metal-organic compounds

A bicapped trigonal–prismatic lead complex: catena-poly[[[aquabis(1,10-phenanthroline-κ^2N,N')lead(II)]-μ-squarato-κO^1:κ^2O^2,O^3] dihydrate]

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The asymmetric unit of the title compound, {[Pb(C$_4$O$_4$)-(C$_{12}$H$_8$N$_2$)$_2$(H$_2$O)]·2H$_2$O}$_n$, contains one squarate dianion, two phenanthroline (phen) ligands and one aqua ligand all coordinated to Pb, and two solvent water molecules. The eight-coordinate Pb metal ion displays a distorted bicapped trigonal–prismatic coordination environment, defined by three squarate O atoms, four N atoms from two chelating phen ligands and one O atom from the coordinated water molecule. The crystal structure contains chains of squarate-1,2,3-bridged Pb^{II} ions running in the [010] direction. These polymeric chains are linked to one another via offset face-to-face π–π interactions between the phen ligands, which lead to a two-dimensional network extending along the (001) plane. The crystal structure is also stabilized by O—H···O intermolecular hydrogen-bond interactions, forming a three-dimensional network.

Comment

Increasing attention has been devoted to the study of the coordination chemistry of the squarate ligand, C$_4$O$_4^{2-}$, by both inorganic and bioinorganic chemists during the past few years (van Ooijen et al., 1978; Reinprecht et al., 1980; Yufit et al., 1999). Squarate acts as a bridge between two or more metal atoms in mono- or polydentate coordination modes when acting as a ligand towards first row transition metal ions (Trombe et al., 2002; Millet et al., 2003). It coordinates to Fe^{II}, Fe^{III}, Ni^{II} and Cu^{II} complexes in a μ-1,3 fashion, giving binuclear (Bernardinelli et al., 1989) and chain structures (Lee et al., 1996), whereas the μ-1,2 coordination mode has been reported for binuclear and chain complexes of Cu^{II} and Pd^{II} (Castro et al., 1997; Crispini et al., 2000). It is also observed that the squarate anion, with Cu^{II} and Ni^{II}, acts as a tetra-monodentate ligand and forms polynuclear compounds (Castro et al., 1995). The chelating and bis-chelating coordination modes are only possible in complexes with larger metal

ions, such as alkaline and rare-earth cations (Lisnard et al., 2003; Modec et al., 2003). In all the cases reported so far, metal–squarate complexes have been found interesting in terms of the structural relationships between their respective solid-state architectures.

(I)
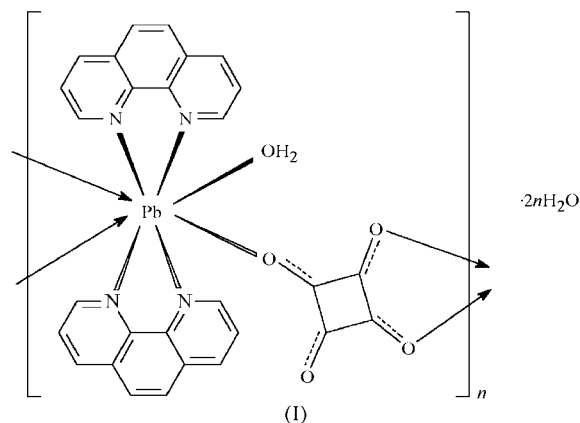
On the other hand, Pb^{II} compounds have been increasingly studied owing to their possible applications in different fields, especially in environmental protection, because of the toxicity of lead, and in biological systems, for the diverse interactions of lead with biological molecules. In Pb^{II}, lanthanide and actinide compounds, the coordination number eight is most commonly found (Oldham et al., 2002; Fan et al., 2003; Gao et al., 2005). For eight-coordination, there are three main structure types, viz. (i) cubic, (ii) square antiprismatic and (iii) dodecahedral, the last two of which are preferred for molecules. Geometry (iii) is observed in the title compound, (I). In our ongoing research on squaric acid, we have synthesized some mixed-ligand metal(II) complexes of squaric acid, and their structures have been reported. In these compounds,
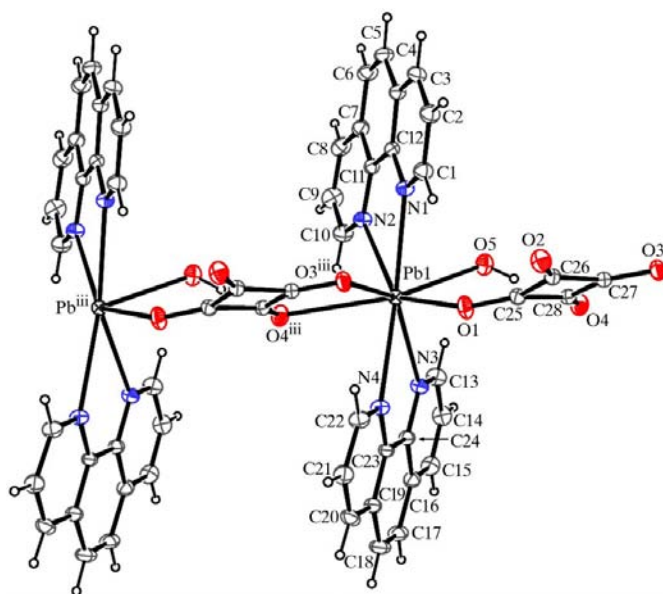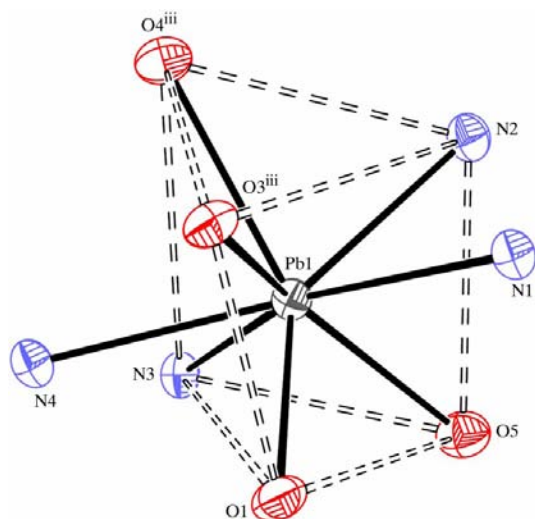

