# research communications

## $\mu_3$-Chlorido-$\mu_2$-chlorido-($\mu_3$-pyrrolidine-1-carbo-dithioato-$\kappa^4S:S,S':S'$)tris[(triethylphosphane-$\kappa P$)-copper(I)]: crystal structure and Hirshfeld surface analysis

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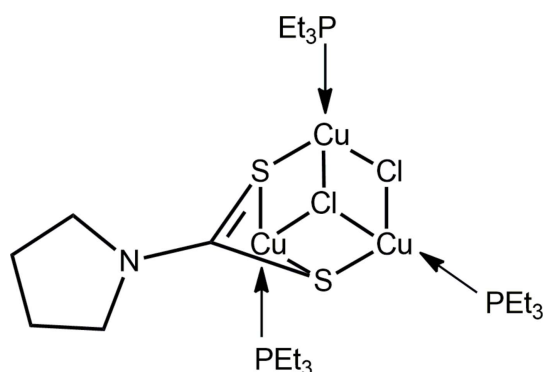
The title trinuclear compound, [Cu₃(C₅H₈NS₂)Cl₂(C₆H₁₅P)₃], has the dithiocarbamate ligand symmetrically chelating one Cu$^{I}$ atom and each of the S atoms bridging to another Cu$^{I}$ atom. Both chloride ligands are bridging, one being $\mu_3$- and the other $\mu_2$-bridging. Each Et₃P ligand occupies a terminal position. Two of the Cu$^{I}$ atoms exist within Cl₂PS donor sets and the third is based on a ClPS₂ donor set, with each coordination geometry based on a distorted tetrahedron. The constituents defining the core of the molecule, $i.e.$ Cu₃Cl₂S₂, occupy seven corners of a distorted cube. In the crystal, linear supramolecular chains along the $c$ axis are formed $via$ phosphane–methylene-C—H···Cl and pyrrolidine–methylene-C—H···$\pi$(chelate) interactions, and these chains pack without directional interactions between them. An analysis of the Hirshfeld surface points to the predominance of H atoms at the surface, $i.e.$ contributing 86.6% to the surface, and also highlights the presence of C—H···$\pi$(chelate) interactions.

## 1. Chemical context

Recent studies have highlighted the potential of ternary coinage metal phosphane/dithiocarbamates as anti-microbial agents. Motivated by the quite significant activity exhibited by $R_3$PAu(S₂CN$RR'$), $R$, $R'$ = alkyl/aryl (Sim $et$ $al.$, 2014; Chen $et$ $al.$, 2016), lower congeners, $i.e.$ (Ph₃P)₂$M$(S₂CN$RR'$), $M$ = Cu$^{I}$ and Ag$^{I}$, were investigated and shown to be also potent in this context (Jamaludin $et$ $al.$, 2016). A prominent lead compound, Et₃PAu(S₂CNEt₂), was shown to possess broad-range activity against Gram-positive and Gram-negative bacteria and, notably, was also bactericidal against methicillin-resistant $Staphylococcus$ $aureus$ (MRSA) (Chen $et$ $al.$, 2016). Given that Et₃PAu(S₂CNEt₂) exhibited the most exciting potential amongst the phosphanegold dithiocarbamates, it was thought of interest to extend the chemistry/biological investigations of ($R_3$P)₂$M$(S₂CN$RR'$), $M$ = Cu$^{I}$ and Ag$^{I}$, to include trialkylphosphane species. It was during these studies that the title compound, (I), was isolated as an incomplete reaction product from the 1:2:1 reaction between CuCl, Et₃P and NH₄[S₂CN(CH₂)₄]. Herein, the crystal and molecular structures of (I) are described along with a detailed analysis of the Hirshfeld surface.

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

| | | | |
|---|---|---|---|
| Cu1—Cl1 | 2.3474 (5) | Cu2—P2 | 2.2018 (6) |
| Cu1—Cl2 | 2.5809 (5) | Cu3—Cl2 | 2.3912 (5) |
| Cu1—S1 | 2.3282 (5) | Cu3—S1 | 2.4002 (5) |
| Cu1—P1 | 2.1936 (5) | Cu3—S2 | 2.4939 (5) |
| Cu2—Cl1 | 2.3640 (5) | Cu3—P3 | 2.1841 (5) |
| Cu2—Cl2 | 2.5324 (5) | S1—C1 | 1.7367 (19) |
| Cu2—S2 | 2.3556 (5) | S2—C1 | 1.7330 (19) |
| | | | |
| Cl1—Cu1—Cl2 | 96.188 (18) | Cl2—Cu2—S2 | 97.904 (18) |
| Cl1—Cu1—S1 | 104.585 (19) | Cl2—Cu2—P2 | 112.82 (2) |
| Cl1—Cu1—P1 | 115.51 (2) | S2—Cu2—P2 | 124.87 (2) |
| Cl2—Cu1—S1 | 100.954 (18) | Cl2—Cu3—S1 | 104.566 (18) |
| Cl2—Cu1—P1 | 108.90 (2) | Cl2—Cu3—S2 | 98.030 (18) |
| S1—Cu1—P1 | 125.81 (2) | Cl2—Cu3—P3 | 118.56 (2) |
| Cl1—Cu2—Cl2 | 97.080 (18) | S1—Cu3—S2 | 74.935 (17) |
| Cl1—Cu2—S2 | 106.406 (19) | S1—Cu3—P3 | 127.39 (2) |
| Cl1—Cu2—P2 | 113.35 (2) | S2—Cu3—P3 | 123.04 (2) |

## 2. Structural commentary

The molecular structure of (I), Fig. 1, represents a neutral, trinuclear $Cu^I$ complex comprising three monodentate phosphane ligands, two chlorido anions, one $\mu_3$- and the other $\mu_2$-bridging, and a dithiocarbamate ligand. The latter is tetra-coordinating, chelating the Cu3 atom, and each sulfur atom also bridges another $Cu^I$ atom. As highlighted in Fig. 2, the $Cu_3Cl_2S_2$ atoms of the core occupy the corners of a distorted cube with the putative eighth position being occupied by the quaternary-carbon atom of the dithiocarbamate ligand. As listed in Table 1, there are systematic trends in the Cu—donor-atom bond lengths. To a first approximation, the Cu—P bond lengths are about the same. As anticipated for the Cu1 and Cu2 atoms, the Cu—Cl bond lengths involving the $\mu_3$-chlorido ligand are systematically longer than those formed with the $\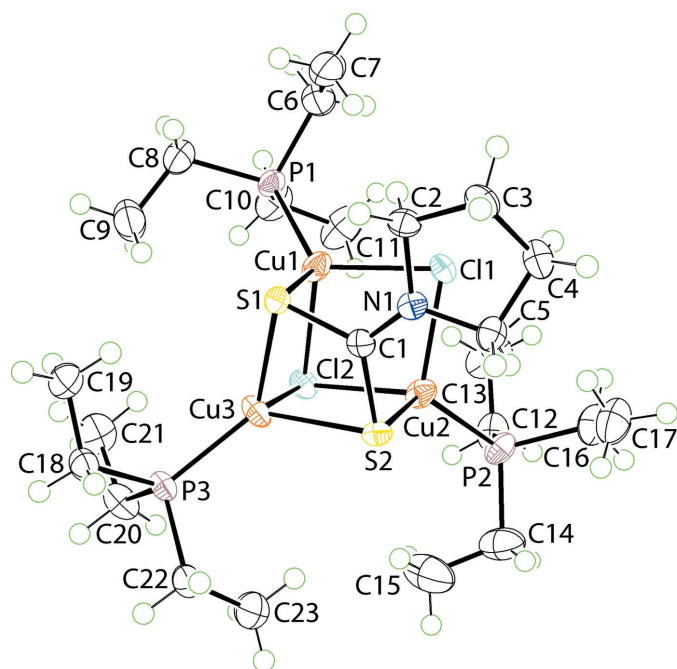mu_2$-chlorido ligand. Despite being chelated by the dithio-carbamate ligand, the Cu3 atom forms longer Cu—S bond lengths than do the Cu1 and Cu2 atoms, an observation correlated with the presence of two electronegative chloride anions in the donor sets for the latter.

