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Synthesis and crystal structures of copper(I) iodide complexes chelating with bis(ethylamidophosphine)

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Abstract

Two copper(I) iodide complexes with polydentate bis(ethylamidophosphine) ligands were synthesized, characterized with crystal structures. They include a dimeric complex $[\mathrm{Cu}(\mu\text{-I})(\mathrm{CH_2NHCOC_2H_4PPh_2})_2]_2$ **1** containing a planar $\mathrm{Cu_2I_2}$ rhombohedron with two doubly bridged ligands and a tetrameric complex $\{\mathrm{Cu_4}(\mu\text{-I})_4[(\mathrm{CH_2NHCOC_2H_4PPh_2})_2]_2\}$ **3** with all the coppers and iodines forming a highly distorted cubane geometry.

Keywords: Copper(I) iodide complex; Bis(ethylamidophosphine); Cubane; Crystal structure

In recent years the cuprous halide complexes have drawn much attention. It is well known that these d^{10} complexes display rich coordination chemistry with a great diversity of stoichiometries and geometries [1–5] due to their relatively flat ground state potential energy surfaces. Herein, we report the synthesis, crystal structures and the coordination chemistry of copper(I) iodide complexes, $[\mathrm{Cu}(\mu\text{-I})(\mathrm{CH_2NHCOC_2H_4PPh_2})_2]_2$ **1** and $\{\mathrm{Cu_4}(\mu\text{-I})_4[(\mathrm{CH_2NHCOC_2H_4PPh_2})_2]_2\}$ **3** from the reaction Bis(ethylamidophosphine) [6] of with CuX. To our knowledge, **3** is the first example of $\mathrm{Cu_4I_4}$ cubane complex bridging with a polydentate ligand, and its electrochemical and photo-physical behavior is under active investigation.

Single crystals were grown from their appropriate solvent systems under favorable conditions. Intensity data were collected at ambient temperature on a MAR research image plate scanner using Mo-Kα radiation and ω scan technique. $60 \times 3^\circ$ frames with an exposure time of 3–15 min per frame were used. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallograhic Data Centre as supplementary publication no. CCDC 209664–209665. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

The synthesis of copper(I) iodide complexes are summarized in Scheme 1. An ORTEP plot showing the atomic-numbering scheme of **1** is depicted in Fig. 1, together with the relevant bond lengths and angles. The dimeric molecule contains two pseudotetrahedrally coordinated copper atoms bridged by two iodine atoms. Each copper atom is further coordinated with the phosphorus atoms of bis(ethylamidophosphine) ligand, which act as a bidentate bridge. This kind of bridging structure is uncommon in copper(I) iodide dimeric systems with bidentate ligands [7]; more often each ligand binds to the one copper atom owing to the great repulsion of the bridging iodine atoms [8]. This molecule exhibits a planar $\mathrm{Cu_2I_2}$ rhombohedron, where the Cu–I [2.695(2) and 2.722(1) Å] and Cu–P [2.262(2) and 2.256(2) Å] bond distances are comparable to the relevant bond lengths observed in $[\mathrm{CuI}(\mathrm{C_6H_5PH_2})_2]_2$ [9] or $[\mathrm{CuI}\{(\mathrm{C_6H_5})_2\mathrm{CH_3P}\}_2]_2$ [10]. However, it is noteworthy that the extensively ligand bridged non-bonding Cu···Cu [3.69 Å] distance is significantly elongated, correspond-

