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Short Communication

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Molecular structure of novel heterobimetallic thiolate $[Cu(PPh_3)]_4(ZnCl)_2(SEt)_6.6THF$

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Abstract: Heterobimetallic thiolate $[Cu(PPh_3)]_4(ZnCl)_2(SEt)_6$ has been synthesised and characterised by X-ray crystallography as a THF solvate. It contains the first structurally characterised example of a Cu^I-S(R)-Zn^{II} linkage and only the second species type to embody the Cu^I-S-Zn^{II} triad.

Keywords: copper; heterobimetallic; thiolate; X-ray; zinc.

In the search for efficient absorber materials for photovoltaic cells derived from earth-abundant elements, Cu_2ZnSnS_4 (CZTS) has attracted significant attention (Ito and Nakazawa, 1988; Ramasamy et al., 2012); cells with efficiencies, which have increased from *ca*. 7% to in excess of 11%, have now been reported (Guo et al., 2010; Todorov et al., 2010, 2013; Barkhouse et al., 2012; Repins et al., 2012; Shin et al., 2013).

While several methods for forming CZTS are known (Ramasamy et al., 2012; Kociok-Köhn et al., 2014a and references therein), deposition in thin film form has been problematic. We (Kociok-Köhn et al., 2014a) and others (Ramasamy et al., 2011) have noted the specificity of conditions required to bring at least three precursors (one for each metal, which may, or may not, incorporate the chalcogen) together to generate CZTS in the correct stoichiometry. One way to simplify this problem is the use of precursors that embody more than one metal, which thereby reduces the overall number of precursors involved in the process. To this end, we have previously reported the synthesis of several M-Cl-M′ species (M=Cu, Zn, Sn *inter alia*), which could plausibly act as starting points for the synthesis of M-S-M′-containing precursors (Kociok-Köhn et al., 2014b). Unfortunately, to date, our attempts to produce such species by salt metathesis of the M-Cl-M′ reagents with thiolate anions have been unsuccessful. However, we now wish to report an initial success from the combination of $(Ph_3P)_2CuCl$ and $[(EtS)_3Zn]Na$ and the structural characterisation of the first Cu^I-S(R)-Zn^{II} linkage.

$[Cu(PPh_3)]_4(ZnCl)_2(SEt)_6$ (**1**) was synthesised from the reaction of $Na[Zn(SEt)_3]$, prepared by partially following the methodology used to prepare $[(EtS)_6Zn_2]Na_2$, (Watson et al., 1985) and $Cu(PPh_3)_2Cl$:

$$4(Ph_3P)_2CuCl+2[(EtS)_3Zn]Na \xrightarrow[-4Ph_3P,\ -2NaCl]{(i)\ toluene,\ (ii)\ THF} \underset{(\mathbf{1})}{[(Ph_3P)Cu]_4(ZnCl)_2(SEt)_6}$$

Although the reaction was carried out at 1:1 reagent stoichiometry, this is not translated to the ratio of metals in the final product. Moreover, the reaction involves (perhaps unsurprisingly) loss of Ph_3P and also, but less anticipated, migration of a halogen from the softer copper to the harder zinc.

Crystals of **1**.6THF were isolated from the solution, but microanalysis implies that the molecules of solvation are easily lost from the solid when the initially prepared compound was pumped dry. Spectroscopic data are unexceptional, and despite NMR integrals revealing the ratio of EtS:Ph_3P ligands, the structure is revealed only by crystallography (Figure 1; Table 1). **1** consists of two Cu_2ZnS_3 rings, each in a distorted boat conformation, joined co-facially *via* two Cu-S [Cu(2)-S(1) 2.3650(11) Å] and two Zn-S [Zn(1)-S(1) 2.3836(11) Å] bonds. This results in a cage embodying both six-membered Cu_2ZnS_3 and four-membered $CuZnS_2$ heterocycles. In addition to bonds to sulphur, each zinc is bonded to chlorine [Zn(1)-Cl(1) 2.2505(11) Å], while each copper has a Ph_3P group external to the cage [Cu(1)-P(1) 2.2087(10) Å; Cu(2)-P(2) 2.2214(10) Å]. Cu(1) is three-coordinate in a trigonal planar environment, while both Cu(2) and Zn(1) are four-coordinate and tetrahedral, although the formation of fused rings requires significant bond