The coordination geometries for the Cu1 and Cu2 atoms are based on $Cl_2PS$ donor sets while that of Cu3 is based on a $ClPS_2$ donor set, Table 1. While being based on tetrahedra, the coordination geometries exhibit wide ranges of angles subtended at the copper atoms, i.e. 30, 28 and 53°, respectively. The wider range of angles about the Cu3 atom can be traced, in part, to the acute angle subtended by the dithiocarbamate ligand. A measure of the geometry defined by a four-atom donor set is $\tau_4$ (Yang et al., 2007). Based on this index, $\tau_4$ values of 1 and 0 are computed for ideal tetrahedral and square-planar geometries, respectively. The $\tau_4$ values calculated for the Cu1–Cu3 atoms in (I) are 0.84, 0.86 and 0.78, respectively, i.e. consistent with distortions from tetrahedral geometries.

Reflecting the near equivalence in the pairs of Cu—S1 and Cu—S2 bonds, the associated C—S bond lengths are equal within experimental error, Table 1. Finally, the pyrrolidine ring is twisted about the C3—C4 bond.



**Figure 1**
The molecular structure of (I), showing the atom-labelling scheme and displacement ellipsoids at the 70% probability level.
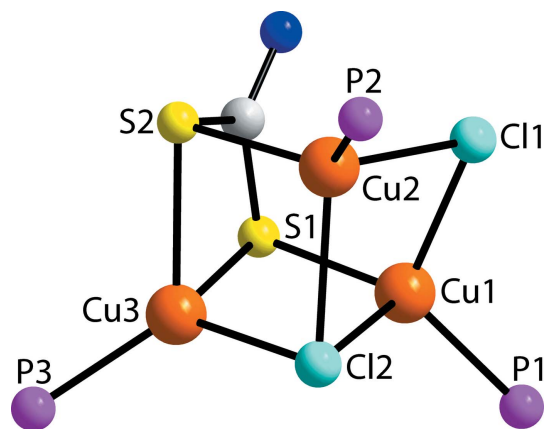


**Figure 2**
The molecular core in (I) highlighting the 'incomplete cube'.
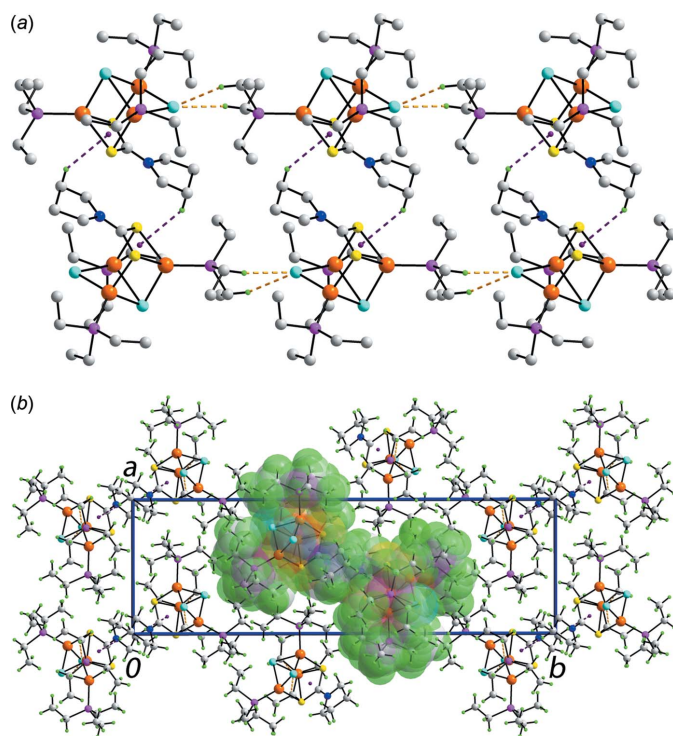
**Table 2**
Hydrogen-bond geometry (Å, °).

$Cg1$ is the centroid of the (Cu,S1,S2,C1) chelate ring.

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|---|---|---|---|---|
| C20—H20B$\cdots$Cl1[i] | 0.99 | 2.81 | 3.722 (2) | 154 |
| C22—H22B$\cdots$Cl1[i] | 0.99 | 2.80 | 3.720 (2) | 154 |
| C3—H3B$\cdots$Cg1[ii] | 0.99 | 2.83 | 3.705 (2) | 148 |

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

## 3. Supramolecular features

The key feature of the molecular packing in (I) is the formation of linear supramolecular chains along the $c$ axis, Fig. 3$a$ and Table 2. The $\mu_2$-chlorido ligand accepts two phosphane-methylene-C—H$\cdots$Cl type interactions to form a linear chain. Centrosymmetrically related chains are connected *via* pyrrolidine–methylene-C—H$\cdots\pi$(chelate) interactions where the chelate ring is defined by the Cu1,S1,S2,C1 atoms. Such C—H$\cdots\pi$(chelate) interactions are now well established in dithiocarbamate structural chemistry (Tiekink & Zukerman-Schpector, 2011) and are gaining greater recognition in coordination chemistry (Tiekink, 2017). The supramolecular chains pack in the crystal with no directional interactions between them, Fig. 3$b$.



**Figure 3**
The molecular packing in (I): ($a$) linear supramolecular chain mediated by methylene-C—H$\cdots$Cl (orange dashed lines) and methylene-C—H$\cdots\pi$(chelate) (blue) interactions aligned along the $c$ axis and ($b$) view of the unit-cell contents in projection down the $c$ axis. One chain is highlighted in space-filling mode.

## 4. Hirshfeld surface analysis

The Hirshfeld surface analysis of (I) was performed in accord with a recent study of a related dithiocarbamate complex (Jotani *et al.*, 2016). The presence of tiny red spots near the Cl1 and methylene-H20$B$ and H22$B$ atoms on the Hirshfeld surfaces mapped over $d_{\text{norm}}$ in Fig. 4 is indicative of the double-acceptor (C—H)$_2\cdots$Cl interaction. In the view of the Hirshfeld surface mapped over the calculated electrostatic potential in Fig. 5, the light-blue and pale-red regions around the electropositive and electronegative atoms result from the polarization of charges about the donors and acceptors, respectively, of the intermolecular interactions. The immediate environments about a reference molecule within the shape-index-mapped Hirshfeld surfaces in Fig. 6$a$ and $b$ highlight the intermolecular C—H$\cdots$Cl and C—H$\cdots\pi$(chelate) interactions, respectively.



