C3*B*—H3*B*···N6	2.709 (6)	3.706 (6)	142.27 (12)
C3*C*—H3*C*···N7	2.916 (6)	3.731 (6)	143.11 (11)
C3*A*—H3*A*···N8	3.030 (6)	3.614 (6)	136.54 (11)

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

H atoms were located in a difference synthesis and refined with a riding model and with $U_{iso}(H) = 1.2U_{eq}$(C or O).

Data collection: *XSCANS* (Siemens, 1993). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990*a*). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1990*b*). Software used to prepare material for publication: *SHELXTL/PC*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1210). Services for accessing these data are described at the back of the journal.

References

Aakeröy, C. B. & Seddon, K. R. (1993). *Chem. Soc. Rev.* **22**, 397–407.
Blandamer, M. J., Burgess, J. & Shraydeh, B. (1993). *J. Chem. Soc. Faraday Trans.* **89**, 531–533.
Blundell, N. J., Burgess, J. & Hubbard, C. J. (1989). *Inorg. Chim. Acta*, **155**, 165–171.
Brewer, K. J., Murphy, W. R. Jr & Petersen, J. D. (1987). *Inorg. Chem.* **26**, 3376–3379.
Brewer, K. J., Murphy, W. R. Jr & Petersen, J. D. (1989). *Inorg. Chim. Acta*, **159**, 93–98.
Brewer, K. J., Murphy, W. R. Jr, Petersen, J. D., Ruminski, R. R. & Sahai, R. (1985). *Coord. Chem. Rev.* **64**, 261–273.
Burgess, J., Drasdo, D. N. & Shraydeh, B. J. (1992). *J. Chem. Res.* (*S*), pp. 288–289.
Buser, H. J., Schwarzenbach, D., Petter, W. & Ludi, A. (1977). *Inorg. Chem.* **16**, 2704–2710.
Christoph, G. G. & Goedken, V. L. (1973). *J. Am. Chem. Soc.* **95**, 3869–3875.
Garcia Posse, M. E., Juri, M. A., Aymonino, P. J., Piro, O. E., Negri, H. A. & Castellano, E. E. (1984). *Inorg. Chem.* **23**, 948–952.
Herren, F., Fischer, P., Ludi, A. & Hälg, W. (1980). *Inorg. Chem.* **19**, 956–959.
Kotowsky, M., van Eldik, R., Ali, R. B., Burgess, J. & Radulovic, S. (1987). *Inorg. Chim. Acta*, **131**, 225–229.
Lanfranconi, A. H., Alverez, A. G. & Castellano, E. E. (1973). *Acta Cryst.* B**29**, 1733–1734.
Manoharan, P. T. & Hamilton, W. C. (1963). *Inorg. Chem.* **2**, 1043–1047.
Pierrot, P. M., Kern, R. & Wiess, R. (1966). *Acta Cryst.* **20**, 425–428.
Ruminski, R. R., van Tassel, K. D. & Petersen, J. D. (1984). *Inorg. Chem.* **23**, 4380–4382.
Schilt, A. A. & Cresswell, A. M. (1966). *Talanta*, **13**, 911–918.
Sheldrick, G. M. (1990*a*). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1990*b*). *SHELXTL/PC. An Integrated System for Data Collection, Processing, Structure Solution and Refinement.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Siemens (1993). *XSCANS. X-ray Single Crystal Analysis System.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Swanson, B. I., Hamburg, S. I. & Ryan, R. R. (1974). *Inorg. Chem.* **13**, 1685–1687.
Tullberg, A. & Vannerburg, N. G. (1974). *Acta Chem. Scand. Ser. A*, **28**, 551–562.

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Diaquachlorobis(4-pyridinioacetate-*O*)copper(II) Perchlorate

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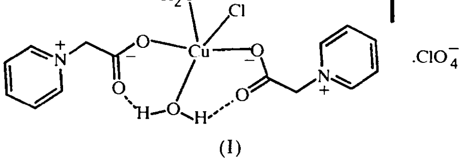
Abstract

In the title compound, $[CuCl(C_7H_7NO_2)_2(H_2O)_2]ClO_4$, the metal atom is coordinated in a distorted square-pyramidal environment with one aqua ligand [Cu—O 1.944 (4) Å], one chloride ion [Cu—Cl 2.2538 (15) Å] and two monodentate carboxylate O atoms [Cu—O 1.994 (4) and 2.004 (4) Å] in basal positions. The apical position is occupied by another aqua ligand [Cu—O 2.367 (4) Å].