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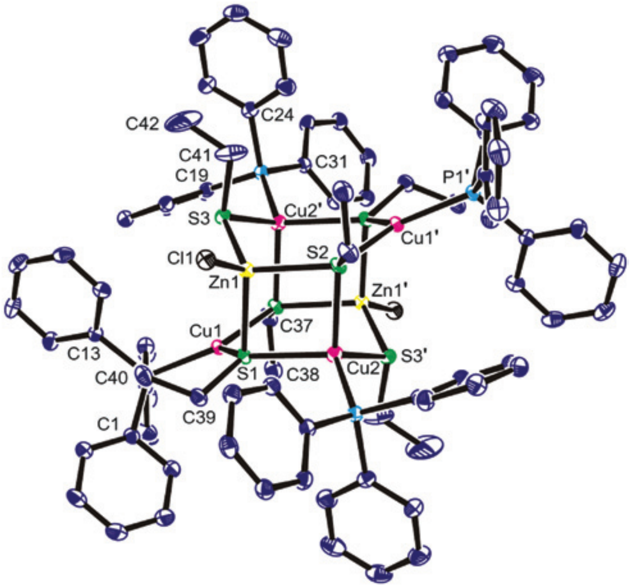

Figure 1: The asymmetric unit of **1** showing the labelling scheme used; thermal ellipsoids are at the 30% probability level. P(1) and C(7) are hidden behind C(40). Symmetry operation: 1-*x*, -*y*, 2-*z*.

Table 1: Selected bond distances (Å) and angles (°) for **1**.

Bond lengths			
Zn-S(1)	2.3836(11)	Cu(1)-S(2′)	2.2404(10)
Zn-S(2)	2.3907(10)	Cu(2)-S(1)	2.3650(11)
Zn-S(3)	2.3000(10)	Cu(2)-S(2)	2.4342(10)
Zn-Cl(1)	2.2505(11)	Cu(2)-S(3′)	2.3219(11)
Cu(1)-P(1)	2.2087(10)	Cu(2)-P(2)	2.2214(10)
Cu(1)-S(1)	2.2204(11)		
Bond angles			
S(1)-Zn(1)-S(2)	98.45(4)	S(1)-Cu(2)-S(2)	97.75(4)
S(1)-Zn(1)-S(3)	112.96(4)	S(1)-Cu(2)-S(3′)	104.41(4)
S(1)-Zn(1)-Cl(1)	103.56(4)	S(1)-Cu(2)-P(2)	114.35(4)
S(2)-Zn(1)-S(3)	107.60(4)	S(2)-Cu(2)-S(3′)	112.21(4)
S(2)-Zn(1)-Cl(1)	114.30(4)	S(2)-Cu(2)-P(2)	113.02(4)
S(3)-Zn(1)-Cl(1)	118.24(4)	S(3′)-Cu(2)-P(2)	113.76(4)
S(1)-Cu(1)-S(2′)	108.76(4)		
S(1)-Cu(1)-P(1)	126.52(4)		
P(1)-Cu(1)-S(2′)	124.73(4)		

Symmetry operation: 1-*x*, -*y*, 2-*z*.

angle distortion [angles about Zn(1) 98.45(4)–118.24(4)°; Cu(1) 108.76(4)–124.73(4)°; Cu(2) 97.75(4)–114.35(4)°]; the shorter bond lengths to Cu(1) in comparison to Cu(2) reflect this coordination number difference. S(1) and S(2) act in a μ_3-bridging mode, while S(3) is only μ_2 and has the shorter bond lengths to its neighbouring metals. Despite the two distinct copper (and hence phosphorus and thiolate) environments, separate signals are not seen in either the ^{31}P or ^{13}C NMR spectra, suggesting some structural fluxionality in solution.