**Figure 4**
Two views of the Hirshfeld surface for (I) mapped over $d_{\text{norm}}$ over the range −0.016 to 1.529 au.

**Table 3**
Percentage contribution of interatomic contacts to the Hirshfeld surface for (I).

| Contact | percentage contribution |
|---|---|
| H···H | 86.6 |
| Cl···H/H···Cl | 5.8 |
| S···H/H···S | 5.7 |
| C···H/H···C | 1.1 |
| Cu···H/H···Cu | 0.4 |
| N···H/H···N | 0.3 |
| C···N / N···C | 0.1 |

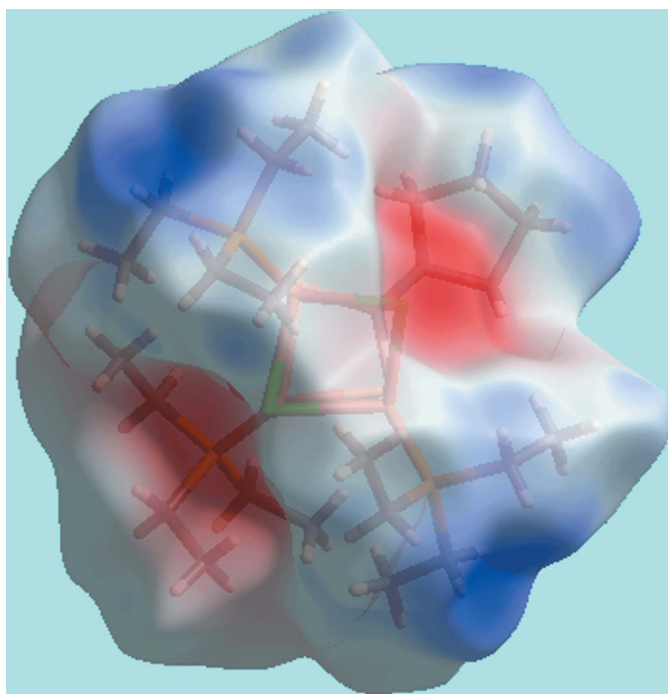The two-dimensional fingerprint plots for (I), *i.e.* the overall, Fig. 7a, and those delineated into H···H, Cl···H/H···Cl and S···H/H···S contacts (McKinnon *et al.*, 2007) in Fig. 7b–d, respectively, provide further information on the intermolecular interactions present in the crystal. It is evident from the fingerprint plot delineated into H···H contacts, Fig. 7b, that the hydrogen atoms of the triethylphosphane and pyrrolidine ligands make the greatest contribution, *i.e.* 86.6%, to the Hirshfeld surface, but at distances greater than the sum of the van der Waals radii. The pair of tips at $d_e + d_i \sim 2.8$ Å in the arrow-like distribution of points in the plot for Cl···H/H···Cl contacts, Fig. 7c, represent the intermolecular C—H···Cl interactions. A pair of short spikes at $d_e + d_i \sim 3.0$ Å in the S···H/H···S delineated plot, Fig. 7d, and the 5.8% contribution to Hirshfeld surfaces along with the small but significant contributions from C···H/H···C and Cu···H/H···Cu contacts, Table 3, to the Hirshfeld surface are all indicative of the C—H···$\pi$(chelate) interaction, Fig. 3a and Table 2. The small contributions from the other interatomic contacts, namely N···H/H···N and C···N/N···C, have little effect on the packing of the crystal.

## 5. Database survey

The isolated $Cu_3(\mu_3$-Cl$)(\mu_2$-Cl$)S_2$ core observed in (I) appears to be rare in the literature, being structurally observed only in one other structure with general formula, $M_3(\mu_3$-X$)(\mu_2$-X$)S_2$, incidentally, a dithiocarbamate complex. Thus, in the Ru$^{II}$ species, $Ru_3(CO)_3(S_2CNEt_2)_4Cl_2$, a discrete $Ru_3(\mu_3$-Cl$)(\mu_2$-Cl$)S_2$ core is found but where the $\mu_2$-S sulfur atoms are derived from four dithiocarbamate ligands and each Ru$^{II}$ atom is coordinated by two additional sulfur donor atoms leading to *trans*-RuCClS$_4$ octahedral coordination geometries (Raston & White, 1975). While other structures are known with the specified core, the core is embedded within higher nuclearity clusters or in coordination polymers.



(a)

(b)

**Figure 6**
Views of Hirshfeld surface for a reference molecule in (I) mapped over the shape-index property highlighting the: (a) C—H···Cl interactions as red dashed lines and (b) C—H···$\pi$(chelate) interactions as white dashed lines
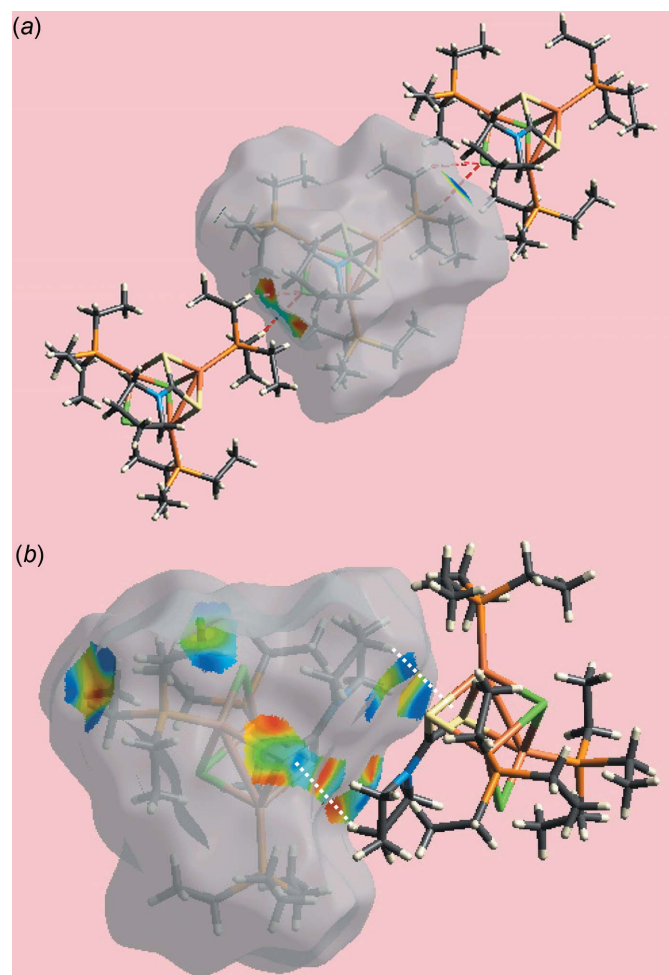


**Figure 5**
A view of the Hirshfeld surface for (I) mapped over the calculated electrostatic potential in the range −0.071 to 0.030 au. The red and blue regions represent negative and positive electrostatic potentials, respectively.
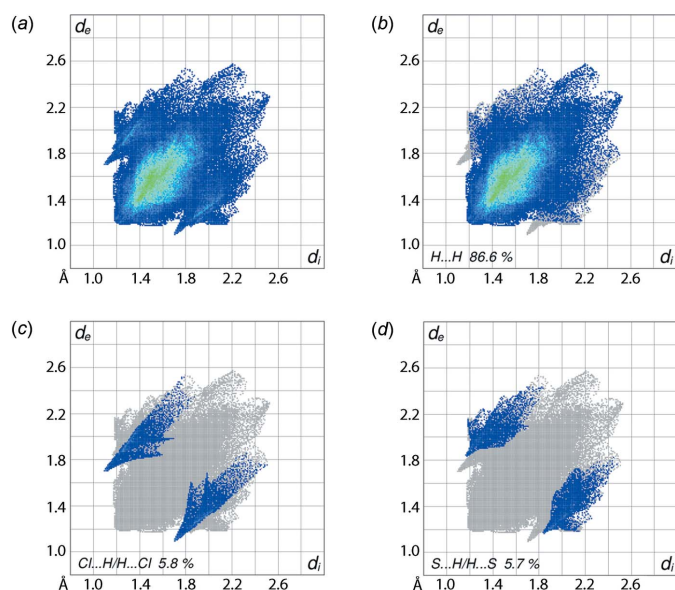
**Figure 7**
(*a*) The full two-dimensional fingerprint plot for (I) and fingerprint plots delineated into (*b*) H⋯H, (*c*) Cl⋯H/H⋯Cl and (*d*) S⋯H/H⋯S contacts.

