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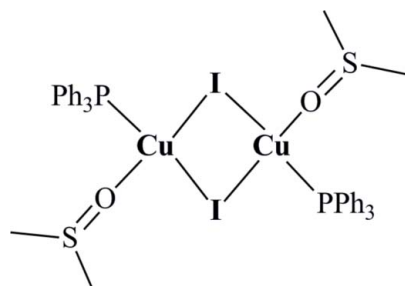
Crystal structure of di- μ -iodido-bis[(dimethyl sulfoxide- κ O)(triphenylphosphane- κ P)copper(I)]

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The centrosymmetric dinuclear title compound, [Cu₂I₂(C₂H₆OS)₂(C₁₈H₁₅P)₂], represents the first example of a Cu^I complex ligated by an *O*-bound dimethyl sulfoxide ligand. In the crystal, the two tetrahedrally coordinated Cu^I atoms are bridged by two μ_2 -iodido ligands in an almost symmetrical rhomboid geometry. The loose Cu \cdots Cu contact of 2.9874 (8) Å is longer than the sum of the van der Waals radii of two Cu atoms (2.8 Å), excluding a significant cupriophilic interaction in the actual dimer. C—H \cdots O and C—H \cdots I hydrogen bonding interactions as well as C—H \cdots π (aryl) interactions stabilize the three-dimensional supramolecular network.

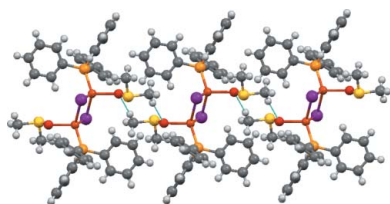
1. Chemical context

There exists a large family of dinuclear Cu^I \cdots Cu^I-halide-bridged complexes of the type [PPh₃(*L*)Cu(μ_2 -I)₂Cu(*L'*)-PPh₃], with the ligands *L* commonly bearing the coordinating N and S atoms, in which cupriophilic interactions may play a crucial role in determining their photophysical properties (Lobana *et al.*, 2012 and references therein; Engelhardt *et al.*, 1989). The title compound, [PPh₃(DMSO)Cu(μ_2 -I)₂Cu-(DMSO)PPh₃] (1), belongs to this family of compounds for which an association of *L* = PPh₃ and *L'* = DMSO has never been mentioned before.



2. Database survey

The polar aprotic solvent (CH₃)₂S=O (DMSO) is frequently used in organic chemistry for reactions involving salts such nucleophilic substitutions reactions, but it has also found widespread use as a ligating solvent in the coordination chemistry of transition metals, where it may act both as an *S*-donor and an *O*-donor ligand towards a metal centre (Selbin *et al.*, 1961). A survey of the Cambridge Structural Database (CSD; Groom & Allen, 2014) reveals a large number of structurally characterized Cu^{II} halide complexes ligated by *O*-bound DMSO ligands. However, we found just one entry concerning a Cu^I halide complex, namely the tetrametallic



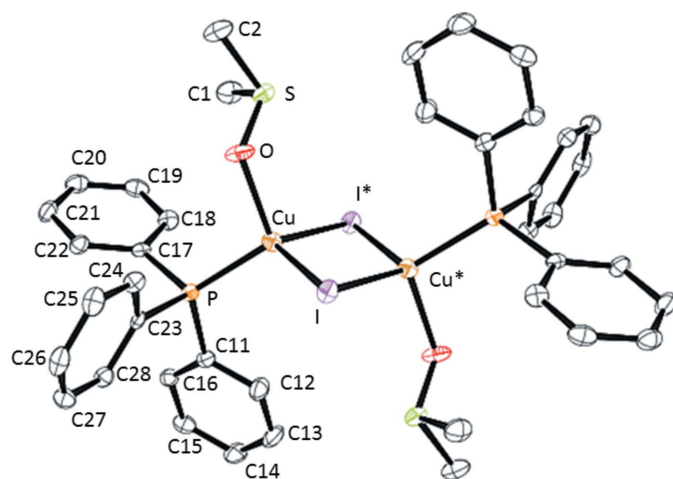


Figure 1
The molecular structure of title compound built over a symmetry centre, with atom labels and 50% probability displacement ellipsoids for non-H atoms. Symmetry code for unlabelled atoms is (1 - *x*, -*y*, -*z*).

chain complex $[\text{Cu}_4\text{Br}(\mu\text{-Br})_3(\mu\text{-dpmppm})_2(\text{DMSO})_2]$ (dpmppm = bis[(diphenylphosphinomethyl)phenylphosphino]methane) reported by Takemura *et al.* (2009). Note that in the case of a soft Cu^{I} ion (compared with a harder Cu^{II} ion according the HSAB principle), DMSO could be *a priori* coordinating either *via* the sulfur or *via* the oxygen atom. Surprisingly, we found no Cu^{I} complex ligated by DMSO in the CSD.

