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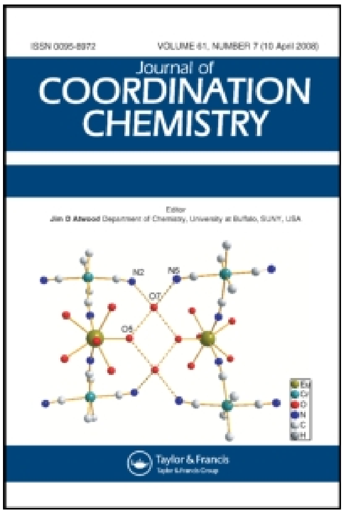

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# Copper(I) *O*,*O*′-dialkyldithiophosphate clusters: EXAFS, NMR and X-ray diffraction studies

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Copper K-edge EXAFS data for six polycrystalline cubic cluster compounds, $\{Cu_8[S_2P(OR)_2]_6(\mu_8\text{-}S)\}$ with R = Et, $^n$Pr, $^i$Pr, $^n$Bu, $^i$Bu and $^i$Am, show that the architecture of their $Cu_8(S_2P)_2S$ cores is fairly rigid and independent of both length and branching of the alkyl chain, and that the structure of the cluster is maintained in acetone solution. Solid-state $^{31}$P CP-MAS and static $^{65}$Cu NMR data for $\{Cu_8[S_2P(O^nPr)_2]_6(\mu_8\text{-}S)\}$ and $\{Cu_8[S_2P(OEt)_2]_6(\mu_8\text{-}S)\}$ show similarities in the icosahedral *O*,*O*′-dialkyldithiophosphate shells and in the 'cubic' copper cores in these cluster compounds. The crystal structure of $\{Cu_8[S_2P(O^nPr)_2]_6(\mu_8\text{-}S)\}$ was resolved using single-crystal X-ray diffraction.

*Keywords*: Copper(I) *O*,*O*′-dialkyldithiophosphate clusters; EXAFS; NMR; X-ray structure

## 1. Introduction

The coordination chemistry of monovalent copper is strongly dominated by two-(linear), three-(trigonal) and four-(tetrahedral) coordination, while higher coordination numbers occur rarely [1]. It is well known that copper(I) is preferentially stabilized (over copper(II)) by sulfur-donor ligands and the most common coordination geometry in this case is the tetrahedron [2]. The tetrahedral arrangement is often considerably distorted and the primary expected coordination number is lower than

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that sterically possible, indicating a strong covalent bonding character. Chemical interest in sulfur bridging cubic-copper(I) clusters arises from the specific configuration of eight copper ions, each of which lies in a distorted tetrahedral configuration of sulfur-donor ligands, and six *O*,*O*′-dialkyldithiophosphate ligands, which form a nearly perfect icosahedron around copper(I) centers [3]. Investigations of these structures are particularly relevant to the construction of surface-capped copper(I) dithiophosphate nanotemplates [4], properties of modified lubricating oils [5] and identification of species formed on chalcocite ($Cu_2S$) surfaces when they are treated with *O*,*O*′-dialkyldithiophosphate collectors [6].

Due to difficulties in producing single-crystals suitable for X-ray measurements, however, only the structures of the ethyl- and *iso*-propyl sulfur-centred cubic copper(I) *O*,*O*′-dialkyldithiophosphate clusters have been characterised so far [7]. Furthermore, while there are numerous data reported for the properties of mononuclear copper(II) *O*,*O*′-dialkyldithiophosphate complexes in solution [8], no structural studies are reported for corresponding polynuclear copper(I) clusters and therefore the structures of such systems in solution are unknown.