Comment

Recently, we used zwitterionic betaines to prepare metal carboxylate complexes containing anionic ligands. The compounds included some dimeric copper(II) complexes in which the anionic ligands are axial (Chen & Mak, 1993; Chen *et al.*, 1997). In order to relate their magnetic properties and structures, we have synthesized several new dimeric copper(II)–carboxylate complexes containing different types of carboxylate bridge, as well as different types of axial ligand. The title complex, the mononuclear species $[CuCl(pybet)_2(H_2O)_2]ClO_4$, (I) (pybet is pyridinioacetate, $C_5H_5N^+CH_2O_2^-$), was obtained as a minor product (Chen *et al.*, 1998). We describe its crystal structure herein.



(I)

The crystals consist of discrete monomeric $[CuCl(pybet)_2(H_2O)_2]^+$ cations and perchlorate anions. The Cu^{II} atom is in a distorted square-pyramidal environment, being coordinated at the basal positions by one aqua ligand [Cu—O1*w* 1.944 (4) Å], one chloro ligand [Cu—Cl 2.2538 (15) Å] and two *trans* monodentate carboxylate ligands [Cu—O 1.994 (4) and 2.004 (4) Å],

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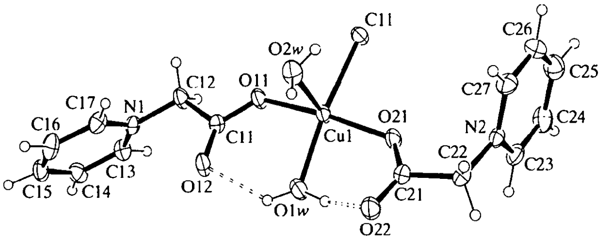

Fig. 1. *ORTEP*3 (Farrugia, 1997) plot (35% probability displacement ellipsoids for non-H atoms; H atoms as spheres of arbitrary size).

and at the apical position by another aqua ligand [Cu—O2*w* 2.367 (4) Å]. The metal atom is displaced from the basal plane by 0.172 (2) Å.

It is noteworthy that copper(II) carboxylates commonly have dimeric or polymeric structures, monomeric structures being quite uncommon (Chen *et al.*, 1998). There is a previous report of such a monomeric complex with distorted square-pyramidal geometry, in which the basal positions are occupied by two aqua ligands, one Cl ligand and one monodentate carboxylate ligand, and the apical position is occupied by another Cl ligand (Chen & Mak, 1992).

Hydrogen bonding plays an important role in consolidating the crystal structure. Each aqua ligand forms two donor hydrogen bonds. The O1*w* atom forms two strong intramolecular hydrogen bonds with the two uncoordinated carboxylate O atoms [O1*w*···O22 2.623 (7) and O1*w*···O12 2.642 (6) Å], whereas the O2*w* atom forms two intermolecular hydrogen bonds, one with a ligated carboxylate oxygen atom O11^{i} [2.834 (6) Å] and the other with a chloro ligand Cl^{i} [3.299 (4) Å] of the adjacent cation [symmetry code: (i) *x*, *y* − 1, *z*].

Experimental

The title compound was obtained in our attempt to prepare a dinuclear tetrakis(carboxylate)-bridged copper(II) complex (Chen *et al.*, 1998). A mixture of pybet (0.412 g, 3 mmol) and $CuCl_2.2H_2O$ (0.256 g, 1.5 mmol) was dissolved in distilled water (8 ml) and heated at 333 K for 10 min, then an aqueous solution (2 ml) of $NaClO_4.H_2O$ (0.106 g, 1.5 mmol) was added with stirring for 20 min. The solution was allowed to evaporate slowly at room temperature. After about 4 d, light-blue polyhedral crystals began to appear. The main product was characterized as $[Cu_2Cl(pybet)_4(H_2O)](ClO_4)_3.2H_2O$; a small quantity of a deep-blue crystalline compound was also isolated as a minor product. This minor product was carefully separated by hand under a microscope and characterized by elemental analysis and X-ray crystallography as the monomeric complex $[CuCl(pybet)_2(H_2O)_2]ClO_4$.