3. Structural commentary

CuI is known to afford with DMSO in the presence of P_2S_5 the 2D coordination polymer $[(\text{Me}_2\text{S})_3\{\text{Cu}_4(\mu\text{-I})_4\}]_n$, the production of SMe_2 being explained by the deoxygenation of Me_2SO by P_2S_5 (Zhou *et al.*, 2006). In the context of our research on the coordination of thioethers $R\text{-S-R}$ on CuX salts (Knorr *et al.*, 2010; Lapprand *et al.*, 2013), we reacted a CuI solution in hot DMSO with a stoichiometric amount of PPh_3 and succeeded in isolating in moderate yield X-ray-suitable crystals of (1). Structural analysis revealed that a centrosymmetric dinuclear complex is formed (Fig. 1), in which the two tetra-

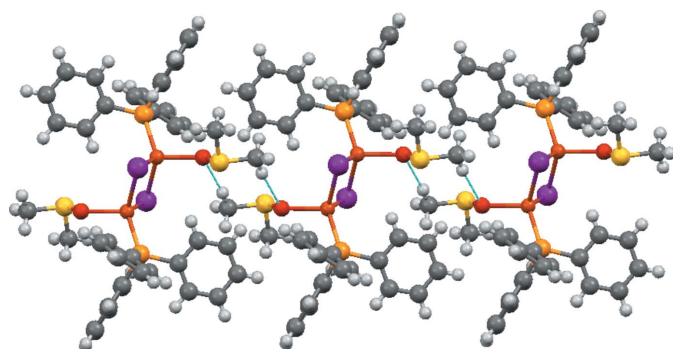


Figure 2
One-dimensional chain along [110] built *via* C—H...O intermolecular interactions between the DMSO ligands.

Table 1
Hydrogen-bond geometry (\AA , $^\circ$).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C2—H2A...O ⁱ	0.98	2.46	3.434 (5)	173
C1—H1B...I ⁱⁱ	0.98	3.12	3.931 (4)	142
C2—H2B...I ⁱⁱ	0.98	3.15	3.978 (4)	143
C26—H26...C16 ⁱⁱⁱ	0.95	2.85	3.781 (5)	168

Symmetry codes: (i) $-x + 2, -y + 1, -z$; (ii) $-x + 2, -y, -z$; (iii) $x, y + 1, z$.

hedrally coordinated Cu^{I} atoms are bridged by two μ_2 -iodido ligands in a slightly asymmetric rhomboid manner. Despite the soft character of CuI , the DMSO ligands are *O*-bound. The Cu—O bond length of 2.140 (2) \AA is considerably longer than those of polymeric Cu^{II} compounds $[(\text{DMSO})_2\text{CuBr}_2]_n$ [1.962 (9) \AA ; Willett *et al.*, 1977] and $[(\text{DMSO})_2\text{CuCl}_2]_n$ [1.955 (4) \AA ; Willett & Chang, 1970], but is in the same range as found for $[\text{Cu}_4\text{Br}(\mu\text{-Br})_3(\mu\text{-dpmppm})_2(\text{DMSO})_2]$ [2.200 (7) \AA]. The Cu...Cu contact of 2.9874 (8) \AA is longer than the sum of the van der Waals radii of two Cu atoms (2.8 \AA), excluding any cupriophilic interaction. This separation is in the same range as reported for $[\text{PPh}_3(\text{pyridine})\text{Cu}(\mu_2\text{-I})_2\text{Cu}(\text{pyridine})\text{PPh}_3]$ (2.97 \AA) (Bowmaker *et al.*, 1994), and the P—Cu bond lengths are also quite similar in the two compounds [2.2295 (10) vs 2.24 \AA].

