Electrochemical synthesis and structural characterization of the trinuclear copper(I)–copper(II) complex: bis[bis(triphenylphosphine)copper(I)] [bis(thiosalicylate)copper(II)]

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Received (in Cambridge) 2nd September 1998, Accepted 2nd October 1998

A novel, symmetrical trinuclear copper(I)–copper(II) complex, bis[bis(triphenylphosphine)copper(I)][bis(thiosalicylate)copper(II)], [{Cu(PPh$_3$)$_2$}$_2${Cu(C$_7$H$_4$O$_2$S)$_2$}], has been prepared by anodic dissolution of copper into a solution of triphenylphosphine and thiosalicylic acid in acetonitrile and characterized by single crystal X-ray structure determination as its acetonitrile solvate; characterized also is the 1 : 3 copper(I) complex, [tris(triphenylphosphine)(thiosalicylic acid-*S*)copper(I)], formed as an intermediate in the electrosynthesis.

In our ongoing studies on the synthesis, structural and spectroscopic characterization of the adducts of triphenylphosphine with copper(I) carboxylates, [Cu(PPh$_3$)$_n$(O$_2$CR)],[1,2] we have been investigating the feasibility of preparing the compounds by anodic dissolution of copper into an acetonitrile solution of RCO$_2$H and PPh$_3$ with concomitant reduction of the acidic protons to hydrogen gas at a platinum cathode [eqn. (1)].

$$\mathrm{Cu} + n\mathrm{PPh_3} + \mathrm{RCO_2H} \longrightarrow [\mathrm{Cu(PPh_3)}_n\mathrm{(O_2CR)}] + 1/2\mathrm{H_2} \quad (1)$$

As part of this work, we recently turned our attention to the reaction with thiosalicylic acid in order to ascertain the effects on the products obtained due to the presence of the thiol group *ortho* to the carboxylic acid. Initial electrolysis† resulted in the deposition of colourless crystalline material which was shown by X-ray structure determination‡ to be the acetonitrile solvated [tris(triphenylphosphine)(thiosalicylic acid-*S*)copper(I)] complex [Cu(PPh$_3$)$_3$(C$_7$H$_5$O$_2$S)]·MeCN **1** with a four-coordinate distorted tetrahedral CuP$_3$S copper coordination sphere (Fig. 1). In this complex the carboxylic acid proton forms a strong internal hydrogen bond (O–H···S 1.91 Å) between the oxygen and sulfur atoms. This result is reflected in the IR spectrum of the complex which shows a broad absorption band centred at 2540 cm^{-1} and ascribed to the hydrogen-bonded O–H stretching vibration, together with a moderately strong carbonyl vibration at 1703 cm^{-1}. Continued electrolysis resulted in change in colour of the solution from pale yellow to pale green and then to a darker green during which time crystals of **1** redissolved and new deep green–black crystals slowly formed in their place. The broad absorption band at 2540 cm^{-1} was absent from the IR spectrum of this compound and the band at 1703 cm^{-1} was replaced by two bands at 1620 and 1434 cm^{-1} assignable to asymmetric and symmetric carboxylate stretching vibrations with the difference in wavenumbers indicative of unidentate coordination.[3] This complex was shown by X-ray structure determination to be the acetonitrile solvate of a trinuclear copper(I)–copper(II) complex, bis[bis(triphenylphosphine)copper(I)] [bis(thiosalicylate-*O*, *S*)copper(II)] [{Cu(PPh$_3$)$_2$}$_2${Cu(C$_7$H$_4$O$_2$S)$_2$}]·MeCN **2**. Here we report a description of the structural characteristics of this unusual and interesting compound.

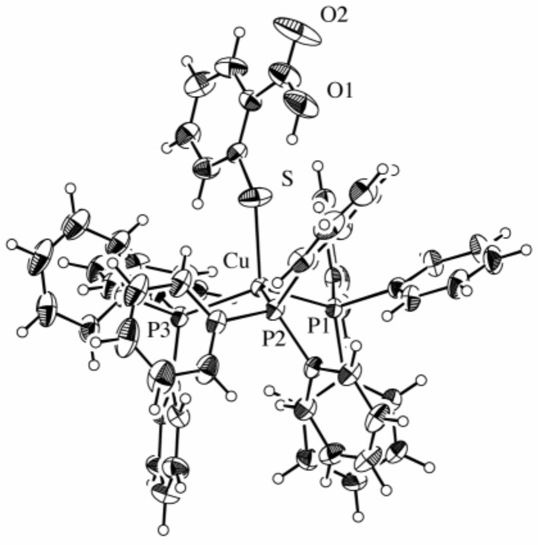

Fig. 1 View of the molecular structure of **1**. Copper coordination sphere: Cu–S 2.369(1), Cu–P(n) 2.367(2), 2.345(2), 2.362(2) Å; S–Cu–P(n) 110.71(7), 96.06(5), 108.94(8)°, P(*n*)–Cu–P(*n* + 1) 109.68(6), 112.02(6), 117.37(5)°. Carboxylate: C–O(*n*) 1.34(1), 1.197(8) Å.