Often, the most detailed description of such cluster compounds in the solid state is not through the crystallographic data due to imperfections in available crystals or misinterpretation of X-ray-absorption data for complex systems. Therefore, a combination of symmetry-sensitive spectroscopic techniques, preferably non-lattice dependent, is desirable, especially for this particular type of octanuclear clusters for which crystallographic studies are lacking. In this communication we show how a combination of NMR and EXAFS spectroscopy can be used to probe the $Cu_8(S_2P)_6S_{centre}$ architecture in several octameric copper(I) cluster compounds and provide information for identification of these systems when single crystals are not readily achievable. Novel copper K-edge EXAFS data for the cubic sulfur-centred polycrystalline compounds, $\{Cu_8[S_2P(OR)_2]_6(\mu_8\text{-}S)\}$, R = Et, $^n$Pr, $^i$Pr, $^n$Bu, $^i$Bu and $^i$Am, combined with $^{31}$P CP-MAS NMR data for polycrystalline $\{Cu_8[S_2P(O^nPr)_2]_6(\mu_8\text{-}S)\}$, (**1**), and $\{Cu_8[S_2P(OEt)_2]_6(\mu_8\text{-}S)\}$ (**2**), are given followed by a discussion of the $^{65}$Cu NMR response for the two systems. The single-crystal X-ray structure of **1** is resolved and the data are compared to those for the two clusters with known structures. In addition, EXAFS and $^{31}$P NMR data for **1** and **2** in acetone and dichloromethane solutions are discussed.

## 2. Results and discussion

EXAFS is a lattice-independent structural method and provides information about the structure around the absorbing atom in the sample, in this case copper, independent of the state of aggregation of the material. In order to find whether or not the alkyl chain of the ligands may affect the architecture of the $Cu_8$-cube we applied EXAFS to study six polycrystalline cluster compounds, $\{Cu_8[S_2P(OR)_2]_6(\mu_8\text{-}S)\}$, R = Et, $^n$Pr, $^i$Pr, $^n$Bu, $^i$Bu and $^i$Am. EXAFS data for all six compounds are shown in figure 1. The refined structure parameters from the EXAFS study are summarised in table 1 together with XRD data reported to date. The average bond distances from the EXAFS data are in an agreement with the data obtained by XRD for $\{Cu_8[S_2P(OR)_2]_6(\mu_8\text{-}S)\}$ R = Et, $^n$Pr and $^i$Pr. The average $Cu\cdots Cu$, Cu–S, $Cu\cdots S_{centre}$ bond lengths of the

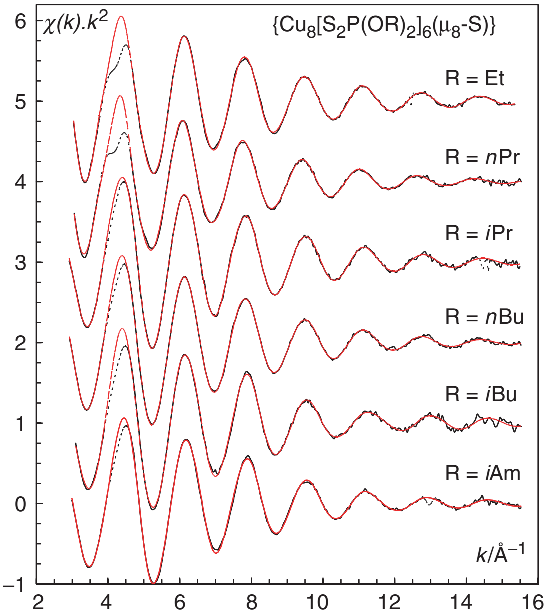

Figure 1. EXAFS data and curve fitting functions for the $\{Cu_8[S_2P(OR)_2]_6(\mu_8\text{-}S)\}$ clusters, R = Et, $^{n}$Pr, $^{i}$Pr, $^{n}$Bu, $^{i}$Bu and $^{i}$Am; solid line: experimental data (regions with dotted points have been omitted in calculations); dashed line: refined model using parameters listed in table 1.

Table 1. Structure parameters of $\{Cu_8[S_2P(OR)_2]_6(\mu_8\text{-}S)\}$ with R = Et, $^{n}$Pr, $^{i}$Pr, $^{n}$Bu, $^{i}$Bu and $^{i}$Am, as determined by EXAFS; d (Å), distance, $\beta^2$ (Å)$^2$, Debye–Waller coefficient and $N$, number at that distance. Corresponding parameters obtained from crystallographic studies are given for comparison.