4. Supramolecular features

The assembly of the crystal structure seems to be first governed by C—H...O-type hydrogen bonds (intermolecular ligand-to-ligand DMSO interactions), leading to a 1D chain

Table 2
Experimental details.

Crystal data	
Chemical formula	$[\text{Cu}_2\text{I}_2(\text{C}_2\text{H}_6\text{OS})_2(\text{C}_{18}\text{H}_{15}\text{P})_2]$
M_r	1061.67
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	115
<i>a</i> , <i>b</i> , <i>c</i> (\AA)	8.6099 (2), 9.3435 (2), 14.5279 (4)
α , β , γ ($^\circ$)	91.016 (1), 104.049 (1), 116.004 (1)
<i>V</i> (\AA^3)	1008.60 (4)
<i>Z</i>	1
Radiation type	Mo $K\alpha$
μ (mm^{-1})	2.80
Crystal size (mm)	0.17 \times 0.05 \times 0.05
Data collection	
Diffractometer	Nonius KappaCCD
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	8368, 4586, 3541
R_{int}	0.036
$(\sin \theta/\lambda)_{\text{max}}$ (\AA^{-1})	0.649
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, <i>S</i>	0.035, 0.077, 0.99
No. of reflections	4586
No. of parameters	228
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e \AA^{-3})	0.78, -0.98

Computer programs: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997), *SIR97* (Altomare *et al.*, 1999), *SHELXL2012* (Sheldrick, 2008), *ORTEP-3 for Windows* and *WinGX* (Farrugia, 2012).

structure extending in the [110] direction (Fig. 2). Further, the very weak C—H...I interactions (for a 2D structure), followed by those of the C—H... π (aryl) type are probably responsible for the 3D assembly (Table 1).

5. Synthesis and crystallization

Triphenylphosphane (262 mg, 1.0 mmol) was added to a solution of CuI (192 mg, 1.0 mmol) in 10 ml of DMSO. The reaction mixture was first stirred at room temperature for 30 min and then heated for further 30 min to 368 K. After allowing the mixture to reach ambient temperature, yellowish crystals were formed (36% yield). Characterization data: ^1H NMR (CDCl_3): 2.62 (s, 6H, Me), 7.30–7.57 (m, 15H, Ph).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All H atoms were placed in calculated positions and treated in a riding-model approximation. C—H distances were set to 0.95 (aromatic) and 0.98 Å (methyl) with $U_{\text{iso}}(\text{H}) = xU_{\text{eq}}(\text{C})$, where $x = 1.5$ for methyl and 1.2 for aromatic H atoms.

Acknowledgements

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References

- Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
- Bowmaker, G. A., Hanna, J. V., Hart, R. D., Healy, P. C. & White, A. H. (1994). *J. Chem. Soc. Dalton Trans.* pp. 2621–2629.
- Engelhardt, L. M., Healy, P. C., Kildea, J. D. & White, A. H. (1989). *Aust. J. Chem.* **42**, 913–922.
- Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
- Groom, C. R. & Allen, F. H. (2014). *Angew. Chem. Int. Ed.* **53**, 662–671.
- Knorr, M., Pam, A., Khatyr, A., Strohmman, C., Kubicki, M. M., Rousselin, Y., Aly, S. M., Fortin, D. & Harvey, P. D. (2010). *Inorg. Chem.* **49**, 5834–5844.
- Lapprand, A., Bonnot, A., Knorr, M., Rousselin, Y., Kubicki, M. M., Fortin, D. & Harvey, P. D. (2013). *Chem. Commun.* pp. 8848–8850.
- Lobana, T. S., Sharma, R., Hundal, G., Castineiras, A. & Butcher, R. J. (2012). *Polyhedron*, **47**, 134–142.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
- Selbin, J., Bull, W. E. & Holmes, L. H. Jr (1961). *J. Inorg. Nucl. Chem.* **16**, 219–224.
- Sheldrick, G. M. (2008). *Acta Cryst. A* **64**, 112–122.
- Takemura, Y., Nakajima, T. & Tanase, T. (2009). *Dalton Trans.* pp. 10231–10243.
- Willett, R. D. & Chang, K. U. (1970). *Inorg. Chim. Acta*, **4**, 447–451.
- Willett, R. D., Jardine, F. H. & Roberts, S. A. (1977). *Inorg. Chim. Acta*, **25**, 97–101.
- Zhou, J., Bian, G.-Q., Dai, J., Zhang, Y., Zhu, Q.-Y. & Lu, W. (2006). *Inorg. Chem.* **45**, 8486–8488.