**Table 4**
Experimental details.

| | |
|---|---|
| Crystal data | |
| Chemical formula | $[Cu_3(C_5H_8NS_2)Cl_2(C_6H_{15}P)_3]$ |
| $M_r$ | 762.21 |
| Crystal system, space group | Monoclinic, $P2_1/n$ |
| Temperature (K) | 100 |
| $a$, $b$, $c$ (Å) | 10.6489 (2), 31.7578 (4), 10.7212 (2) |
| $\beta$ (°) | 108.607 (2) |
| $V$ (Å$^3$) | 3436.24 (11) |
| $Z$ | 4 |
| Radiation type | Cu $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 6.14 |
| Crystal size (mm) | $0.20 \times 0.09 \times 0.07$ |
| | |
| Data collection | |
| Diffractometer | Agilent SuperNova, Dual, Cu at zero, AtlasS2 |
| Absorption correction | Multi-scan (*CrysAlis PRO*; Rigaku Oxford Diffraction, 2015) |
| $T_{min}$, $T_{max}$ | 0.684, 1.000 |
| No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections | 34566, 7186, 6699 |
| $R_{int}$ | 0.027 |
| $(\sin\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.631 |
| | |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.028, 0.073, 1.04 |
| No. of reflections | 7186 |
| No. of parameters | 316 |
| H-atom treatment | H-atom parameters constrained |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 1.50, −0.79 |

Computer programs: *CrysAlis PRO* (Rigaku Oxford Diffraction, 2015), *SHELXS* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012), *DIAMOND* (Brandenburg, 2006) and *publCIF* (Westrip, 2010).

There are twenty crystal structure containing copper with dithiocarbamate and phosphane ligands in the crystallographic literature (Groom *et al.*, 2016). The majority, *i.e.* 12 conform to the tetrahedral CuP$_2$S$_2$ motif observed in the biologically active bis(phosphane)copper(I) dithiocarbamate compounds mentioned in the *Chemical Context* (Jamaludin *et al.* 2016; Tan *et al.*, 2016). Similar coordination geometries are found in two binuclear structures with bis(dithiocarbamate) ligands, as exemplified in (Ph$_3$P)$_2$CuS$_2$CN(CH$_2$CH$_2$)$_2$NCS$_2$Cu(PPh$_3$)$_2$ (Kumar *et al.*, 2009). There are two related complexes but with a 1:1:1 ratio of copper, dithiocarbamate and phosphane, as exemplified by [Et$_3$PCu(S$_2$CNEt$_2$)]$_2$ (Afzaal *et al.*, 2011). One of the remaining structures is neutral and octanuclear with formula (Ph$_3$P)$_4$Cu$_8$($\mu_4$-SC$_6$H$_4$Br-4)$_4$($\mu_2$-SC$_6$H$_4$Br-4)$_2$(S$_2$CNMe$_2$)$_2$·MeO(CH$_2$)$_2$OMe (Langer *et al.*, 2009). Here, each sulfur atom of the dithiocarbamate ligand bridges two different Cu$^I$ atoms. The common feature of the remaining three structures is that they are charged and feature bidentate phosphane ligands. The simplest of these is formulated as [(dppm)$_2$Cu$_2$(S$_2$CNMe$_2$)][ClO$_4$]$_2$·EtOH·0.25H$_2$O where the dithiocarbamate ligand is bidentate bridging as is the dppm ligand (Huang & Situ, 2003); dppm = Ph$_2$PCH$_2$PPh$_2$. In the trinuclear mono-cation {(dppm)$_3$Cu$_3$($\mu_3$-I)[S$_2$CN-(CH$_2$Ph)CH$_2$(2-thienyl)]}I, the dithiocarbamate ligand bridges two Cu$^I$ atoms and simultaneously coordinates a third Cu$^I$ atom *via* one of the sulfur atoms only (Rajput *et al.*, 2015). The final structure to be described is related to the former whereby one bis(phosphane) ligand has been replaced by a dithiocarbamate ligand with the ejection of the $\mu_3$-iodido species, *i.e.* {(dppf)$_2$Cu$_3$[S$_2$CN(CH$_2$Ph)CH$_2$Fc]$_2$}PF$_6$·CHCl$_3$ (Kishore *et al.*, 2016); dppf = Ph$_2$P($\eta^5$-C$_5$H$_4$)Fe($\eta^5$-C$_5$H$_4$)PPh$_2$ and Fc is ($\eta^5$-C$_5$H$_4$)Fe($\eta^5$-C$_5$H$_5$). In this structure, each dithiocarbamate ligand is tri-coordinate, binding to three different Cu$^I$ atoms.

From the foregoing, it is obvious there is considerable structural variability in these systems arising in part from the ability of the dithiocarbamate ligands to adopt quite diverse coordination modes.

## 6. Synthesis and crystallization

Complex (I) is an unexpected product from the *in situ* reaction of CuCl, Et$_3$P, and NH$_4$[S$_2$CN(CH$_2$)$_4$] in a 1:2:1 ratio. The preparation was as follows: NH$_4$[S$_2$CN(CH$_2$)$_4$] (Sigma–Aldrich, 0.5 mmol, 0.082 g) dissolved in isopropanol (5 ml) was added to an isopropanol solution (5 ml) of CuCl (Sigma–Aldrich, 0.5 mmol, 0.05 g) at room temperature. Then, a THF solution of Et$_3$P (Sigma–Aldrich; 1 ml (= 0.118 g), 1.0 mmol) was added to the reaction mixture followed by stirring for 2 h. The resulting mixture was filtered, diluted with hexane (2 ml) and mixed well. The mixture was left for evaporation at 227 K. A small number of yellow crystals of (I) were obtained after 5 d. Yield: 0.0095 g (4.26%), m.p. 330.8 K. IR (cm$^{-1}$): 1429(*s*) $\nu$(C—N); 1045(*m*), 993(*m*) $\nu$(C—S).

## 7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. Carbon-bound H atoms were placed in calculated positions (C—H = 0.98–0.99 Å) and were

included in the refinement in the riding model approximation, with $U_{iso}$(H) set to 1.2–1.5$U_{eq}$(C).

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# supporting information

## *μ*₃-Chlorido-*μ*₂-chlorido-(*μ*₃-pyrrolidine-1-carbodithioato-*κ*⁴*S:S,S′:S′*)tris[(tri-ethylphosphane-*κP*)copper(I)]: crystal structure and Hirshfeld surface analysis

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**Computing details**

Data collection: *CrysAlis PRO* (Rigaku Oxford Diffraction, 2015); cell refinement: *CrysAlis PRO* (Rigaku Oxford Diffraction, 2015); data reduction: *CrysAlis PRO* (Rigaku Oxford Diffraction, 2015); program(s) used to solve structure: *SHELXS* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

**μ₃-Chlorido-μ₂-chlorido-(μ₃-pyrrolidine-1-carbodithioato-κ⁴S:S,S′:S′)tris[(triethylphosphane-κP)copper(I)]**

*Crystal data*

| | |
|---|---|
| $[Cu_3(C_5H_8NS_2)Cl_2(C_6H_{15}P)_3]$ | $F(000) = 1584$ |
| $M_r = 762.21$ | $D_x = 1.473$ Mg m⁻³ |
| Monoclinic, $P2_1/n$ | Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å |
| $a = 10.6489$ (2) Å | Cell parameters from 16968 reflections |
| $b = 31.7578$ (4) Å | $\theta = 2.8–76.3°$ |
| $c = 10.7212$ (2) Å | $\mu = 6.14$ mm⁻¹ |
| $\beta = 108.607$ (2)° | $T = 100$ K |
| $V = 3436.24$ (11) Å³ | Prism, yellow |
| $Z = 4$ | $0.20 \times 0.09 \times 0.07$ mm |