Crystal data

$[CuCl(C_7H_7NO_2)_2(H_2O)_2]$-$ClO_4$
$M_r = 508.74$
Orthorhombic
$Pna2_1$
$a = 13.186$ (6) Å
$b = 5.279$ (1) Å
$c = 27.288$ (4) Å
$V = 1899.5$ (10) Å^3
$Z = 4$
$D_x = 1.779$ Mg m^{-3}
D_m not measured

Mo *Kα* radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 5.2$–12.5°
$\mu = 1.489$ mm^{-1}
$T = 293$ (2) K
Polyhedral
0.32 × 0.28 × 0.26 mm
Pale blue

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: *ψ* scan (Kopfmann & Huber, 1968)
$T_{min} = 0.581$, $T_{max} = 0.679$
2326 measured reflections
2000 independent reflections
1736 reflections with $I > 2\sigma(I)$

$R_{int} = 0.027$
$\theta_{max} = 26.0°$
$h = 0 \rightarrow 16$
$k = 0 \rightarrow 6$
$l = -33 \rightarrow 1$
3 standard reflections every 100 reflections intensity decay: 0.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.083$
$S = 1.077$
2000 reflections
261 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.038P)^2 + 0.4389P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.30$ e Å^{-3}
$\Delta\rho_{min} = -0.38$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.01 (2)

Table 1. *Selected geometric parameters (Å, °)*

Cu1—O1*w*	1.944 (4)	O2*w*···O11^{i}	2.834 (6)
Cu1—O11	1.994 (4)	O2*w*···Cl1^{i}	3.299 (4)
Cu1—O21	2.004 (4)	O11—C11	1.271 (6)
Cu1—Cl1	2.2538 (15)	O12—C11	1.231 (6)
Cu1—O2*w*	2.367 (4)	O21—C21	1.262 (7)
O1*w*···O22	2.623 (7)	O22—C21	1.228 (7)
O1*w*···O12	2.642 (6)		
O1*w*—Cu1—O11	89.8 (2)	O21—Cu1—O2*w*	95.0 (2)
O1*w*—Cu1—O21	86.6 (2)	Cl1—Cu1—O2*w*	91.69 (12)
O11—Cu1—O21	170.1 (2)	C11—O11—Cu1	130.1 (3)
O1*w*—Cu1—Cl1	169.9 (2)	C11—O12···O1*w*	94.3 (3)
O11—Cu1—Cl1	92.16 (11)	O12—C11—O11	127.9 (5)
O21—Cu1—Cl1	89.86 (13)	C21—O21—Cu1	126.9 (4)
O1*w*—Cu1—O2*w*	98.1 (2)	C21—O22···O1*w*	92.2 (4)
O11—Cu1—O2*w*	94.7 (2)	O22—C21—O21	129.2 (5)

Symmetry code: (i) *x*, *y* − 1, *z*.

In retrospect, it is clear that data collection should have been extended beyond *θ*(Mo *Kα*) = 26° to obtain a more acceptable data/parameter ratio.

Data collection: *SHELXTL/PC* (Sheldrick, 1990). Cell refinement: *SHELXTL/PC*. Data reduction: *SHELXTL/PC*. Program(s) used to solve structure: *SHELXTL/PC*. Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*3 (Farrugia, 1997). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: MU1368). Services for accessing these data are described at the back of the journal.