| | Mean Cu–S distance | | | | Mean Cu···S$_{centre}$ distance | | | | Mean Cu···Cu distance | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| R | d (Å) | $\sigma^2$ (Å) | $N$ | d(XRD) (Å) | d(Å) | $\sigma^2$ (Å) | $N$ | d(XRD) (Å) | $D$ (Å) | $\sigma^2$ (Å) | $N$ | d(XRD) (Å) |
| Et[a] | 2.293(3) | 0.0065(4) | 3 | 2.305 | 2.62(3) | 0.032(4) | 1 | 2.606 | 3.01(3) | 0.040(4) | 3 | 3.009 |
| $^{n}$Pr | 2.294(3) | 0.0090(4) | 3 | 2.302 | 2.64(3) | 0.032(4) | 1 | 2.607 | 3.02(3) | 0.037(4) | 3 | 3.011 |
| | 2.290(3)[b] | 0.0075(4) | 3 | | 2.65(2)[b] | 0.033(4) | 1 | | 3.01(3)[b] | 0.043(3) | 3 | |
| $^{i}$Pr[c] | 2.285(3) | 0.0089(4) | 3 | 2.283 | 2.64(2) | 0.015(3) | 1 | 2.694 | 2.99(3) | 0.044(3) | 3 | 3.111 |
| $^{n}$Bu | 2.283(3) | 0.0086(4) | 3 | na | 2.63(2) | 0.020(3) | 1 | na | 2.97(3) | 0.047(4) | 3 | na |
| $^{i}$Bu | 2.290(3) | 0.0102(4) | 3 | na | 2.64(2) | 0.013(3) | 1 | na | 2.99(3) | 0.039(3) | 3 | na |
| $^{i}$Am | 2.285(3) | 0.0099(4) | 3 | na | 2.64(2) | 0.014(3) | 1 | na | 2.98(3) | 0.039(3) | 3 | na |

[a] XRD data are taken from Ref. [7b].
[b] In acetone solution.
[c] XRD data are taken from Ref. [7c]; na – not available.

compounds with R = $^{n}$Bu, $^{i}$Bu and $^{i}$Am are basically the same within error limits. This shows that the structures around the copper(I) ions in all six sulfur-centred cluster compounds are essentially identical and the structure of the $Cu_8(S_2P)_6S$ core is independent of the length and branching of the alkyl chain in the *O*,*O*′-dialkyldithiophosphate ligands. However, it should be pointed out that the symmetries of these clusters are likely to be different as an increase of the length and branching in the hydrocarbon chains often results in breaking the high symmetry of the methyl- and ethyl-analogues. Additionally, for compound **1**, the Cu···Cu, Cu–S, Cu···S$_{centre}$ bond lengths were determined by EXAFS when the compound was dissolved in acetone. The data are identical within error limits to those obtained in the solid-state (table 1) and unambiguously show that the same poly-nuclear structure is maintained in acetone solution.

The *O*,*O*′-dialkyldithiophosphate ligand shells in **1** and **2** were probed with solid-state $^{31}$P NMR. $^{31}$P CP-MAS NMR spectra are shown in figure 2. The compounds display a single $^{31}$P NMR resonance line with isotropic shifts at 100.6 and 99.3 ppm, respectively. This indicates that the $PO_2S_2$ tetrahedra in the ligands are very similar to each other and all phosphorus sites in both clusters are chemically equivalent. The spinning sideband patterns of the samples are very similar and provide a qualitative indication of the similarities of the $^{31}$P chemical shift anisotropies (CSA) in the copper(I) clusters. The CSA parameters estimated from the $^{31}$P CP-MAS spectra are shown in table 2 [9]. The similar negative values of the $\delta_{\text{aniso}}$ parameter for all phosphorus sites reflect similar, relatively large S–P–S bond angles, and the same bridging mode of the ligands. This is in accordance with our previous reports for