Figure 1
A view of the Pb^{II} coordination in (I), shown with 30% probability displacement ellipsoids and arbitrary spheres for the H atoms. The water molecules have been omitted for clarity. [Symmetry code: (iii) x, $y - 1$, z.]

squaric acid behaves as a monodentate ligand (Bulut *et al.*, 2004; Uçar *et al.*, 2005), while in (I), it acts as both a mono-dentate and a bidentate ligand.

A view of the molecule of (I) and its atom-numbering scheme are shown in Fig. 1. The Pb^{II} ion is an eight-coordinate environment, defined by four O atoms from squarate and aqua ligands, and four N atoms from two chelating 1,10-phenan-throline (phen) ligands. Although the coordination geometry around the Pb^{II} ion is irregular, presumably as a result of the steric constraints arising from the shape of the ligands, it can be described as a distorted bicapped trigonal prism (Fig. 2).

In the bicapped trigonal prism, the O1/O5/N3 and O3[iii]/O4[iii]/N2 triangular planes form the bases; the dihedral angle between these planes is 21.49 (17)°. The rectangular faces, O1/O3[iii]/O4[iii]/N3 (plane 1), O1/O3[iii]/N2/O5 (plane 2) and N2/O4[iii]/N3/O5 (plane 3), are almost planar, with r.m.s. deviations of 0.1167, 0.0160 and 0.4530 Å, respectively; the maximum deviations from these planes are, respectively, 0.148 (2) for atom O3[iii], 0.019 (2) for atom O1 and 0.516 (2) Å for atom N2. The dihedral angles between these least-squares planes are 50.88 (8)° between planes 1 and 2, 61.23 (10)° between planes 2 and 3, and 68.18 (9)° between planes 1 and 3. The dihedral angles between plane 1 and the nearly parallel triangular bases are 76.41 (10) and 68.19 (9)°. From the bond angles (see Table 1), it is suggested that four O atoms form the equatorial plane (O1/O3[iii]/O4[iii]/O5) of the bicapped trigonal prism, while the N1/N2 and N3/N4 atom pairs occupy the pseudo-axial positions. The capped Pb1—N4 and Pb1—N1 distances [2.821 (4) and 2.699 (3) Å] are the longest and shortest of the Pb—N bond distances, respectively, while the other Pb—N distances are in the range 2.772 (4)–2.799 (3) Å. The Pb—O bond distances range from 2.436 (3) to 2.869 (4) Å. These bond distances are in agreement with those observed in other Pb^{II} complexes (Furutachi *et al.*, 2000; Li *et al.*, 2004; Dale *et al.*, 2004; Xiao *et al.*, 2004).