The structure determination shows **2** to crystallize as discrete neutral molecules with one acetonitrile molecule of solvation. Views of the molecule in Figs. 2(a) and 2(b) reveal a symmetrical cylindrical topology built about a central axis defined by the three copper atoms with approximately $D_{\infty h}$ local symmetry. The stoichiometry of the molecule and the coordination geometries about the coppers are consistent with oxidation states of +2 for the central and +1 for the two peripheral coppers. The phenyl groups on the triphenylphosphine and thiosalicylate ligands form a hydrophobic surface to the molecule which encapsulates the P$_2$CuO$_2$CuS$_2$CuP$_2$ core. The respective CuP$_2$, CuO$_2$, CuS$_2$ and CuP$_2$ planes spiral around the central copper axis with dihedral angles that appear to be determined primarily by C–H···π interactions between the phenyl groups [Fig. 2(b)]. The dianionic thiosalicylate ligands coordinate to the central copper(II) atom as bidentate ligands to give a *cis* S$_2$O$_2$ distorted square planar coordination sphere (Fig. 3). The S–Cu–S, O–Cu–O and *cis* S–Cu–O angles range from 86.2(3) to 99.7(1)° while the *trans* S–Cu–O angles are 148.1(2) and 149.0(2)°. The sulfur and oxygen atoms also function as bridging ligands between the copper(II) and copper(I) sites with the Cu(II)–S and Cu(II)–O bonds both *ca.* 0.2 Å shorter than the Cu(I)–S and Cu(I)–O bonds. The PPh$_3$ ligands coordinated to the copper(I) sites each adopt a distorted three-bladed propellor type conformation of the same chirality with each pair of ligands eclipsed with respect to each other and related by an approximate twofold rotation axis bisecting the P–Cu–P angle. We have shown previously that the transition from oxygen donor atoms in [Cu(PPh$_3$)$_2$(O$_2$CPh)] to sulfur donor atoms in the isomorphous [Cu(PPh$_3$)$_2$(S$_2$CPh)] complex results in an increase in the Cu–P distances and a decrease in the P–Cu–P angle, these variations being justified on the grounds of the greater covalency of Cu–S bonds compared to Cu–O bonds.[2] No such trends in the Cu–P bond lengths are apparent for the