*Data collection*

| | |
|---|---|
| Agilent SuperNova, Dual, Cu at zero, AtlasS2 diffractometer | 34566 measured reflections |
| | 7186 independent reflections |
| Radiation source: micro-focus sealed X-ray tube | 6699 reflections with $I > 2\sigma(I)$ |
| Mirror monochromator | $R_{int} = 0.027$ |
| Detector resolution: 10.4607 pixels mm⁻¹ | $\theta_{max} = 76.6°$, $\theta_{min} = 2.8°$ |
| $\omega$ scans | $h = -13 \rightarrow 12$ |
| Absorption correction: multi-scan | $k = -39 \rightarrow 29$ |
| (CrysAlisPro; Rigaku Oxford Diffraction, 2015) | $l = -13 \rightarrow 13$ |
| $T_{min} = 0.684$, $T_{max} = 1.000$ | |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Hydrogen site location: inferred from neighbouring sites |
| Least-squares matrix: full | |
| $R[F^2 > 2\sigma(F^2)] = 0.028$ | H-atom parameters constrained |
| $wR(F^2) = 0.073$ | $w = 1/[\sigma^2(F_o^2) + (0.0334P)^2 + 3.4591P]$ |
| $S = 1.04$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| 7186 reflections | $(\Delta/\sigma)_{max} = 0.002$ |
| 316 parameters | $\Delta\rho_{max} = 1.50$ e Å⁻³ |
| 0 restraints | $\Delta\rho_{min} = -0.79$ e Å⁻³ |

*Special details*

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

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)*

|  | $x$ | $y$ | $z$ | $U_{iso}*/U_{eq}$ |
|---|---|---|---|---|
| Cu1 | 0.15403 (3) | 0.60427 (2) | 0.46213 (3) | 0.02150 (8) |
| Cu2 | 0.41213 (3) | 0.65484 (2) | 0.54323 (3) | 0.02075 (8) |
| Cu3 | 0.29958 (3) | 0.60979 (2) | 0.26251 (3) | 0.02196 (8) |
| Cl1 | 0.29973 (4) | 0.62046 (2) | 0.67210 (4) | 0.01860 (9) |
| Cl2 | 0.21102 (4) | 0.66892 (2) | 0.34453 (4) | 0.01933 (9) |
| S1 | 0.26010 (4) | 0.55091 (2) | 0.38531 (4) | 0.01620 (9) |
| S2 | 0.50822 (4) | 0.60146 (2) | 0.45081 (4) | 0.01641 (9) |
| P1 | −0.05739 (5) | 0.60624 (2) | 0.44227 (5) | 0.01844 (10) |
| P2 | 0.51349 (5) | 0.71293 (2) | 0.63413 (5) | 0.02172 (11) |
| P3 | 0.29464 (5) | 0.61039 (2) | 0.05729 (5) | 0.01832 (10) |
| N1 | 0.46529 (16) | 0.53980 (5) | 0.60120 (15) | 0.0162 (3) |
| C1 | 0.41813 (18) | 0.56133 (6) | 0.49156 (18) | 0.0152 (3) |
| C2 | 0.38664 (19) | 0.50826 (6) | 0.64599 (19) | 0.0190 (4) |
| H2A | 0.3621 | 0.4843 | 0.5840 | 0.023* |
| H2B | 0.3049 | 0.5210 | 0.6546 | 0.023* |
| C3 | 0.4799 (2) | 0.49415 (6) | 0.78003 (19) | 0.0222 (4) |
| H3A | 0.4297 | 0.4867 | 0.8403 | 0.027* |
| H3B | 0.5338 | 0.4697 | 0.7709 | 0.027* |
| C4 | 0.5667 (2) | 0.53283 (6) | 0.82932 (19) | 0.0238 (4) |
| H4A | 0.5202 | 0.5540 | 0.8665 | 0.029* |
| H4B | 0.6510 | 0.5250 | 0.8972 | 0.029* |
| C5 | 0.59098 (19) | 0.54950 (6) | 0.70556 (19) | 0.0201 (4) |
| H5A | 0.6084 | 0.5802 | 0.7119 | 0.024* |
| H5B | 0.6666 | 0.5349 | 0.6896 | 0.024* |
| C6 | −0.0943 (2) | 0.58600 (9) | 0.5866 (2) | 0.0350 (5) |
| H6A | −0.0571 | 0.6055 | 0.6612 | 0.042* |
| H6B | −0.1916 | 0.5853 | 0.5674 | 0.042* |
| C7 | −0.0388 (3) | 0.54232 (9) | 0.6268 (3) | 0.0417 (6) |
| H7A | −0.0801 | 0.5224 | 0.5558 | 0.063* |
| H7B | −0.0576 | 0.5337 | 0.7068 | 0.063* |
| H7C | 0.0572 | 0.5426 | 0.6437 | 0.063* |
| C8 | −0.1738 (2) | 0.57717 (7) | 0.3059 (2) | 0.0285 (4) |
| H8A | −0.1613 | 0.5466 | 0.3233 | 0.034* |
| H8B | −0.2656 | 0.5844 | 0.3014 | 0.034* |
| C9 | −0.1549 (3) | 0.58705 (9) | 0.1739 (2) | 0.0379 (6) |
| H9A | −0.1690 | 0.6172 | 0.1553 | 0.057* |
| H9B | −0.2189 | 0.5709 | 0.1043 | 0.057* |
| H9C | −0.0647 | 0.5794 | 0.1772 | 0.057* |
| C10 | −0.1319 (2) | 0.65879 (8) | 0.4228 (3) | 0.0332 (5) |

| H10A | −0.1436 | 0.6691 | 0.3326 | 0.040* |
|------|---------|--------|--------|--------|
| H10B | −0.2207 | 0.6569 | 0.4335 | 0.040* |
| C11 | −0.0480 (3) | 0.69041 (8) | 0.5220 (3) | 0.0432 (6) |
| H11A | −0.0424 | 0.6817 | 0.6112 | 0.065* |
| H11B | −0.0890 | 0.7183 | 0.5040 | 0.065* |
| H11C | 0.0412 | 0.6915 | 0.5144 | 0.065* |
| C12 | 0.4059 (2) | 0.75778 (7) | 0.6313 (2) | 0.0287 (5) |
| H12A | 0.4587 | 0.7807 | 0.6861 | 0.034* |
| H12B | 0.3690 | 0.7683 | 0.5400 | 0.034* |
| C13 | 0.2925 (3) | 0.74600 (9) | 0.6827 (3) | 0.0435 (6) |
| H13A | 0.2441 | 0.7219 | 0.6328 | 0.065* |
| H13B | 0.2322 | 0.7700 | 0.6723 | 0.065* |
| H13C | 0.3284 | 0.7385 | 0.7761 | 0.065* |
| C14 | 0.6344 (3) | 0.73513 (8) | 0.5657 (3) | 0.0387 (6) |
| H14A | 0.6573 | 0.7640 | 0.5999 | 0.046* |
| H14B | 0.7163 | 0.7180 | 0.5937 | 0.046* |
| C15 | 0.5811 (4) | 0.73634 (9) | 0.4171 (3) | 0.0517 (8) |
| H15A | 0.5621 | 0.7076 | 0.3830 | 0.078* |
| H15B | 0.6471 | 0.7491 | 0.3828 | 0.078* |
| H15C | 0.4995 | 0.7531 | 0.3893 | 0.078* |
| C16 | 0.6077 (2) | 0.70895 (7) | 0.8114 (2) | 0.0322 (5) |
| H16A | 0.6675 | 0.7335 | 0.8377 | 0.039* |
| H16B | 0.5451 | 0.7098 | 0.8626 | 0.039* |
| C17 | 0.6886 (3) | 0.66909 (9) | 0.8443 (3) | 0.0393 (6) |
| H17A | 0.6292 | 0.6447 | 0.8289 | 0.059* |
| H17B | 0.7439 | 0.6697 | 0.9369 | 0.059* |
| H17C | 0.7454 | 0.6669 | 0.7884 | 0.059* |
| C18 | 0.2471 (2) | 0.56150 (6) | −0.03875 (19) | 0.0223 (4) |
| H18A | 0.2167 | 0.5687 | −0.1335 | 0.027* |
| H18B | 0.3265 | 0.5434 | −0.0219 | 0.027* |
| C19 | 0.1383 (2) | 0.53638 (7) | −0.0080 (2) | 0.0291 (5) |
| H19A | 0.1670 | 0.5292 | 0.0858 | 0.044* |
| H19B | 0.1209 | 0.5105 | −0.0604 | 0.044* |
| H19C | 0.0573 | 0.5533 | −0.0297 | 0.044* |
| C20 | 0.1873 (2) | 0.65065 (7) | −0.0452 (2) | 0.0262 (4) |
| H20A | 0.2228 | 0.6788 | −0.0128 | 0.031* |
| H20B | 0.1890 | 0.6478 | −0.1366 | 0.031* |
| C21 | 0.0443 (2) | 0.64775 (8) | −0.0457 (2) | 0.0336 (5) |
| H21A | 0.0058 | 0.6210 | −0.0855 | 0.050* |
| H21B | −0.0069 | 0.6712 | −0.0969 | 0.050* |
| H21C | 0.0422 | 0.6492 | 0.0448 | 0.050* |
| C22 | 0.4553 (2) | 0.62219 (7) | 0.0359 (2) | 0.0237 (4) |
| H22A | 0.5156 | 0.5980 | 0.0675 | 0.028* |
| H22B | 0.4427 | 0.6259 | −0.0590 | 0.028* |
| C23 | 0.5198 (3) | 0.66167 (8) | 0.1099 (2) | 0.0358 (5) |
| H23A | 0.4631 | 0.6861 | 0.0754 | 0.054* |
| H23B | 0.6064 | 0.6660 | 0.0981 | 0.054* |
| H23C | 0.5312 | 0.6583 | 0.2038 | 0.054* |