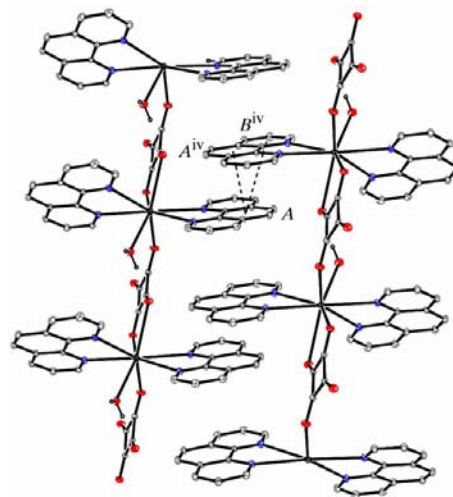In the crystal structure, the squarate dianion adopts a bridging position between the Pb^{II} atoms, coordinating *via* three of its O atoms in a μ-1,2,3 fashion, forming 'zigzag' chains in the direction of the crystallographic *b* axis (Figs. 3 and 4). The squarate dianion coordinates to one Pb^{II} ion as a bidentate ligand (*via* atoms O3 and O4), forming a five-membered chelate ring, while it coordinates to another Pb^{II} ion as a monodentate ligand (*via* O1). The O3—C27—C28—O4 torsion angle is 3.0 (7)°, while the O2—C26—C25—O1 angle is 4.4 (8)°. The O3···O4 distance in the five-membered squarate chelate ring is 3.107 (5) Å, whereas the distance between other squarate O atoms, *viz.* the monodentate squarate O1 and uncoordinated O2 atoms, is 3.183 (5) Å. The phen ligands are approximately planar, with r.m.s. deviations of 0.0427 and 0.0141 Å for N1/N2/C1–C12 and N3/N4/C13–C24, respectively. The dihedral angles between the squarate plane and the phen mean planes are 85.31 (8) and 69.79 (9)°, while that between the phen mean planes is 40.29 (5)°.

The crystal packing of (I) is formed *via* intermolecular hydrogen bonding (Fig. 3) and strong π–π interactions (Fig. 4). The two solvent water molecules, the aqua ligand, and squarate atoms O2 and O3 are involved in interchain hydrogen bonding (see Table 2 for details). The one-dimensional poly-
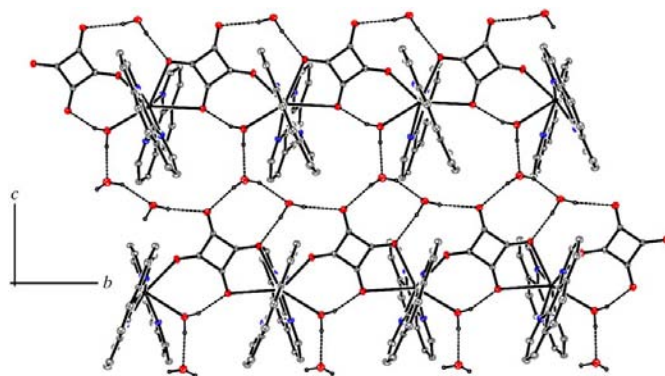
Figure 3
The zigzag chain structure of the title Pb^{II} complex, with intra- and interchain interactions indicated by dashed lines.

Figure 2
A detail of (I), illustrating the bicapped trigonal–prismatic geometry of the Pb atom. [Symmetry code: (iii) *x*, *y* − 1, *z*.]

Figure 4
The extended two-dimensional structure of (I); the interchain offset face-to-face π–π interactions are indicated by dashed lines. [Symmetry code: (iv) −*x* + 1, −*y*, −*z* + 2.]

