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Bis(tetraphenylphosphonium) (μ-tetrathiotungstenio-$\kappa^4 S,S'$:S'':S''')-bis[(cyano-κC)cuprate](2–) acetonitrile solvate monohydrate

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The reaction of CuCN and KCN with $(NH_4)_2[WS_4]$ followed by cation exchange with PPh_4Br produced the title compound, $(C_{24}H_{20}P)_2[Cu_2WS_4(CN)_2]\cdot CH_3CN\cdot H_2O$ or $(PPh_4)_2[(NC)Cu(\mu\text{-}S)_2W(\mu\text{-}S)_2Cu(CN)]\cdot MeCN\cdot H_2O$. In the structure of the dianion, $[(NC)Cu(\mu\text{-}S)_2W(\mu\text{-}S)_2Cu(CN)]^{2-}$, the WS_4 moiety acts as a bidentate ligand that binds two CuCN groups, thus forming a slightly bent WCu_2 core with approximate D_{2d} symmetry. The W—Cu distances are in the range 2.6463 (6)–2.6545 (6) Å.

Comment

In the past decade, the third-order non-linear optical (NLO) properties of group IB–VIB chalcogenide clusters derived from tetrathiometallate anions ($[MS_4]^{2-}$; M = Mo and W) have been studied extensively (Shi *et al.*, 1994; Shi, 1998; Yu *et al.*, 2001). However, only a few Mo(W)/Cu(Ag)/S clusters containing cyanides have been prepared and confirmed to exhibit good NLO properties in solution (Hou *et al.*, 1999; Zhang *et al.*, 2000). To find clusters with better NLO properties, we carried out the reaction of CuCN and KCN with $(NH_4)_2[WS_4]$. We report here the structure of the title trinuclear W/Cu/S cluster, (I).

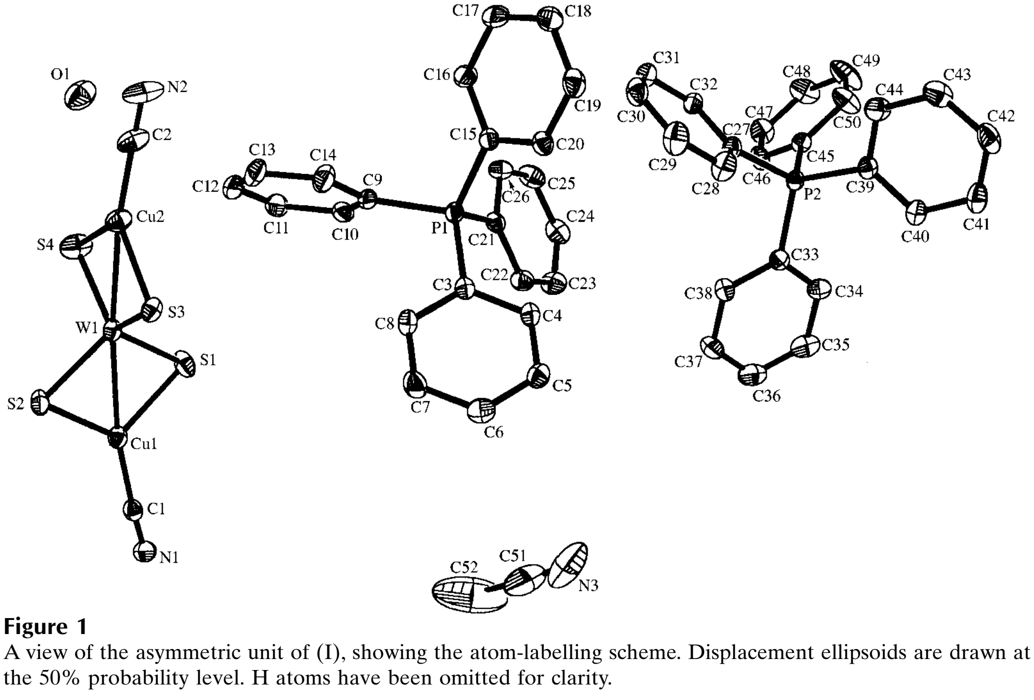
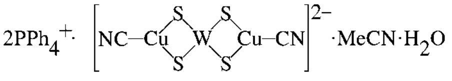


Figure 1
A view of the asymmetric unit of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity.