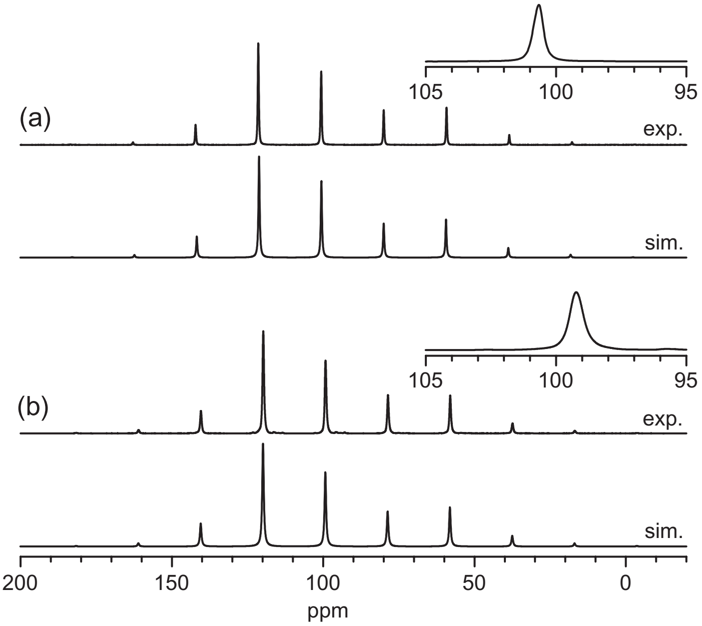

Figure 2. $^{31}$P CPMAS spectra (at 8.46T) of copper(I) *O*,*O*′-dialkyldithiophosphate cluster compounds **1** (a) and **2** (b) together with spectra calculated by the SIMPSON program; 32 signal transients; spinning frequency 3 kHz. Expanded regions with centre bands are shown in insets.

Table 2. $^{31}$P chemical shift and chemical shift anisotropy data (with 68.3% confidence limits) for the copper(I) *O*,*O*′-dialkyldithiophosphate clusters **1** and **2**.

| Cluster | $\delta_{\text{iso}}$ (ppm) | $\delta_{\text{aniso}}$ (ppm) | $\eta$ | $\delta_{xx}$ | $\delta_{yy}$ | $\delta_{zz}$ |
|---|---|---|---|---|---|---|
| **1**[a] | $100.6 \pm 0.1$ | $-63.7 \pm 0.2$ | $0.10 \pm 0.05$ | $135.6 \pm 1.5$ | $129.3 \pm 3.3$ | $36.9 \pm 0.2$ |
| **2**[b] | $99.3 \pm 0.1$ | $-64.9 \pm 0.6$ | $0.18 \pm 0.07$ | $137.6 \pm 2.3$ | $125.6 \pm 5.1$ | $34.4 \pm 0.6$ |

[a] In acetone: $\delta_{\text{iso}} = 102.0$ and 102.6 ppm; in $CH_2CL_2$: 100.7 and 101.0 ppm.
[b] In $CH_2CH_2$: 100.2 and 100.7 ppm.

polycrystalline tetra-nuclear zinc(II)-, hexa- and octanuclear copper(I) *O*,*O*′-dialkyldithiophosphate clusters [6b, 10, 11]. The asymmetry parameter $\eta$ is close to zero, which is indicative of the near axial symmetry of the $^{31}$P chemical shift tensor in both cases.

The SIMPSON program [12] was used to calculate $^{31}$P CP-MAS spectra of **1** and **2** for the $^{31}$P CSA parameters given in table 2, and the spectra are shown in figure 2. $^{31}$P NMR data were additionally obtained for the octanuclear clusters with R = Et and $^{n}$Pr in solution. It was found that these compounds display two $^{31}$P NMR resonance lines with different intensities which vary in different solvents with no particular correlation. These results need additional consideration as it is unlikely that two resonances originate from a chemical inequivalence of the P sites in the clusters in solution. Our previous studies on $\{Cu_8[S_2P(O^iPr)_2]_6(\mu_8\text{-}S)\}$ [13] in different solvents have shown the presence of only single resonance lines in the $^{31}$P NMR spectra for this compound in all solvents used. This is an indication that the clusters with linear and branched hydrocarbon chains may have different properties in solution.