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meric chains are also linked together *via* offset face-to-face π–π interactions between the phen ligands, which lead to a two-dimensional network extending along the (001) plane (Fig. 4). These intermolecular interactions occur between two symmetry-related phen rings (ring *A*; C16–C19/C23/C24). Ring *A* is oriented in such a way that the perpendicular distance from *A* to *A*^{iv} is 3.423 Å, the closest interatomic distance being C17$\cdots$C24^{iv} [3.427 (7) Å; symmetry code: (iv) $-x + 1, -y, -z + 2$]; the distance between the ring centroids is 3.766 (4) Å. The other π–π contact occurs between phen rings *A* and *B* (C13–C16/C24/N3). The perpendicular distance between rings *A* and *B*^{iv} (*B*^{iv} to *A*) is 3.423 Å, the closest interatomic distance is C15$\cdots$C19^{iv} [3.421 (7) Å], and the dihedral angle between the planes of these rings is 0.37 (17)°. The distance between the ring centroids is 3.635 (4) Å. The shortest interchain Pb$\cdots$Pb distance is 9.946 (3) Å for Pb1$\cdots$Pb1($x, -y + \frac{1}{2}, z - \frac{1}{2}$), whereas the intrachain equivalent is 7.2746 (3) Å for Pb1$\cdots$Pb1($x, -1 + y, z$).

Experimental

Squaric acid (0.57 g, 5 mmol) dissolved in water (25 ml) was neutralized with NaOH (0.40 g, 10 mmol) and the mixture was added to a hot solution of Pb(NO$_3$)$_2$·2H$_2$O (1.83 g, 5 mmol) dissolved in water (50 ml). The mixture was stirred at 333 K for 12 h and then cooled to room temperature. The white crystals of PbSq·2H$_2$O that formed were filtered off, washed with water and alcohol, and dried in a vacuum. A solution of 1,10-phenanthroline (0.36 g, 2 mmol) in methanol (50 ml) was added dropwise with stirring to a suspension of PbSq·2H$_2$O (0.35 g, 1 mmol) in water (50 ml). The resulting white solution was refluxed for about 2 h and then cooled to room temperature. A few days later, well formed white crystals were selected for X-ray studies.

Crystal data

[Pb(C$_4$O$_4$)(C$_{12}$H$_8$N$_2$)$_2$(H$_2$O)]·2H$_2$O	$D_x = 1.896$ Mg m^{-3}
$M_r = 733.70$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 5847
$a = 18.5438$ (10) Å	reflections
$b = 7.2746$ (3) Å	$\theta = 1.8$–27.1°
$c = 19.8774$ (11) Å	$\mu = 6.62$ mm^{-1}
$\beta = 106.578$ (4)°	$T = 297$ (2) K
$V = 2570.0$ (2) Å^3	Prism, white
$Z = 4$	$0.23 \times 0.21 \times 0.16$ mm

Data collection

Stoe IPDS-II diffractometer	4842 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.066$
Absorption correction: integration	$\theta_{max} = 27.1°$
(*X-RED32*; Stoe & Cie, 2002)	$h = -23 \rightarrow 23$
$T_{min} = 0.255$, $T_{max} = 0.666$	$k = -9 \rightarrow 9$
39366 measured reflections	$l = -25 \rightarrow 25$
5638 independent reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0451P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.027$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.068$	$(\Delta/\sigma)_{max} = 0.006$
$S = 1.02$	$\Delta\rho_{max} = 1.33$ e Å^{-3}
5638 reflections	$\Delta\rho_{min} = -1.21$ e Å^{-3}
386 parameters	Extinction correction: *SHELXL97*
H atoms treated by a mixture of independent and constrained refinement	Extinction coefficient: 0.00113 (11)

Table 1
Selected geometric parameters (Å, °).

N1—Pb1	2.699 (3)	O1—Pb1	2.436 (3)
N2—Pb1	2.772 (4)	O3—Pb1^i	2.623 (3)
N3—Pb1	2.799 (3)	O4—Pb1^i	2.869 (4)
N4—Pb1	2.821 (4)	O5—Pb1	2.675 (3)
O1—Pb1—O5	80.41 (11)	N1—Pb1—N2	60.40 (10)
O1—Pb1—N1	82.01 (11)	O1—Pb1—N3	101.61 (11)
O5—Pb1—N1	75.94 (10)	O5—Pb1—N3	77.52 (10)
O1—Pb1—N2	138.21 (10)	N1—Pb1—N3	152.20 (11)
O5—Pb1—N2	73.66 (11)	N2—Pb1—N3	104.00 (10)

Symmetry code: (i) $x, y + 1, z$.