References

Chen, X.-M., Feng, X.-L., Xu, Z.-T., Zhang, X.-H., Xue, F. & Mak, T. C. W. (1998). *Polyhedron*. In the press.
Chen, X.-M., Feng, X.-L., Yu, X.-L. & Mak, T. C. W. (1997). *Inorg. Chim. Acta*, **266**, 121–124.
Chen, X.-M. & Mak, T. C. W. (1992). *Struct. Chem.* **3**, 369–374.
Chen, X.-M. & Mak, T. C. W. (1993). *Struct. Chem.* **4**, 247–259.
Farrugia, L. J. (1997). *ORTEP3 for Windows*. Version 1.02 Beta. University of Glasgow, Scotland.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Kopfmann, G. & Huber, R. (1968). *Acta Cryst.* A**24**, 348–351.
Sheldrick, G. M. (1990). *SHELXTL/PC Users Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

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Tetraphenylphosphonium Hexatungstate(VI) Acetonitrile Solvate

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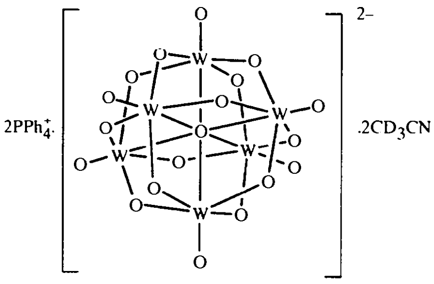
Abstract

Crystals of the title compound, $(C_{24}H_{20}P)_2[W_6O_{19}]$.-$2CD_3CN$, are composed of $[W_6O_{19}]^{2-}$ anions lying on inversion centres, and Ph_4P^+ cations and acetonitrile molecules of solvation in general positions. In the anion, each W atom is bonded to a central O atom, which lies on an inversion centre, a terminal O and four bridging O atoms, with average W—O distances of 2.323 (4), 1.714 (13) and 1.917 (15) Å, respectively.

Comment

It is known that alkylation of the tetrathiotungstate ion with alkyl bromides leads initially to unstable alkylated intermediates and eventually to polytungsten sulfide clusters as condensation products (Dhar & Chandrasekaran, 1989; Boorman *et al.*, 1995). While investigating analogous reactions of the dioxodithiotungstate ion with *tert*-butyl bromide, an NMR-scale reaction was performed in CD_3CN and red crystals were obtained. The crystals were believed to be the alkylated dioxodithiotungstate ion but were shown to be tetraphenylphosphonium hexatungstate acetonitrile solvate, (I), by X-ray diffraction. This finding was unexpected since the W atoms are coordinated exclusively to O atoms in the hexatungstate product, indicating displacement of the S atoms in the starting material.



(I)

The crystal structure is composed of $[W_6O_{19}]^{2-}$ anions (Fig. 1), $C_{24}H_{20}P^+$ cations and acetonitrile (CD_3CN) of solvation, all separated by normal van der Waals distances. The anion has a cage structure in which each W atom is octahedrally bonded to a central O atom, lying on an inversion centre, a terminal O and four bridging O atoms, with mean W—O distances of 2.323 (4), 1.714 (13) and 1.917 (15) Å, respectively. The central O atom exhibits octahedral geometry, with W—O—W angles in the narrow range 89.89 (2)–90.11 (2)°. Similar cage structures for the anion have been reported (Fuchs *et al.*, 1978; Fedin *et al.*, 1992; Hou *et al.*, 1995; Lehtonen & Sillanpää, 1995). The PPh_4 cation

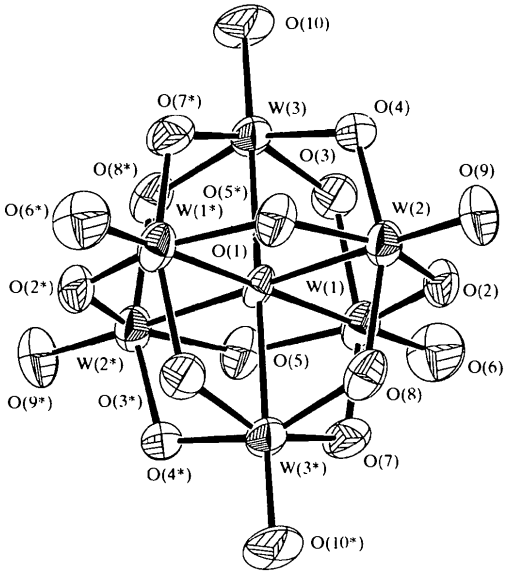


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the title anion. Displacement ellipsoids are plotted at 50% probability. The symmetry operation for the starred (*) atoms is $2-x, -y, -z$.