The presence of an equilibrium between copper(II) and copper(I) dithiophosphato-derivatives was reported when alkyl- and alkylenedithiophosphates with branched hydrocarbon chains were studied in dichloromethane by means of $^{31}$P NMR [14].

$$Cu[S_2P(OR)_2]_2 \rightleftharpoons Cu[S_2P(OR)_2] + 1/2[S_2P(OR)_2]_2$$

In contrast to the alkyldithiophosphato derivatives, the reaction for alkylene derivatives has been found to be considerably slower, allowing the $^{31}$P NMR spectra of copper(I) and the disulfide of the alkylene derivatives to be recorded simultaneously, and the equilibrium to be studied [14]. Thus, it is reasonable to assume that the two resonance lines, for each of the clusters with R = Et or $^{n}$Pr, could be due to an equilibrium either between different types of clusters or between a cluster compound and a disulfide molecule formed in solution. A variable temperature NMR experiment, combined with experiments that include deliberately adding corresponding disulfides, is needed to reveal the actual coordination chemistry of these cluster compounds in solution.

Polycrystalline samples of **1** and **2** were the subject of a $^{65}$Cu NMR study. In the structure of **2**, there are two copper sites with a population distribution of 6 : 2, but with somewhat larger differences in their local environments. The latter two copper atoms are situated at positions of higher symmetry than the other six, and are connected to sulfur atoms by a somewhat longer distance of 2.348 Å; all three S–Cu–S angles are equal to 118.31°. The other six copper atoms are connected to three sulfur atoms by distances in the range 2.274 to 2.310 Å and S–Cu–S angles vary by up to five degrees [7b]. The Cu–S bond distance of 2.348 Å in **2** appears to be considerably longer in comparison with the corresponding crystallographic distance in **1** (see below) and the mean distances obtained by EXAFS for all octanuclear clusters in this study. EXAFS data for **2**, however, are more reliable as the extreme long distance order required in crystallography, which is ensured by a good quality of single crystals, is not a requirement of the EXAFS method. Although the copper sites in **2** seem to be more different from a crystallographic point of view than the sites in **1**, these compounds are expected to show similar $^{65}$Cu NMR spectra due to the fact that the chemical environments around the copper atoms in both cases is represented by four sulfur atoms in a trigonal pyramidal geometry with the $S_{centre}$ at the apical position, $CuS_3 \cdots S_{centre}$.

$^{65}$Cu NMR measurements were performed at two applied magnetic field strengths, 7.05 and 14.1T. No $^{65}$Cu NMR signals were detected at the lower field strength. At 14.1T, both compounds show almost featureless line-shapes, with a width of about 120 kHz for the copper sites in **1** and 170 kHz for those in **2** (see supporting information section). The absence of $^{65}$Cu NMR signals at 7.05T and the weak signal at 14.1T is an indication that the copper nuclei in both compounds have very short transverse relaxation times, $T_2$. The relatively narrow line-width and the absence of a well-defined quadrupolar line-shape means that the quadrupolar coupling constant, $C_Q$, is likely to be less than 12 MHz, which is considerably smaller than is observed for the copper sites in $\{Cu_6[S_2P(OEt)_2]_6\}$ ($C_Q = 46.6$ MHz [11]) and $\{Cu_8[S_2P(O^iBu)_2]_6(\mu_8\text{-}S)\}$ ($C_Q$ between 19 and 46 MHz [15]).

The reason for the observed differences in the $^{65}$Cu NMR data for the clusters with six identical *O*,*O*′-diethyldithiophosphate ligands, forming a nearly regular icosahedral $S_{12}$-shell around the copper cores in $\{Cu_6[S_2P(OEt)_2]_6\}$ and $\{Cu_8[S_2P(OEt)_2]_6(\mu_8\text{-}S)\}$ is due to the geometry around the copper centres in the compounds, planar geometry ($CuS_3$) in the former and a trigonal pyramidal arrangement of sulfur atoms ($CuS_3 \cdots S_{centre}$) in the latter. It is worth noting that coordination of the ligand itself in these compounds is different, tri-connective trimetallic in the former and tetra-connective tetrametallic in the latter. This probably plays a role in stabilising the copper-sulfur planes ($CuS_3$) in both compounds and could be an additional reason for the observed large differences in the quadrupolar interaction parameters ($C_Q$ and $\eta_Q$) in these compounds. Differences between the $^{65}$Cu relaxation time, $T_2$, for the two cubic clusters with considerably shorter, non-branched alkyl chains, **1** and **2**, and that of the polycrystalline compound with longer and branched alkyl chains, $\{Cu_8[S_2P(O^iBu)_2]_6(\mu_8\text{-}S)\}$ [15], is likely to be due to motion in the alkyl chains in the less rigid structures of $\{Cu_8[S_2P(OEt)_2]_6(\mu_8\text{-}S)\}$ and $\{Cu_8[S_2P(O^nPr)_2]_6(\mu_8\text{-}S)\}$. All attempts to record $^{63/65}$Cu NMR spectra in acetone or $CH_2CH_2$ solutions were unsuccessful, probably due to distorted tetrahedral configurations of the copper sites [16].