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

D—H$\cdots$$A$	D—H	H$\cdots$$A$	$D$$\cdots$$A$	D—H$\cdots$$A$
O5—H5$A$$\cdots$O4	0.83 (3)	2.00 (3)	2.792 (5)	161 (5)
O5—H5$B$$\cdots$O6	0.85 (3)	1.97 (3)	2.817 (5)	176 (5)
O6—H6$A$$\cdots$O2^{ii}	0.80 (3)	2.09 (3)	2.878 (5)	168 (7)
O6—H6$B$$\cdots$O7^v	0.83 (3)	2.11 (4)	2.887 (5)	156 (7)
O7—H7$A$$\cdots$O3^{iii}	0.84 (3)	1.96 (3)	2.800 (5)	173 (5)
O7—H7$B$$\cdots$O2	0.82 (3)	2.15 (3)	2.947 (6)	166 (5)

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

H atoms attached to C atoms were placed at calculated positions (C—H = 0.93 Å) and were allowed for as riding atoms [U_{iso}(H) = 1.2U_{eq}(C)]. The remaining H atoms were located in a difference map and were refined with the O—H and H$\cdots$H distances restrained to 0.85 (3) and 1.35 (3) Å, respectively. The highest peak and deepest hole in the final difference map were located 1.00 and 0.73 Å, respectively, from atom Pb1.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

References

Bernardinelli, G., Deguenon, D., Soules, R. & Castan, P. (1989). *Can. J. Chem.* **67**, 1158–1165.
Bulut, B., Uçar, I., Yeşilel, O. Z., Içbudak, H., Ölmez, H. & Büyükgüngör, O. (2004). *Acta Cryst.* **C60**, m526–m528.
Castro, I., Calatayud, M. L., Sletten, J., Lloret, F. & Julve, M. (1997). *J. Chem. Soc. Dalton Trans.* pp. 811–817.
Castro, I., Sletten, J., Calatayud, M. L., Julve, M., Cano, J., Lloret, F. & Caneschi, A. (1995). *Inorg. Chem.* **34**, 4903–4909.
Crispini, A., Pucci, D., Aiello, I. & Ghedini, M. (2000). *Inorg. Chim. Acta*, **304**, 219–223.
Dale, S. H., Elsegood, M. R. J. & Kainth, S. (2004). *Acta Cryst.* **C60**, m76–m78.
Fan, J., Shu, M. H., Okamura, T., Li, Y. Z., Sun, W. Z., Tang, W. X & Ueyama, N. (2003). *New J. Chem.* **27**, 1307–1306.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Furutachi, H., Fujinami, S. & Okawa, H. (2000). *J. Chem. Soc. Dalton Trans.* pp. 2761–2769.

Gao, S., Zhu, Z. B., Huo, L. H. & Ng, S. W. (2005). *Acta Cryst.* E**61**, m528–m530.

Lee, R. R., Wang, C. C. & Wang, Y. (1996). *Acta Cryst.* B**52**, 966–975.

Li, J. F., Zhao, Y. J., Li, X. H. & Hu, M. L. (2004). *Acta Cryst.* E**60**, m1210–m1212.

Lisnard, L., Mialane, P., Dolbecq, A., Marrot, J. & Secheresse, F. (2003). *Inorg. Chem. Commun.* **6**, 503–505.

Millet, P., Sabadié, L., Galy, J. & Trombe, J. C. (2003). *J. Solid State Chem.* **173**, 49–53.

Modec, B., Brencic, J. V., Burkholder, E. M. & Zubieta, J. (2003). *Dalton Trans.* pp. 4618–4625.

Oldham, W. J., Scott, B. L., Abney, K. D., Smith, W. H. & Costa, D. A. (2002). *Acta Cryst.* C**58**, m139–m140.

Ooijen, J. A. C. van, Reedijk, J. & Spek, A. L. (1978). *Inorg. Chem.* **18**, 1184–1189.

Reinprecht, J. T., Miller, J. G., Vogel, G. C., Haddad, M. S. & Hendrikson, D. N. (1980). *Inorg. Chem.* **19**, 927–931.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Stoe & Cie (2002). *X-AREA* (Version 1.18) and *X-RED32* (Version 1.04). Stoe & Cie, Darmstadt, Germany.

Trombe, J. C., Sabadie, L. & Milet, P. (2002). *Solid State Sci.* **4**, 1209–1212.

Uçar, I., Bulut, A. & Büyükgüngör, O. (2005). *Acta Cryst.* C**61**, m218–m220.

Xiao, H.-P., Zhu, N.-W. & Hu, M.-L. (2004). *Acta Cryst.* E**60**, m800–m801.

Yufit, D. S., Price, D. J., Howard, J. A. K., Gutchke, S. O. H., Powell, A. K. & Wood, P. T. (1999). *Chem. Commun.* pp. 1561–1562.