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Crystal structure of di- μ -iodido-bis[(dimethyl sulfoxide- κ O)(triphenylphosphane- κ P)copper(I)]

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Computing details

Data collection: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL2012* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012; software used to prepare material for publication: *WinGX* (Farrugia, 2012).

Di- μ -iodido-bis[(dimethyl sulfoxide- κ O)(triphenylphosphane- κ P)copper(I)]

Crystal data

$[\text{Cu}_2\text{I}_2(\text{C}_2\text{H}_6\text{OS})_2(\text{C}_{18}\text{H}_{15}\text{P})_2]$

$M_r = 1061.67$

Triclinic, $P\bar{1}$

$a = 8.6099$ (2) Å

$b = 9.3435$ (2) Å

$c = 14.5279$ (4) Å

$\alpha = 91.016$ (1)°

$\beta = 104.049$ (1)°

$\gamma = 116.004$ (1)°

$V = 1008.60$ (4) Å³

$Z = 1$

$F(000) = 524$

$D_x = 1.748$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 8449 reflections

$\theta = 1.0\text{--}27.5^\circ$

$\mu = 2.80$ mm⁻¹

$T = 115$ K

Prism, clear light colourless

$0.17 \times 0.05 \times 0.05$ mm

Data collection

Nonius KappaCCD

diffractometer

Radiation source: X-ray tube, Enraf–Nonius

FR590

Horizontally mounted graphite crystal

monochromator

Detector resolution: 9 pixels mm⁻¹

CCD rotation images, thick slices scans

8368 measured reflections

4586 independent reflections

3541 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.036$

$\theta_{\text{max}} = 27.5^\circ$, $\theta_{\text{min}} = 2.9^\circ$

$h = -11 \rightarrow 11$

$k = -12 \rightarrow 12$

$l = -18 \rightarrow 18$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.035$

$wR(F^2) = 0.077$

$S = 0.99$

4586 reflections

228 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-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0332P)^2]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$

$$\Delta\rho_{\max} = 0.78 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.97 \text{ e } \text{\AA}^{-3}$$

Special details

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	1.1097 (5)	0.1762 (5)	0.1426 (3)	0.0287 (9)
H1A	1.2180	0.1767	0.1319	0.043*
H1B	1.0227	0.0656	0.1443	0.043*
H1C	1.1417	0.2424	0.2038	0.043*
C2	1.2026 (5)	0.4468 (4)	0.0613 (3)	0.0289 (10)
H2A	1.2436	0.4995	0.1276	0.043*
H2B	1.1687	0.5138	0.0179	0.043*
H2C	1.2999	0.4324	0.0458	0.043*
C11	0.4456 (4)	-0.0357 (4)	0.2784 (3)	0.0164 (8)
C12	0.2884 (5)	-0.1295 (4)	0.2069 (3)	0.0261 (9)
H12	0.2763	-0.1044	0.1432	0.031*
C13	0.1487 (5)	-0.2598 (4)	0.2276 (3)	0.0309 (10)
H13	0.0407	-0.3222	0.1784	0.037*
C14	0.1662 (5)	-0.2989 (4)	0.3195 (3)	0.0270 (9)
H14	0.0711	-0.3890	0.3335	0.032*
C15	0.3233 (5)	-0.2061 (4)	0.3913 (3)	0.0228 (8)
H15	0.3355	-0.2321	0.4548	0.027*
C16	0.4625 (5)	-0.0756 (4)	0.3707 (3)	0.0178 (8)
H16	0.5703	-0.0130	0.4199	0.021*
C17	0.8273 (4)	0.1580 (4)	0.3337 (3)	0.0154 (7)
C18	0.8942 (5)	0.0488 (4)	0.3218 (3)	0.0193 (8)
H18	0.8316	-0.0358	0.2693	0.023*
C19	1.0498 (5)	0.0623 (4)	0.3852 (3)	0.0235 (9)
H19	1.0937	-0.0127	0.3763	0.028*
C20	1.1422 (5)	0.1862 (4)	0.4623 (3)	0.0244 (9)
H20	1.2490	0.1959	0.5063	0.029*
C21	1.0783 (5)	0.2938 (4)	0.4742 (3)	0.0240 (9)
H21	1.1414	0.3784	0.5267	0.029*
C22	0.9227 (4)	0.2810 (4)	0.4107 (3)	0.0187 (8)
H22	0.8807	0.3573	0.4198	0.022*
C23	0.5978 (4)	0.3083 (4)	0.2747 (2)	0.0145 (7)
C24	0.6736 (5)	0.4388 (4)	0.2269 (3)	0.0201 (8)
H24	0.7384	0.4338	0.1835	0.024*
C25	0.6536 (5)	0.5769 (4)	0.2431 (3)	0.0236 (9)
H25	0.7075	0.6670	0.2119	0.028*
C26	0.5561 (5)	0.5829 (4)	0.3040 (3)	0.0229 (9)