*Atomic displacement parameters (Å²)*

|  | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Cu1 | 0.01310 (14) | 0.02656 (16) | 0.02473 (15) | −0.00123 (11) | 0.00588 (11) | −0.00501 (12) |
| Cu2 | 0.02180 (15) | 0.01514 (14) | 0.02611 (15) | −0.00383 (11) | 0.00876 (12) | −0.00443 (11) |
| Cu3 | 0.03038 (17) | 0.02277 (15) | 0.01416 (14) | 0.00065 (12) | 0.00914 (12) | 0.00068 (11) |
| Cl1 | 0.0220 (2) | 0.0212 (2) | 0.01358 (18) | 0.00073 (16) | 0.00701 (16) | −0.00123 (15) |
| Cl2 | 0.0218 (2) | 0.0185 (2) | 0.0179 (2) | 0.00308 (16) | 0.00661 (17) | 0.00183 (15) |
| S1 | 0.0173 (2) | 0.0152 (2) | 0.0159 (2) | −0.00239 (15) | 0.00490 (16) | −0.00200 (15) |
| S2 | 0.0158 (2) | 0.0155 (2) | 0.0199 (2) | −0.00078 (15) | 0.00855 (17) | −0.00004 (16) |
| P1 | 0.0128 (2) | 0.0219 (2) | 0.0203 (2) | −0.00112 (17) | 0.00482 (18) | −0.00132 (18) |
| P2 | 0.0190 (2) | 0.0146 (2) | 0.0294 (3) | −0.00147 (17) | 0.0047 (2) | −0.00271 (19) |
| P3 | 0.0240 (2) | 0.0181 (2) | 0.0136 (2) | 0.00122 (18) | 0.00702 (18) | −0.00037 (17) |
| N1 | 0.0171 (7) | 0.0130 (7) | 0.0189 (7) | 0.0005 (6) | 0.0064 (6) | −0.0003 (6) |
| C1 | 0.0172 (8) | 0.0131 (8) | 0.0169 (8) | 0.0018 (6) | 0.0078 (7) | −0.0028 (6) |
| C2 | 0.0225 (9) | 0.0150 (9) | 0.0210 (9) | 0.0001 (7) | 0.0088 (8) | 0.0029 (7) |
| C3 | 0.0296 (11) | 0.0186 (9) | 0.0196 (9) | 0.0032 (8) | 0.0096 (8) | 0.0026 (7) |
| C4 | 0.0299 (11) | 0.0213 (10) | 0.0177 (9) | 0.0030 (8) | 0.0038 (8) | −0.0001 (7) |
| C5 | 0.0190 (9) | 0.0173 (9) | 0.0212 (9) | 0.0013 (7) | 0.0024 (7) | 0.0000 (7) |
| C6 | 0.0254 (11) | 0.0531 (15) | 0.0265 (11) | −0.0062 (10) | 0.0082 (9) | 0.0025 (10) |
| C7 | 0.0346 (13) | 0.0498 (16) | 0.0327 (12) | −0.0154 (11) | −0.0005 (10) | 0.0135 (11) |
| C8 | 0.0230 (10) | 0.0317 (11) | 0.0286 (11) | −0.0046 (9) | 0.0050 (8) | −0.0029 (9) |
| C9 | 0.0364 (13) | 0.0504 (15) | 0.0243 (11) | −0.0012 (11) | 0.0062 (10) | −0.0042 (10) |
| C10 | 0.0245 (11) | 0.0307 (12) | 0.0426 (13) | 0.0035 (9) | 0.0083 (10) | −0.0036 (10) |
| C11 | 0.0314 (13) | 0.0334 (13) | 0.0651 (18) | −0.0017 (10) | 0.0159 (12) | −0.0186 (12) |
| C12 | 0.0337 (12) | 0.0184 (10) | 0.0300 (11) | 0.0038 (8) | 0.0045 (9) | −0.0029 (8) |
| C13 | 0.0337 (13) | 0.0317 (13) | 0.0680 (18) | 0.0024 (10) | 0.0204 (13) | −0.0126 (12) |
| C14 | 0.0443 (14) | 0.0300 (12) | 0.0513 (15) | −0.0103 (10) | 0.0286 (13) | −0.0079 (11) |
| C15 | 0.085 (2) | 0.0332 (14) | 0.0538 (17) | −0.0146 (14) | 0.0455 (17) | −0.0111 (12) |
| C16 | 0.0313 (12) | 0.0290 (11) | 0.0310 (11) | −0.0019 (9) | 0.0027 (9) | −0.0041 (9) |
| C17 | 0.0324 (13) | 0.0386 (14) | 0.0374 (13) | −0.0003 (10) | −0.0021 (10) | 0.0007 (11) |
| C18 | 0.0281 (10) | 0.0209 (9) | 0.0181 (9) | −0.0013 (8) | 0.0076 (8) | −0.0014 (7) |
| C19 | 0.0319 (12) | 0.0264 (11) | 0.0281 (11) | −0.0069 (9) | 0.0084 (9) | −0.0022 (8) |
| C20 | 0.0341 (11) | 0.0236 (10) | 0.0232 (10) | 0.0101 (8) | 0.0123 (9) | 0.0034 (8) |
| C21 | 0.0300 (12) | 0.0345 (12) | 0.0349 (12) | 0.0096 (9) | 0.0082 (10) | 0.0020 (10) |
| C22 | 0.0269 (10) | 0.0260 (10) | 0.0185 (9) | −0.0022 (8) | 0.0074 (8) | −0.0019 (8) |
| C23 | 0.0417 (14) | 0.0367 (13) | 0.0304 (12) | −0.0135 (11) | 0.0132 (10) | −0.0083 (10) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Cu1—Cl1 | 2.3474 (5) | C8—H8B | 0.9900 |
| Cu1—Cl2 | 2.5809 (5) | C9—H9A | 0.9800 |
| Cu1—S1 | 2.3282 (5) | C9—H9B | 0.9800 |
| Cu1—P1 | 2.1936 (5) | C9—H9C | 0.9800 |
| Cu2—Cl1 | 2.3640 (5) | C10—C11 | 1.527 (3) |
| Cu2—Cl2 | 2.5324 (5) | C10—H10A | 0.9900 |
| Cu2—S2 | 2.3556 (5) | C10—H10B | 0.9900 |
| Cu2—P2 | 2.2018 (6) | C11—H11A | 0.9800 |