The asymmetric unit of (I) contains one discrete cluster anion, two $[PPh_4]^+$ cations, one acetonitrile molecule and one water molecule (Fig. 1). Being isostructural with its molybdenum analogue (Gheller *et al.*, 1984), the dianion of (I) consists of a central WS_4 moiety and two CuCN groups, which are connected *via* μ-S atoms. However, the dianion is slightly distorted from D_{2d} symmetry by small bends of 6–8° at all three metal atoms along the NC—Cu···W···Cu—CN axis (Table 1). The two Cu—C≡N angles also deviate from linearity (by 2–4°). The two $WCuS_2$ rhombuses are not quite planar but are essentially perpendicular to one another.



$$2PPh_4^+\cdot\left[NC{-}Cu(\mu\text{-}S)_2W(\mu\text{-}S)_2Cu{-}CN\right]^{2-}\cdot MeCN\cdot H_2O$$

(I)

Each of the two Cu atoms adopts an approximately trigonal-planar coordination geometry. The WS_4 moiety is a slightly distorted tetrahedron, with S—W—S bond angles ranging from 107.34 (4) to 112.17 (5)°. The mean W—μ-S bond length shows an apparent elongation of 0.052 (11) Å compared with that in the free $[WS_4]^{2-}$ ion [2.165 (3) Å] (Sasvári, 1963) as a result of binding two CuCN groups. The mean W—Cu distance [2.6504 (6) Å] is comparable to those found in three-coordinate Cu clusters, such as $(PPh_4)_2[(\eta^5\text{-}C_5Me_5)WS_3Cu_3Br_3]_2$ [2.661 (1) Å; Lang *et al.*, 1997] and $(PPh_4)[\{(\eta^5\text{-}C_5Me_5)WS_3Cu_2\}_2S_2]_2$ [2.677 (3) Å; Lang & Tatsumi, 1998]. The mean Cu—μ-S and Cu—C distances are similar to those in the corresponding molybdenum analogue [Cu—μ-S = 2.210 (2) Å and Cu—C = 1.886 (9) Å; Gheller *et al.*, 1984].

Each water molecule acts as a donor for two intermolecular hydrogen bonds (Table 2). The acceptor atoms are the cyano

N atoms from opposite ends of two adjacent anions. These interactions link an alternating sequence of anions and water molecules into extended chains that run in the $[1\bar{1}0]$ direction.

Experimental

$(NH_4)_2[WS_4]$ was prepared according to the method of McDonald *et al.* (1983). To a suspension produced by combining CuCN (0.89 g, 10 mmol) and KCN (0.70 g, 10.77 mmol) in water (20 ml) was added solid $(NH_4)_2[WS_4]$ (1.74 g, 5 mmol). The mixture was stirred for 1 h and filtered. The addition of a solution of PPh_4Br (4.19 g, 10 mmol) in water (10 ml) produced a yellow precipitate, which was filtered off, washed with water and dissolved in acetonitrile (60 ml). Evaporation of the solvent produced yellow platelets of (I), which were collected by filtration, washed with methanol and diethyl ether, and dried *in vacuo* (yield 5.29 g, 86%). IR (KBr , cm^{-1}): ν(C—N) 2123 (*m*); ν(W—S) 457 (*m*), 417 (*w*).

Crystal data

$(C_{24}H_{20}P)_2[Cu_2WS_4(CN)_2]\cdot C_2H_3N\cdot H_2O$
$M_r = 1229.07$
Triclinic, $P\bar{1}$
$a = 10.6193$ (2) Å
$b = 12.7441$ (10) Å
$c = 20.7526$ (3) Å
$\alpha = 72.922$ (9)°
$\beta = 76.449$ (9)°
$\gamma = 77.159$ (10)°
$V = 2574.1$ (3) $Å^3$
$Z = 2$
$D_x = 1.586$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6823 reflections
$\theta = 3.0$–27.5°
$\mu = 3.31$ mm^{-1}
$T = 193.2$ K
Prism, orange
0.40 × 0.35 × 0.30 mm

Data collection

Rigaku Mercury CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (Jacobson, 1998)
$T_{min} = 0.260$, $T_{max} = 0.370$
25 798 measured reflections
11 796 independent reflections
10 551 reflections with $I > 2\sigma(I)$
$R_{int} = 0.030$
$\theta_{max} = 27.5°$
$h = -13 \rightarrow 13$
$k = -16 \rightarrow 16$
$l = -26 \rightarrow 26$

Refinement

Refinement on F^2
$R(F) = 0.039$
$wR(F^2) = 0.089$
$S = 1.02$
11567 reflections
594 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0435P)^2 + 3.3249P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.02$ e $Å^{-3}$
$\Delta\rho_{min} = -0.84$ e $Å^{-3}$

Table 1
Selected geometric parameters (Å, °).