H26	0.5403	0.6760	0.3131	0.028*
C27	0.4813 (5)	0.4551 (4)	0.3520 (3)	0.0219 (8)
H27	0.4160	0.4612	0.3948	0.026*
C28	0.5013 (4)	0.3171 (4)	0.3378 (3)	0.0180 (8)
H28	0.4496	0.2290	0.3708	0.022*
O	0.8790 (3)	0.2915 (3)	0.0820 (2)	0.0270 (6)
P	0.62437 (12)	0.13151 (10)	0.24350 (7)	0.0145 (2)
S	1.01292 (12)	0.25565 (10)	0.04801 (7)	0.0206 (2)
Cu	0.62834 (6)	0.10410 (5)	0.09145 (3)	0.01942 (12)
I	0.60513 (3)	−0.17153 (2)	0.03064 (2)	0.02049 (9)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.023 (2)	0.038 (2)	0.028 (2)	0.0175 (19)	0.0055 (18)	0.0123 (18)
C2	0.0155 (19)	0.023 (2)	0.045 (3)	0.0060 (16)	0.0084 (18)	0.0055 (18)
C11	0.0143 (18)	0.0132 (17)	0.022 (2)	0.0066 (14)	0.0051 (15)	0.0019 (14)
C12	0.024 (2)	0.027 (2)	0.018 (2)	0.0044 (17)	0.0029 (17)	0.0028 (16)
C13	0.016 (2)	0.029 (2)	0.031 (3)	−0.0013 (17)	0.0020 (18)	−0.0011 (18)
C14	0.022 (2)	0.0182 (19)	0.035 (3)	0.0016 (16)	0.0126 (18)	0.0056 (17)
C15	0.026 (2)	0.024 (2)	0.025 (2)	0.0136 (17)	0.0135 (18)	0.0091 (16)
C16	0.0168 (18)	0.0154 (18)	0.021 (2)	0.0070 (15)	0.0063 (15)	0.0023 (15)
C17	0.0111 (17)	0.0169 (18)	0.018 (2)	0.0052 (14)	0.0061 (15)	0.0048 (14)
C18	0.0224 (19)	0.0148 (17)	0.022 (2)	0.0087 (15)	0.0071 (16)	0.0064 (15)
C19	0.024 (2)	0.027 (2)	0.030 (2)	0.0174 (17)	0.0132 (18)	0.0116 (17)
C20	0.0179 (19)	0.032 (2)	0.024 (2)	0.0124 (17)	0.0052 (17)	0.0087 (17)
C21	0.0163 (19)	0.0224 (19)	0.025 (2)	0.0049 (16)	−0.0009 (16)	−0.0038 (16)
C22	0.0152 (18)	0.0184 (18)	0.022 (2)	0.0087 (15)	0.0026 (16)	0.0017 (15)
C23	0.0095 (16)	0.0136 (17)	0.0149 (19)	0.0030 (14)	−0.0016 (14)	−0.0017 (14)
C24	0.0180 (19)	0.0182 (18)	0.023 (2)	0.0073 (15)	0.0049 (16)	0.0033 (15)
C25	0.029 (2)	0.0147 (18)	0.022 (2)	0.0084 (16)	0.0022 (17)	0.0042 (15)
C26	0.024 (2)	0.0166 (19)	0.026 (2)	0.0151 (16)	−0.0068 (17)	−0.0038 (16)
C27	0.0200 (19)	0.024 (2)	0.025 (2)	0.0128 (16)	0.0060 (17)	−0.0005 (16)
C28	0.0162 (18)	0.0177 (18)	0.019 (2)	0.0076 (15)	0.0031 (15)	0.0024 (15)
O	0.0147 (13)	0.0222 (13)	0.0462 (19)	0.0076 (11)	0.0138 (12)	0.0082 (12)
P	0.0139 (4)	0.0123 (4)	0.0175 (5)	0.0062 (4)	0.0042 (4)	0.0020 (4)
S	0.0147 (5)	0.0205 (5)	0.0232 (5)	0.0059 (4)	0.0036 (4)	0.0038 (4)
Cu	0.0195 (2)	0.0204 (2)	0.0200 (3)	0.0100 (2)	0.0066 (2)	0.00351 (19)
I	0.02019 (14)	0.01809 (13)	0.02255 (15)	0.01034 (10)	0.00187 (10)	0.00121 (10)