| | | | |
|---|---|---|---|
| Cu3—Cl2 | 2.3912 (5) | C11—H11B | 0.9800 |
| Cu3—S1 | 2.4002 (5) | C11—H11C | 0.9800 |
| Cu3—S2 | 2.4939 (5) | C12—C13 | 1.526 (4) |
| Cu3—P3 | 2.1841 (5) | C12—H12A | 0.9900 |
| Cu1—Cu3 | 3.0216 (4) | C12—H12B | 0.9900 |
| S1—C1 | 1.7367 (19) | C13—H13A | 0.9800 |
| S2—C1 | 1.7330 (19) | C13—H13B | 0.9800 |
| P1—C10 | 1.831 (2) | C13—H13C | 0.9800 |
| P1—C8 | 1.836 (2) | C14—C15 | 1.511 (4) |
| P1—C6 | 1.830 (2) | C14—H14A | 0.9900 |
| P2—C14 | 1.816 (2) | C14—H14B | 0.9900 |
| P2—C12 | 1.822 (2) | C15—H15A | 0.9800 |
| P2—C16 | 1.849 (2) | C15—H15B | 0.9800 |
| P3—C20 | 1.830 (2) | C15—H15C | 0.9800 |
| P3—C22 | 1.836 (2) | C16—C17 | 1.508 (3) |
| P3—C18 | 1.842 (2) | C16—H16A | 0.9900 |
| N1—C1 | 1.313 (2) | C16—H16B | 0.9900 |
| N1—C5 | 1.477 (2) | C17—H17A | 0.9800 |
| N1—C2 | 1.480 (2) | C17—H17B | 0.9800 |
| C2—C3 | 1.530 (3) | C17—H17C | 0.9800 |
| C2—H2A | 0.9900 | C18—C19 | 1.526 (3) |
| C2—H2B | 0.9900 | C18—H18A | 0.9900 |
| C3—C4 | 1.527 (3) | C18—H18B | 0.9900 |
| C3—H3A | 0.9900 | C19—H19A | 0.9800 |
| C3—H3B | 0.9900 | C19—H19B | 0.9800 |
| C4—C5 | 1.526 (3) | C19—H19C | 0.9800 |
| C4—H4A | 0.9900 | C20—C21 | 1.523 (3) |
| C4—H4B | 0.9900 | C20—H20A | 0.9900 |
| C5—H5A | 0.9900 | C20—H20B | 0.9900 |
| C5—H5B | 0.9900 | C21—H21A | 0.9800 |
| C6—C7 | 1.515 (4) | C21—H21B | 0.9800 |
| C6—H6A | 0.9900 | C21—H21C | 0.9800 |
| C6—H6B | 0.9900 | C22—C23 | 1.525 (3) |
| C7—H7A | 0.9800 | C22—H22A | 0.9900 |
| C7—H7B | 0.9800 | C22—H22B | 0.9900 |
| C7—H7C | 0.9800 | C23—H23A | 0.9800 |
| C8—C9 | 1.524 (3) | C23—H23B | 0.9800 |
| C8—H8A | 0.9900 | C23—H23C | 0.9800 |
| | | | |
| Cl1—Cu1—Cl2 | 96.188 (18) | C9—C8—P1 | 112.35 (16) |
| Cl1—Cu1—S1 | 104.585 (19) | C9—C8—H8A | 109.1 |
| Cl1—Cu1—P1 | 115.51 (2) | P1—C8—H8A | 109.1 |
| Cl2—Cu1—S1 | 100.954 (18) | C9—C8—H8B | 109.1 |
| Cl2—Cu1—P1 | 108.90 (2) | P1—C8—H8B | 109.1 |
| S1—Cu1—P1 | 125.81 (2) | H8A—C8—H8B | 107.9 |
| Cl1—Cu2—Cl2 | 97.080 (18) | C8—C9—H9A | 109.5 |
| Cl1—Cu2—S2 | 106.406 (19) | C8—C9—H9B | 109.5 |
| Cl1—Cu2—P2 | 113.35 (2) | H9A—C9—H9B | 109.5 |

| | | | |
|---|---|---|---|
| Cl2—Cu2—S2 | 97.904 (18) | C8—C9—H9C | 109.5 |
| Cl2—Cu2—P2 | 112.82 (2) | H9A—C9—H9C | 109.5 |
| S2—Cu2—P2 | 124.87 (2) | H9B—C9—H9C | 109.5 |
| Cl2—Cu3—S1 | 104.566 (18) | C11—C10—P1 | 112.60 (17) |
| Cl2—Cu3—S2 | 98.030 (18) | C11—C10—H10A | 109.1 |
| Cl2—Cu3—P3 | 118.56 (2) | P1—C10—H10A | 109.1 |
| S1—Cu3—S2 | 74.935 (17) | C11—C10—H10B | 109.1 |
| S1—Cu3—P3 | 127.39 (2) | P1—C10—H10B | 109.1 |
| S2—Cu3—P3 | 123.04 (2) | H10A—C10—H10B | 107.8 |
| P1—Cu1—Cu3 | 132.231 (19) | C10—C11—H11A | 109.5 |
| S1—Cu1—Cu3 | 51.338 (13) | C10—C11—H11B | 109.5 |
| Cl1—Cu1—Cu3 | 109.575 (16) | H11A—C11—H11B | 109.5 |
| Cl2—Cu1—Cu3 | 49.769 (12) | C10—C11—H11C | 109.5 |
| P3—Cu3—Cu1 | 149.44 (2) | H11A—C11—H11C | 109.5 |
| Cl2—Cu3—Cu1 | 55.492 (13) | H11B—C11—H11C | 109.5 |
| S1—Cu3—Cu1 | 49.237 (13) | C13—C12—P2 | 111.61 (16) |
| S2—Cu3—Cu1 | 86.926 (14) | C13—C12—H12A | 109.3 |
| Cu1—Cl1—Cu2 | 81.004 (17) | P2—C12—H12A | 109.3 |
| Cu3—Cl2—Cu2 | 81.010 (16) | C13—C12—H12B | 109.3 |
| Cu3—Cl2—Cu1 | 74.739 (16) | P2—C12—H12B | 109.3 |
| Cu2—Cl2—Cu1 | 73.508 (15) | H12A—C12—H12B | 108.0 |
| C1—S1—Cu1 | 96.15 (6) | C12—C13—H13A | 109.5 |
| C1—S1—Cu3 | 84.76 (6) | C12—C13—H13B | 109.5 |
| Cu1—S1—Cu3 | 79.425 (17) | H13A—C13—H13B | 109.5 |
| C1—S2—Cu2 | 94.21 (6) | C12—C13—H13C | 109.5 |
| C1—S2—Cu3 | 81.97 (6) | H13A—C13—H13C | 109.5 |
| Cu2—S2—Cu3 | 82.517 (17) | H13B—C13—H13C | 109.5 |
| C10—P1—C8 | 102.12 (11) | C15—C14—P2 | 111.1 (2) |
| C10—P1—C6 | 102.40 (12) | C15—C14—H14A | 109.4 |
| C8—P1—C6 | 102.94 (11) | P2—C14—H14A | 109.4 |
| C10—P1—Cu1 | 115.53 (8) | C15—C14—H14B | 109.4 |
| C8—P1—Cu1 | 118.31 (8) | P2—C14—H14B | 109.4 |
| C6—P1—Cu1 | 113.48 (8) | H14A—C14—H14B | 108.0 |
| C14—P2—C12 | 102.29 (12) | C14—C15—H15A | 109.5 |
| C14—P2—C16 | 102.70 (13) | C14—C15—H15B | 109.5 |
| C12—P2—C16 | 101.70 (11) | H15A—C15—H15B | 109.5 |
| C14—P2—Cu2 | 117.20 (8) | C14—C15—H15C | 109.5 |
| C12—P2—Cu2 | 115.53 (8) | H15A—C15—H15C | 109.5 |
| C16—P2—Cu2 | 115.24 (8) | H15B—C15—H15C | 109.5 |
| C20—P3—C22 | 102.17 (10) | C17—C16—P2 | 112.33 (17) |
| C20—P3—C18 | 104.21 (10) | C17—C16—H16A | 109.1 |
| C22—P3—C18 | 101.71 (10) | P2—C16—H16A | 109.1 |
| C20—P3—Cu3 | 114.89 (7) | C17—C16—H16B | 109.1 |
| C22—P3—Cu3 | 113.81 (7) | P2—C16—H16B | 109.1 |
| C18—P3—Cu3 | 118.01 (7) | H16A—C16—H16B | 107.9 |
| C1—N1—C5 | 124.37 (16) | C16—C17—H17A | 109.5 |
| C1—N1—C2 | 123.24 (16) | C16—C17—H17B | 109.5 |
| C5—N1—C2 | 111.41 (15) | H17A—C17—H17B | 109.5 |

