2.18	3.071 (14)	169
N12—H12*C*···O8^{v}	0.90	2.30	3.106 (5)	148
N12—H12*D*···Cl3^{iii}	0.90	2.54	3.341 (4)	149
O1*W*—H1*WA*···O10	0.85	1.86	2.663 (4)	157
O1*W*—H1*WB*···Cl3^{viii}	0.85	2.28	3.078 (4)	157
O2*W*—H2*WB*···O7*W*^{i}	0.85	2.46	3.268 (19)	159
O3*W*—H3*WD*···O2*W*	0.85	2.23	3.081 (18)	174
O4*W*—H4*WA*···O6*W*^{i}	0.85	1.97	2.773 (19)	157
O4*W*—H4*WC*···O9^{iii}	0.85	1.59	2.429 (15)	169
O6*W*—H6*WC*···O4*W*^{i}	0.85	1.98	2.773 (19)	156
O7—H7*E*···O5^{vii}	0.82	1.91	2.717 (5)	167
O9*W*—H9*WD*···Cl1^{iv}	0.85	2.57	3.270 (12)	140
O14—H14*D*···O11^{viii}	0.82	1.94	2.679 (5)	150

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

All H atoms were positioned geometrically and refined as riding, with U_{iso} values of 1.2–1.5 times U_{eq} of the parent atom, and C—H distances of 0.96 and 0.97 Å, N—H distances of 0.90 Å and O—H distances of 0.82–1.17 Å.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1174). Services for accessing these data are described at the back of the journal.

References

Alberti, G. (1996). In *Comprehensive Supramolecular Chemistry*, edited by J. M. Lehn, Vol. 7. Oxford: Pergamon.

Bruker (2000). *SMART*, *SAINT*, *SHELXTL*, *XPREP* and *XP*. Bruker AXS Inc., Madison, Wisconsin, USA.

Cao, G., Hong, H.-G. & Mallouk, T. E. (1992). *Acc. Chem. Res.* **25**, 420–427.

Clearfield, A. (1998). *Prog. Inorg. Chem.* **47**, 371–510.

Katz, H. E., Scheller, G., Putvinski, T. M., Schilling, M. L., Wilson, W. L. & Chidsey, C. E. D. (1991). *Science*, **254**, 1485–1486.

McCann, M., Murphy, E., Cardin, C. & Convery, M. (1993). *Polyhedron*, **12**, 1725–1729.

Yi, X.-Y., Zheng, L.-M., Xu, W. & Feng, S. (2003). *Inorg. Chem.* **42**, 2847–2829.

Zheng, L.-M., Song, H.-H. & Xin, X.-Q. (2000). *Comments Inorg. Chem.* **22**, 129–149.