The cluster compound **1** was structurally characterised by single-crystal X-ray diffraction [17]. A thermal ellipsoid plot for **1**, with the unique atoms labelled, is shown in figure 3. The structure reveals a sulfur-centred $Cu_8$-cage with six *O*,*O*′-di-*n*-propyl-dithiophosphate ligands bridging across each face of the cube, analogously to the $\{Cu_8[S_2P(OEt)_2]_6(\mu_8\text{-}S)\}$ and $\{Cu_8[S_2P(O^iPr)_2]_6(\mu_8\text{-}S)\}$ structures [7b–c]. The copper atoms form a nearly perfect cube with an average $Cu \cdots Cu$ distance of 3.011 Å along the edges. Two crystallographically different copper atoms are present in the unit cell; two Cu(1) and six Cu(2) atoms form the $Cu_8$-cube in which the Cu(1) atoms exhibit a somewhat higher local symmetry. Each Cu(1) atom is connected to three S(1)-type sulfur atoms at a distance of 2.299 Å and the three S(1)–Cu(1)–S(1) angles are equal to 118.88°. Cu(2) atoms are connected to three sulfur atoms (one S(1) and two S(2)) with bond lengths in the range 2.288–2.317 Å and S–Cu–S angles vary from 118.26 to 119.23°. Additionally, each of the copper atoms is connected to the central sulfur atom, S(3). The mean $Cu \cdots S(3)$ distance is 2.607 Å, which is similar to that in $\{Cu_8[S_2P(OEt)_2]_6(\mu_8\text{-}S)\}$ [7b] but shorter than the distance of 2.69 Å in $\{Cu_8[S_2P(O^iPr)_2]_6(\mu_8\text{-}S)\}$ [7c]. The geometry around both Cu(1) and Cu(2) is trigonal pyramidal with $\mu_8$-S(3) at the common apical position. These crystallographic data are in very good agreement with the copper K-edge EXAFS data for the system.

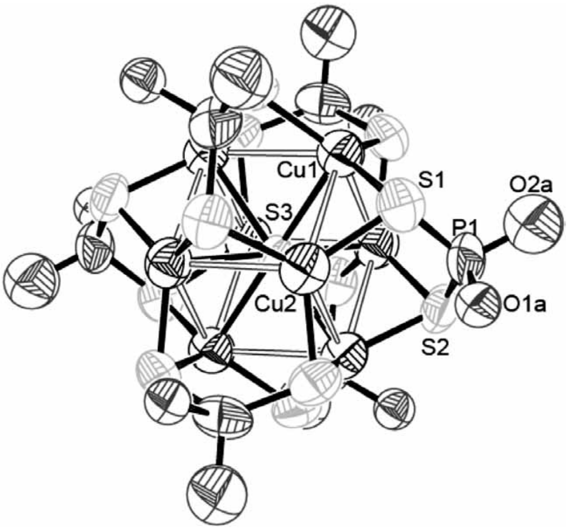

Figure 3. Thermal ellipsoid plot of $\{Cu_8[S_2P(O^nPr)_2]_6(\mu_8\text{-}S)\}$ shown at the 50% probability level. The *n*-propyl groups are omitted for clarity. Selected bond lengths, Å, and bond angles, degrees: Cu(1)–S(1) 2.299, Cu(1)–S(3) 2.610, Cu(2)–S(1) 2.288, Cu(2)–S(2) 2.303, Cu(2)–S(3) 2.606, P(1)–S(1) 1.976, P(1)–S(2) 1.988, P(1)–O(1a) 1.556, P(1)–O(2a) 1.496, S(1)–Cu(1)–S(1) 118.88, S(1)–Cu(2)–S(2) 118.20, S(2)–Cu(2)–S(1) 118.88, Cu(1)–S(1)–Cu(2) 81.87, Cu(2)–S(2)–Cu(2) 81.52.