W1—S1	2.2087 (11)	Cu1—C1	1.897 (4)
W1—S4	2.2151 (12)	Cu1—S2	2.2295 (11)
W1—S3	2.2178 (9)	Cu1—S1	2.2404 (12)
W1—S2	2.2243 (11)	Cu2—C2	1.885 (5)
W1—Cu2	2.6463 (6)	Cu2—S4	2.2316 (13)
W1—Cu1	2.6545 (6)	Cu2—S3	2.2449 (11)
S1—W1—S4	110.51 (5)	C2—Cu2—S4	129.30 (14)
S1—W1—S3	108.45 (4)	C2—Cu2—S3	124.32 (14)
S4—W1—S3	107.78 (4)	S4—Cu2—S3	106.27 (5)
S1—W1—S2	107.34 (4)	C2—Cu2—W1	173.86 (17)
S4—W1—S2	112.17 (5)	W1—S1—Cu1	73.26 (3)
S3—W1—S2	110.54 (4)	W1—S2—Cu1	73.17 (3)
Cu2—W1—Cu1	173.961 (16)	W1—S3—Cu2	72.74 (3)
C1—Cu1—S2	133.75 (12)	W1—S4—Cu2	73.04 (4)
C1—Cu1—S1	120.18 (12)	N1—C1—Cu1	176.2 (4)
S2—Cu1—S1	106.06 (4)	N2—C2—Cu2	177.7 (5)
C1—Cu1—W1	172.31 (11)		

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1W*A*···N1^{i}	0.90 (6)	2.05 (6)	2.947 (5)	175 (5)
O1—H1W*B*···N2	0.84 (9)	2.20 (9)	3.038 (7)	179 (10)

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

The positions of the H atoms of the water molecule were located from a difference Fourier map and were refined freely, along with their isotropic displacement parameters. The acetonitrile H atoms were constrained to an ideal geometry [C—H = 0.96 Å, with $U_{iso}(H) = 1.5U_{eq}(C)$]. All other H atoms were placed in idealized positions (C—H = 0.93 Å) and constrained to ride on their parent atoms [$U_{iso}(H) = 1.2U_{eq}(C)$].

Data collection: *CrystalClear* (Rigaku/MSC, 2001); cell refinement: *CrystalClear*; data reduction: *CrystalStructure* (Rigaku/MSC, 2003); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2000).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1179). Services for accessing these data are described at the back of the journal.

References

Burnett, M. N. & Johnson, C. K. (1996). *ORTEP*III. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
Gheller, S. F., Hambley, T. W., Rodgers, J. R., Brownlee, R. T. C., O'Connor, M. J., Snow, M. R. & Wedd, A. G. (1984). *Inorg. Chem.* **23**, 2519–2528.
Hou, H.-W., Zheng, H.-G., Ang, H.-G., Fan, Y.-T., Low, M. K. M., Zhu, Y., Wang, W.-L., Xin, X.-Q., Ji, W. & Wong, W.-T. (1999). *J. Chem. Soc. Dalton Trans.* pp. 2953–2957.
Jacobson, R. (1998). Private communication.
Lang, J.-P., Kawaguchi, H., Ohnishi, S. & Tatsumi, K. (1997). *Chem. Commun.* pp. 405–406.
Lang, J.-P. & Tatsumi, K. (1998). *Inorg. Chem.* **37**, 160–162.
McDonald, J. W., Friesen, G. D., Rosenhein, L. D. & Newton, W. E. (1983). *Inorg. Chim. Acta*, **72**, 205–210.
Rigaku/MSC (2001). *CrystalClear Software User's Guide.* Version 1.30. Rigaku/MSC, 9009 New Trails Drive, The Woodlands, TX 77381, USA.
Rigaku/MSC (2003). *CrystalStructure.* Version 3.16. Rigaku/MSC, 9009 New Trails Drive, The Woodlands, TX 77381, USA.
Sasvári, K. (1963). *Acta Cryst.* **16**, 719–724.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Sheldrick, G. M. (2000). *SHELXTL.* Version 6.10. Bruker AXS Inc., Madison, Wisconsin, USA.
Shi, S. (1998). *Optoelectronic Properties of Inorganic Compounds*, edited by D. M. Roundhill & J. P. Fackler Jr, pp. 55–105. New York: Plenum Press.
Shi, S., Ji, W., Tang, S.-H., Lang, J.-P. & Xin, X.-Q. (1994). *J. Am. Chem. Soc.* **116**, 3615–3616.
Yu, H., Xu, Q.-F., Sun, Z.-R., Ji, S.-J., Chen, J.-X., Liu, Q., Lang, J.-P. & Tatsumi, K. (2001). *Chem. Commun.* pp. 2614–2615.
Zhang, C., Song, Y.-L., Xu, Y., Fun, H.-K., Fang, G.-Y., Wang, Y.-X. & Xin, X.-Q. (2000). *J. Chem. Soc. Dalton Trans.* pp. 2823–2829.

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