Geometric parameters (Å, °)

C1—H1A	0.9800	C19—C20	1.393 (5)
C1—H1B	0.9800	C20—H20	0.9500
C1—H1C	0.9800	C20—C21	1.367 (5)
C1—S	1.777 (4)	C21—H21	0.9500
C2—H2A	0.9800	C21—C22	1.384 (5)
C2—H2B	0.9800	C22—H22	0.9500

C2—H2C	0.9800	C23—C24	1.396 (5)
C2—S	1.781 (3)	C23—C28	1.401 (5)
C11—C12	1.387 (5)	C23—P	1.828 (3)
C11—C16	1.388 (5)	C24—H24	0.9500
C11—P	1.834 (3)	C24—C25	1.398 (4)
C12—H12	0.9500	C25—H25	0.9500
C12—C13	1.386 (5)	C25—C26	1.374 (5)
C13—H13	0.9500	C26—H26	0.9500
C13—C14	1.382 (5)	C26—C27	1.379 (5)
C14—H14	0.9500	C27—H27	0.9500
C14—C15	1.387 (5)	C27—C28	1.392 (4)
C15—H15	0.9500	C28—H28	0.9500
C15—C16	1.386 (5)	O—S	1.514 (2)
C16—H16	0.9500	O—Cu	2.140 (2)
C17—C18	1.399 (4)	P—Cu	2.2295 (10)
C17—C22	1.388 (5)	Cu—Cu ⁱ	2.9874 (8)
C17—P	1.825 (3)	Cu—I	2.6144 (4)
C18—H18	0.9500	Cu—I ⁱ	2.6463 (5)
C18—C19	1.381 (5)	I—Cu ⁱ	2.6463 (5)
C19—H19	0.9500		
H1A—C1—H1B	109.5	C22—C21—H21	119.6
H1A—C1—H1C	109.5	C17—C22—H22	119.6
H1B—C1—H1C	109.5	C21—C22—C17	120.8 (3)
S—C1—H1A	109.5	C21—C22—H22	119.6
S—C1—H1B	109.5	C24—C23—C28	119.5 (3)
S—C1—H1C	109.5	C24—C23—P	115.5 (3)
H2A—C2—H2B	109.5	C28—C23—P	124.9 (3)
H2A—C2—H2C	109.5	C23—C24—H24	120.2
H2B—C2—H2C	109.5	C23—C24—C25	119.6 (3)
S—C2—H2A	109.5	C25—C24—H24	120.2
S—C2—H2B	109.5	C24—C25—H25	119.9
S—C2—H2C	109.5	C26—C25—C24	120.3 (3)
C12—C11—C16	119.1 (3)	C26—C25—H25	119.9
C12—C11—P	117.3 (3)	C25—C26—H26	119.7
C16—C11—P	123.6 (3)	C25—C26—C27	120.6 (3)
C11—C12—H12	119.8	C27—C26—H26	119.7
C13—C12—C11	120.5 (4)	C26—C27—H27	120.0
C13—C12—H12	119.8	C26—C27—C28	120.0 (3)
C12—C13—H13	119.9	C28—C27—H27	120.0
C14—C13—C12	120.2 (4)	C23—C28—H28	120.0
C14—C13—H13	119.9	C27—C28—C23	119.9 (3)
C13—C14—H14	120.1	C27—C28—H28	120.0
C13—C14—C15	119.7 (4)	S—O—Cu	121.91 (13)
C15—C14—H14	120.1	C11—P—Cu	116.27 (11)
C14—C15—H15	120.0	C17—P—C11	102.77 (16)
C16—C15—C14	120.1 (4)	C17—P—C23	103.83 (14)
C16—C15—H15	120.0	C17—P—Cu	115.71 (12)