The central sulfur atom sits on the crystallographically imposed inversion centre and the intraligand bite distance is 3.45 Å, which is slightly shorter than those for $\{Cu_8[S_2P(OEt)_2]_6(\mu_8\text{-}S)\}$ and $\{Cu_8[S_2P(O^iPr)_2]_6(\mu_8\text{-}S)\}$ (3.48 and 3.53 Å, respectively). The six *O*,*O*′-di-*n*-propyldithiophosphate ligands, forming an almost regular icosahedron of $S_{12}$ atoms around the copper core, exhibit a tetrametallic tetra-connective coordination mode [18]. The phosphorus atoms are structurally equivalent; the two P–S and P–O bond distances are 1.976 and 1.988, and 1.556 and 1.496 Å, respectively. The S–P–S angle is 120.76° for all six P atoms, which correlates well with 120.57 and 121.61° reported for $\{Cu_8[S_2P(OEt)_2]_6(\mu_8\text{-}S)\}$ [7b] and $\{Cu_8[S_2P(O^iPr)_2]_6(\mu_8\text{-}S)\}$ [7c], respectively. The crystallographic equivalence of the P sites causes the chemical equivalence that it is observed in the $^{31}$P CP-MAS NMR spectrum.

## Supporting material

Synthesis and characterization of $\{Cu_8[S_2P(OR)_2]_6(\mu_8\text{-}S)\}$, R = Et, $^n$Pr, $^i$Pr, $^n$Bu, $^i$Bu and $^i$Am, $^{31}$P CP/MAS and $^{65}$Cu NMR experimental conditions, $^{65}$Cu NMR spectra of **1** and **2**, and the detailed fit to the copper K-edge EXAFS spectra for the cluster compounds are available from the authors upon request. CCDC 290833 contains the supplementary crystallographic data for this article. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033.

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[9] Definitions: $\delta_{\mathrm{aniso}} = \delta_{zz} - \delta_{\mathrm{iso}}$; $\delta_{\mathrm{iso}} = (\delta_{xx} + \delta_{yy} + \delta_{zz})/3$ where $\delta_{xx}$, $\delta_{yy}$ and $\delta_{zz}$ are the principal values of the chemical shift tensor, $|\delta_{zz} - \delta_{\mathrm{iso}}| \geq |\delta_{xx} - \delta_{\mathrm{iso}}| \geq |\delta_{yy} - \delta_{\mathrm{iso}}|$; the asymmetry parameter, $\delta = (\delta_{yy} - \delta_{xx})/\delta_{\mathrm{aniso}}$.

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[17] $Cu_8S_{13}P_6(OC_3H_7)_{12}$, hexagonal, space group $R\bar{3}$, $a = 22.4397(17)$, $c = 11.9937(10)$ Å, $Z = 3$, $V = 5230.2(7)$ Å$^3$, $D_c = 1.733\ \mathrm{g\,cm^{-3}}$. X-ray diffraction data were collected at 297 K from a single crystal ($0.10 \times 0.07 \times 0.04\ \mathrm{mm^3}$) on an Xcalibur Sapphire 3-CCD diffractometer (Oxford diffraction) with Kappa geometry using Mo-K$\alpha$ radiation ($\lambda = 0.7107$ Å). A total of 12009 reflections (1413 unique, $R(\mathrm{int}) = 0.0288$) were collected in the region $3.99^\circ < \theta < 21.95^\circ$. Data collection was carried out using the program Crysalis CCD and cell refinement, data reduction and absorption correction

($T_{\mathrm{max}}/T_{\mathrm{min}} = 0.8906/0.7559$) were performed by Crysalis RED. The structure was solved and refined using SHELX97 within the interface program WinGX. Drawings of the structure were made using ORTEP. The *n*-propyl groups ($OC_3H_7$) were disordered and therefore only refined isotropically. The rest of the structure was refined anisotropically; $R_1 = 0.0729$ for 1183 reflections with $F_o > 2\sigma(F_o)$ and 0.0863 for all 1413 reflections, $wR_2 = 0.2271$, GOF = 1.146.
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