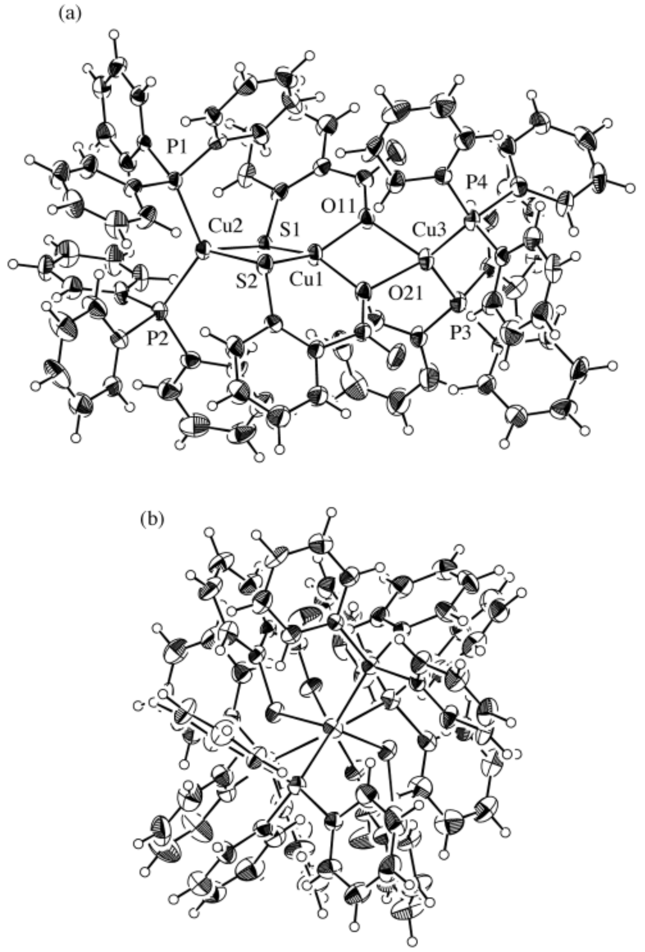

Fig. 2 View of the molecular structure of **2** (a) along and (b) down the Cu···Cu···Cu axis. Copper (II) coordination sphere: Cu(1)–O(*n*1) 1.97(1), 1.94(1) Å, Cu(1)–S(*n*) 2.196(3), 2.208(3) Å, S(1)–Cu(1)–S(2) 99.7(1)°, O(11)–Cu–O(21) 86.2(3)°; S-Cu(1)–O 148.1(2), 149.0(2), 96.4(2) and 93.6(2)°. Copper(I) P_2S_2 coordination sphere: Cu(2)–P(*n*) 2.257(3), 2.258(3), Cu(2)–S(n) 2.451(3), 2.396(3) Å; P(1)–Cu(2)–P(2) 125.0(1)°, S(1)–Cu(2)–S(2) 88.0(1)°. Copper(I) P_2O_2 coordination sphere: Cu(3)–P(n) 2.254(4), 2.229(3) Å, Cu(3)–O(*n*1) 2.20(1), 2.18(1) Å, P(3)–Cu(3)–P(4) 120.4(1)°, O(11)–Cu(3)–O(21) 75.1(2)°. Cu_3 geometry: Cu(1)···Cu(2), 3.159(2), Cu(1)···Cu(3), 3.160(2) Å, Cu(1)–Cu(2)–Cu(3), 178.90(6)°.

present molecule while the P–Cu–P angle of 125.0(1)° for the P_2CuS_2 site is, in fact, greater than the value of 120.4(1)° for the P_2CuO_2 site.

Compound **2** is a new and unusual member of an interesting class of polynuclear adducts between $[M(PPh_3)_2]^+$ (M = Cu, Ag) and anionic metal complexes that were prepared over 20 years ago by Coucouvanis and coworkers by the reaction of $[MX(PPh_3)_2]$ with salts of dianionic metal dithiolate complexes (*e.g.* refs. 4 and 5). The electrochemical synthesis used in the present study provides a new, uncomplicated approach to the preparation of this type of complex with the advantage that prior synthesis of the parent dianionic copper(II) complex is not required. In addition, the formation of crystalline products from the reaction mixtures is favoured by the very slow rate of dissolution of the metal as a result of the inherently low concentration of ionic species in the solution.

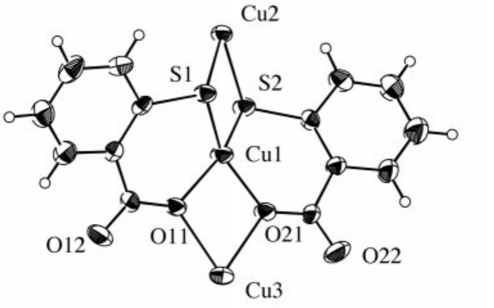

Fig. 3 View of the coordination sphere about the copper(II) atom.

Notes and references

† *Experimental details*: electrosynthesis. A copper anode and platinum coil cathode were inserted into a solution of 0.154 g (0.001 mol) of thiosalicylic acid (TSA) and 1.05 g (0.004 mol) of triphenylphosphine in 80 ml acetonitrile. Potentiostatic oxidation of the copper anode at 5 V resulted in the colourless solution initially turning a pale and then deeper shade of yellow. After 6–7 h compound **1** crystallized from the solution as large colourless blocky crystals (yield 0.6 g). After electrolysis for *ca.* 15 h, the solution changed to pale green and then to a darker green. During this time some of the crystals of **1** re-dissolved and deep green–black crystalline material (**2**) slowly formed (yield 0.2 g). Repetition of the experiment with PPh_3 to TSA mole ratios ranging from 2 : 1 to 5 : 1 resulted in the synthesis proceeding as above with only variations in the amount of **1** isolated.

Microanalysis: **1.** Found: C, 72.4; H, 5.1; N, 1.3. $C_{63}H_{53}CuNO_2P_3S$ requires C, 72.4; H, 5.1; N, 1.3%. **2.** Found: C, 66.8; H, 4.4; N, 0.5. $C_{88}H_{71}Cu_3O_4NP_4S_2$ requires C, 66.7; H, 4.5; N, 0.9 %.

‡ *Crystal data*: $C_{63}H_{53}CuNO_2P_3S$, **1**: $M = 1044.6$, triclinic, space group $P\bar{1}$ (C_2^2 no. 2), $a = 13.11(1)$, $b = 19.41(3)$, $c = 12.72(1)$ Å, $\alpha = 97.9(1)$, $\beta = 115.87(5)$, $\gamma = 104.1(1)°$, $U = 2713$ Å^3, $Z = 2$, μ (Mo-Kα) = 5.74 cm^{-1}, $T = 295$ K, $N = 9576$, N_o $[I > 3\sigma(I)] = 5006$; $R = 0.044$, $R_w = 0.054$.

$C_{88}H_{71}Cu_3O_4NP_4S_2$ **2**: $M = 1585.2$, triclinic, space group $P\bar{1}$, $a = 13.017(2)$, $b = 13.642(1)$, $c = 22.475(2)$ Å, $\alpha = 97.915(8)$, $\beta = 101.929(9)$, $\gamma = 100.666(4)°$, $U = 3772$ Å^3, $Z = 2$, μ(Mo-Kα) = 10.3 cm^{-1}, $T = 295$ K, $N = 13257$, N_o $[I > 3\sigma(I)] = 5904$; $R = 0.061$, $R_w = 0.045$.

§ We thank Karl Byriel, University of Queensland, for collection of the X-ray data set for compound **2**.

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Communication 8/06813E