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| N1—C1—S2 | 121.62 (14) | C16—C17—H17C | 109.5 |
| N1—C1—S1 | 120.11 (14) | H17A—C17—H17C | 109.5 |
| S2—C1—S1 | 118.25 (11) | H17B—C17—H17C | 109.5 |
| N1—C2—C3 | 103.77 (16) | C19—C18—P3 | 114.33 (14) |
| N1—C2—H2A | 111.0 | C19—C18—H18A | 108.7 |
| C3—C2—H2A | 111.0 | P3—C18—H18A | 108.7 |
| N1—C2—H2B | 111.0 | C19—C18—H18B | 108.7 |
| C3—C2—H2B | 111.0 | P3—C18—H18B | 108.7 |
| H2A—C2—H2B | 109.0 | H18A—C18—H18B | 107.6 |
| C4—C3—C2 | 103.25 (15) | C18—C19—H19A | 109.5 |
| C4—C3—H3A | 111.1 | C18—C19—H19B | 109.5 |
| C2—C3—H3A | 111.1 | H19A—C19—H19B | 109.5 |
| C4—C3—H3B | 111.1 | C18—C19—H19C | 109.5 |
| C2—C3—H3B | 111.1 | H19A—C19—H19C | 109.5 |
| H3A—C3—H3B | 109.1 | H19B—C19—H19C | 109.5 |
| C5—C4—C3 | 103.30 (16) | C21—C20—P3 | 113.07 (16) |
| C5—C4—H4A | 111.1 | C21—C20—H20A | 109.0 |
| C3—C4—H4A | 111.1 | P3—C20—H20A | 109.0 |
| C5—C4—H4B | 111.1 | C21—C20—H20B | 109.0 |
| C3—C4—H4B | 111.1 | P3—C20—H20B | 109.0 |
| H4A—C4—H4B | 109.1 | H20A—C20—H20B | 107.8 |
| N1—C5—C4 | 102.84 (16) | C20—C21—H21A | 109.5 |
| N1—C5—H5A | 111.2 | C20—C21—H21B | 109.5 |
| C4—C5—H5A | 111.2 | H21A—C21—H21B | 109.5 |
| N1—C5—H5B | 111.2 | C20—C21—H21C | 109.5 |
| C4—C5—H5B | 111.2 | H21A—C21—H21C | 109.5 |
| H5A—C5—H5B | 109.1 | H21B—C21—H21C | 109.5 |
| C7—C6—P1 | 113.13 (18) | C23—C22—P3 | 112.66 (16) |
| C7—C6—H6A | 109.0 | C23—C22—H22A | 109.1 |
| P1—C6—H6A | 109.0 | P3—C22—H22A | 109.1 |
| C7—C6—H6B | 109.0 | C23—C22—H22B | 109.1 |
| P1—C6—H6B | 109.0 | P3—C22—H22B | 109.1 |
| H6A—C6—H6B | 107.8 | H22A—C22—H22B | 107.8 |
| C6—C7—H7A | 109.5 | C22—C23—H23A | 109.5 |
| C6—C7—H7B | 109.5 | C22—C23—H23B | 109.5 |
| H7A—C7—H7B | 109.5 | H23A—C23—H23B | 109.5 |
| C6—C7—H7C | 109.5 | C22—C23—H23C | 109.5 |
| H7A—C7—H7C | 109.5 | H23A—C23—H23C | 109.5 |
| H7B—C7—H7C | 109.5 | H23B—C23—H23C | 109.5 |
| | | | |
| C5—N1—C1—S2 | 6.0 (2) | C6—P1—C8—C9 | −176.38 (18) |
| C2—N1—C1—S2 | 173.70 (13) | Cu1—P1—C8—C9 | −50.4 (2) |
| C5—N1—C1—S1 | −172.23 (14) | C8—P1—C10—C11 | −176.76 (19) |
| C2—N1—C1—S1 | −4.5 (2) | C6—P1—C10—C11 | 76.9 (2) |
| Cu2—S2—C1—N1 | −93.58 (15) | Cu1—P1—C10—C11 | −47.0 (2) |
| Cu3—S2—C1—N1 | −175.40 (15) | C14—P2—C12—C13 | 178.71 (19) |
| Cu2—S2—C1—S1 | 84.66 (10) | C16—P2—C12—C13 | −75.3 (2) |
| Cu3—S2—C1—S1 | 2.84 (9) | Cu2—P2—C12—C13 | 50.2 (2) |

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| Cu1—S1—C1—N1 | 96.59 (14) | C12—P2—C14—C15 | −81.4 (2) |
| Cu3—S1—C1—N1 | 175.33 (15) | C16—P2—C14—C15 | 173.45 (19) |
| Cu1—S1—C1—S2 | −81.67 (10) | Cu2—P2—C14—C15 | 46.1 (2) |
| Cu3—S1—C1—S2 | −2.93 (9) | C14—P2—C16—C17 | −84.3 (2) |
| C1—N1—C2—C3 | −176.54 (16) | C12—P2—C16—C17 | 170.03 (19) |
| C5—N1—C2—C3 | −7.4 (2) | Cu2—P2—C16—C17 | 44.3 (2) |
| N1—C2—C3—C4 | 28.69 (19) | C20—P3—C18—C19 | −91.44 (17) |
| C2—C3—C4—C5 | −39.4 (2) | C22—P3—C18—C19 | 162.62 (16) |
| C1—N1—C5—C4 | 152.09 (17) | Cu3—P3—C18—C19 | 37.36 (18) |
| C2—N1—C5—C4 | −16.9 (2) | C22—P3—C20—C21 | 179.63 (16) |
| C3—C4—C5—N1 | 34.37 (19) | C18—P3—C20—C21 | 74.03 (18) |
| C10—P1—C6—C7 | −178.43 (18) | Cu3—P3—C20—C21 | −56.63 (18) |
| C8—P1—C6—C7 | 75.85 (19) | C20—P3—C22—C23 | 73.77 (18) |
| Cu1—P1—C6—C7 | −53.22 (19) | C18—P3—C22—C23 | −178.70 (16) |
| C10—P1—C8—C9 | 77.7 (2) | Cu3—P3—C22—C23 | −50.70 (18) |

*Hydrogen-bond geometry (Å, º)*

Cg1 is the centroid of the (Cu,S1,S2,C1) chelate ring.

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C20—H20*B*···Cl1[i] | 0.99 | 2.81 | 3.722 (2) | 154 |
| C22—H22*B*···Cl1[i] | 0.99 | 2.80 | 3.720 (2) | 154 |
| C3—H3*B*···*Cg*1[ii] | 0.99 | 2.83 | 3.705 (2) | 148 |

Symmetry codes: (i) *x*, *y*, *z*−1; (ii) −*x*+1, −*y*+1, −*z*+1.