1 incorporates the first examples of structurally characterised Cu^I-S(R)-Zn^{II} linkages. Indeed, only one other structure in the Cambridge Crystallographic Database establishes the Cu^I-S-Zn^{II} array, namely, $[(Ph_3P)Cu(\mu\text{-}SCOR)_3Zn(PPh_3)]$ (R = Ph, thiophene), which incorporates μ_2-S thiocarboxylate ligands (Singh et al., 2013).

An analogous approach in search of a similar bimetallic Cu-Sn species only generated a known compound. Thus, $[(PhS)_3Sn]Na$, prepared by adding three equivalents of NaSPh to $SnCl_2$ in MeOH following published methodology (Dean et al., 1985), was added to $Cu(PPh_3)_2Cl$ in CH_2Cl_2 in a 1:1 ratio. The resulting white precipitate was recrystallised from toluene, generating, over time, red crystals of $Sn[Cu(PPh_3)]_2(SPh)_6.2CH_3C_6H_5$, in which the tin had oxidised; the product was identified crystallographically. $Sn[Cu(PPh_3)Cu]_2(SPh)_6.3H_2O$ has been reported by others (Wang et al., 2008) from the reaction of CuCN, PPh_3 and $Sn(SPh)_4$ (1:1:1).

Experimental

$Na[Zn(SEt)_3]$ (Watson et al., 1985) (0.5 g, 1.85 mmol) was stirred with $Cu(PPh_3)_2Cl$ (Reichle, 1971) (1.15 g, 1.85 mmol) in toluene (20 mL) at 80°C for 1 h, forming a pale orange precipitate. On cooling to room temperature, solution was filtered and THF (20 mL) was added to fully dissolve product. On cooling to -20°C, colourless crystals formed (0.53 g, 61%, m.p. 117–9°C). Analysis: (calculated for $C_{84}H_{90}Cl_2Cu_4P_4S_6Zn_2$) C 54.1 (53.9), H 4.63 (4.85)%; ^{1}H NMR (300 MHz, C_6D_6) δ ppm: 1.34–1.50 (m, 18 H), 3.55–3.60 (m, 12 H), 7.00–7.11 (m, 60 H); ^{13}C NMR (75 MHz, C_6D_6) δ ppm: 26.2 (CH_3), 68.2 (CH_2), 129.2 (d, ^3J 7.4 Hz, *m*-CH),

Table 2: Crystal data and structure refinement for **1**.

Chemical formula	$C_{108}H_{138}Cl_2Cu_4O_6P_4S_6Zn_2$
Formula mass	2304.22
Crystal system	Triclinic
a (Å)	13.9563(3)
b (Å)	14.2768(3)
c (Å)	15.5890(3)
α (°)	96.8507(9)
β (°)	113.671(1)
γ (°)	100.6253(9)
V (Å^3)	2730.78(10)
Space group	$P\bar{1}$
Z	1
M(Mo-kα) (mm^{-1})	1.470
No. of reflections measured	39868
No. of independent reflections	12360
R_{int}	0.0850
Final R_1, $wR(F^2)$ ($I>2\sigma(I)$)	0.0590, 0.1427
Final R_1, $wR(F^2)$ (all data)	0.0843, 0.1615

129.8 (br, *p*-CH), 131.4 (d, ^1J 20.5 Hz, *i*-*C*), 134.7 (d, ^2J 17.4 Hz, *o*-CH); ^{31}P NMR (122 MHz, C_6D_6) δ ppm: -3.5.

Crystallography

Experimental details relating to the single-crystal X-ray crystallographic study are summarised in Table 2. Data were collected on a Nonius Kappa CCD diffractometer (Enraf-Nonius B.V., Rotterdam, The Netherlands) at 150(2) K using Mo-K_α radiation (λ=0.71073 Å). Structure solution was followed by full-matrix least squares refinement and was performed using the WinGX-1.70 suite of programmes (Farrugia, 1999). An absorption correction (semi-empirical from equivalents) was applied. One of three THF molecules in the asymmetric unit is disordered over two sites in the ratio 1:1; bond lengths within this disorder have been restrained.

Supporting Information

Crystallographic data for the structural analysis of **1** (in CIF format) have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 1059281. Copies of this information may be obtained from the Director, CCDC, 12 Union Road, Cambridge, CB21EZ, UK (Fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

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