C11—C16—H16	119.8	C23—P—C11	104.58 (15)
C15—C16—C11	120.4 (3)	C23—P—Cu	112.25 (12)
C15—C16—H16	119.8	C1—S—C2	98.10 (19)
C18—C17—P	117.0 (3)	O—S—C1	106.07 (17)
C22—C17—C18	118.1 (3)	O—S—C2	104.70 (16)
C22—C17—P	124.9 (3)	O—Cu—P	106.70 (8)
C17—C18—H18	119.5	O—Cu—Cu ⁱ	116.74 (8)
C19—C18—C17	121.0 (3)	O—Cu—I	108.23 (6)
C19—C18—H18	119.5	O—Cu—I ⁱ	101.47 (7)
C18—C19—H19	120.1	P—Cu—Cu ⁱ	136.38 (3)
C18—C19—C20	119.8 (3)	P—Cu—I ⁱ	114.07 (3)
C20—C19—H19	120.1	P—Cu—I	114.48 (3)
C19—C20—H20	120.2	I—Cu—Cu ⁱ	55.904 (14)
C21—C20—C19	119.6 (3)	I ⁱ —Cu—Cu ⁱ	54.897 (14)
C21—C20—H20	120.2	I—Cu—I ⁱ	110.801 (16)
C20—C21—H21	119.6	Cu—I—Cu ⁱ	69.201 (16)
C20—C21—C22	120.8 (3)		
C11—C12—C13—C14	−1.1 (6)	C22—C17—P—C23	4.7 (4)
C12—C11—C16—C15	−0.9 (5)	C22—C17—P—Cu	128.1 (3)
C12—C11—P—C17	−154.0 (3)	C23—C24—C25—C26	−1.6 (5)
C12—C11—P—C23	97.8 (3)	C24—C23—C28—C27	0.2 (5)
C12—C11—P—Cu	−26.6 (3)	C24—C23—P—C11	−158.7 (3)
C12—C13—C14—C15	0.8 (6)	C24—C23—P—C17	93.8 (3)
C13—C14—C15—C16	−0.5 (5)	C24—C23—P—Cu	−31.8 (3)
C14—C15—C16—C11	0.6 (5)	C24—C25—C26—C27	1.9 (5)
C16—C11—C12—C13	1.2 (5)	C25—C26—C27—C28	−1.1 (5)
C16—C11—P—C17	23.6 (3)	C26—C27—C28—C23	0.1 (5)
C16—C11—P—C23	−84.6 (3)	C28—C23—C24—C25	0.5 (5)
C16—C11—P—Cu	151.0 (2)	C28—C23—P—C11	17.9 (3)
C17—C18—C19—C20	0.0 (5)	C28—C23—P—C17	−89.5 (3)
C18—C17—C22—C21	−0.7 (5)	C28—C23—P—Cu	144.8 (3)
C18—C17—P—C11	78.3 (3)	P—C11—C12—C13	178.8 (3)
C18—C17—P—C23	−172.9 (3)	P—C11—C16—C15	−178.4 (2)
C18—C17—P—Cu	−49.5 (3)	P—C17—C18—C19	178.3 (3)
C18—C19—C20—C21	−0.3 (6)	P—C17—C22—C21	−178.3 (3)
C19—C20—C21—C22	0.1 (6)	P—C23—C24—C25	177.4 (3)
C20—C21—C22—C17	0.4 (6)	P—C23—C28—C27	−176.3 (2)
C22—C17—C18—C19	0.5 (5)	Cu—O—S—C1	−72.7 (2)
C22—C17—P—C11	−104.1 (3)	Cu—O—S—C2	−175.87 (19)

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

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C2—H2A \cdots O ⁱⁱ	0.98	2.46	3.434 (5)	173
C1—H1B \cdots I ⁱⁱⁱ	0.98	3.12	3.931 (4)	142

C2—H2B...I ⁱⁱⁱ	0.98	3.15	3.978 (4)	143
C26—H26...C16 ^{iv}	0.95	2.85	3.781 (5)	168

Symmetry codes: (ii) $-x+2, -y+1, -z$; (iii) $-x+2, -y, -z$; (iv) $x, y+1, z$.