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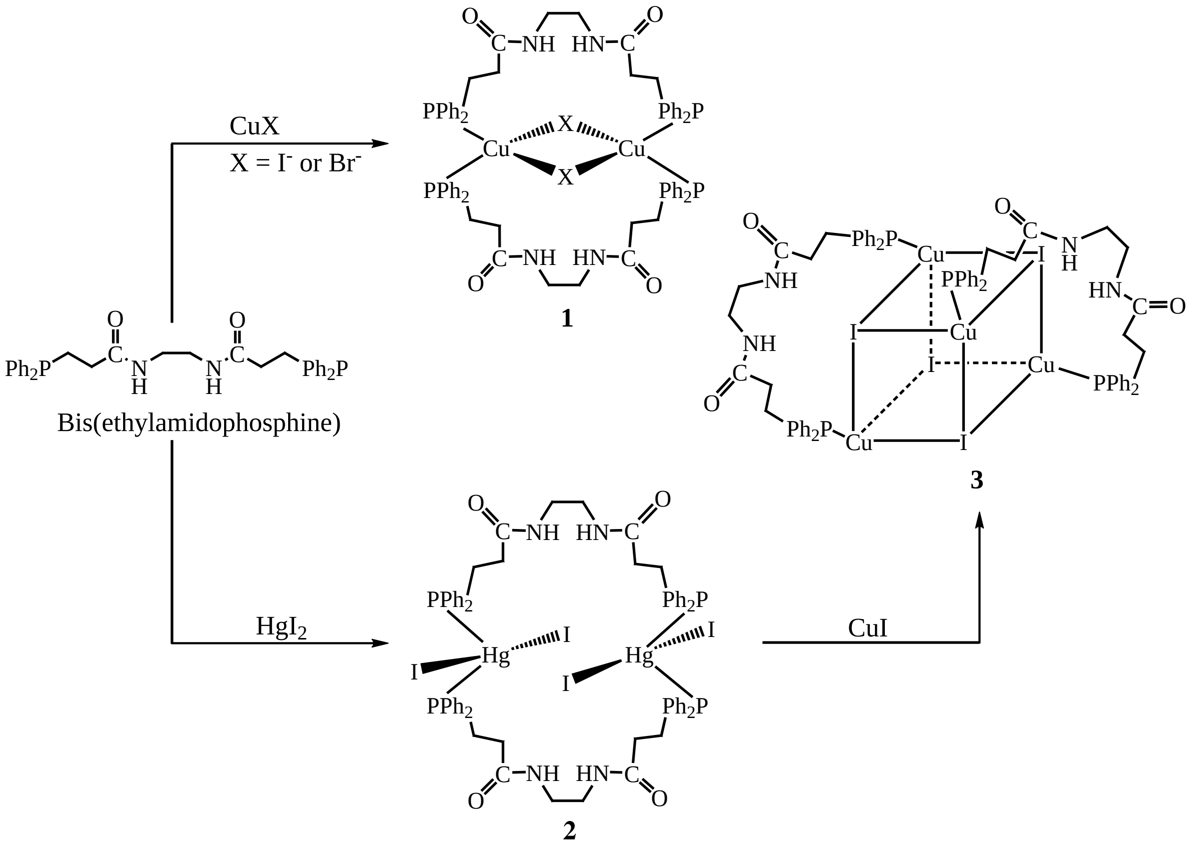

Scheme 1.

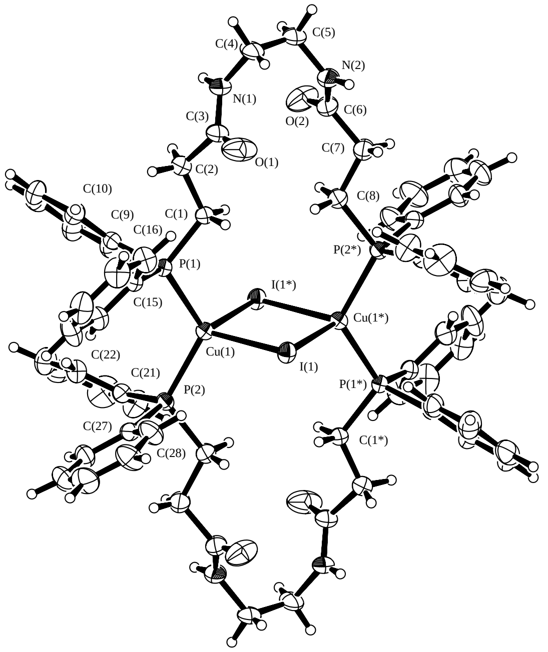

Fig. 1. The molecular structure of $[Cu(\mu\text{-}I)(CH_2NHCOC_2H_4PPh_2)_2]_2$ **1**, with atom numbering scheme. The 30% probability thermal ellipsoids are shown. Selected bond lengths (Å) and angles (°): Cu(1)—Cu(1*) 3.69, I(1)—I(1*) 3.96, Cu(1)—I(1) 2.695(2), Cu(1)—I(1*) 2.722(1), Cu(1)—P(1) 2.262(2), Cu(1)—P(2) 2.256(2); Cu(1)—I(1)—Cu(1*) 85.94(6), I(1)—Cu(1)—I(*) 94.06(6), I(1)—Cu(1)—P(1) 109.44(7), I(1)—Cu(1)—P(2) 110.12(6), I(1*)—Cu(1)—P(1) 111.19(6), I(1*)—Cu(1)—P(2) 107.53(7), P(1)—Cu(1)—P(2) 121.13(8).

ing to that observed in other dimeric copper(I) iodide complexes [11–14]. Consequently, the relatively short I···I [3.96 Å] bond distance and expanded Cu–I–Cu [85.94(6)°] angles are observed. This Cu_2I_2 rhombohedron geometry probably minimizes the lengthening effect of doubly bridging ligands, whilst keeping the minimum iodine–iodine interaction.

The Hg(II) iodide complex $[Hg(CH_2NHCOC_2H_4PPh_2)_2]_2[I]_4$ **2** was prepared according to a similar synthetic method as **1**, and fully characterized by spectroscopic methods. It is interesting to note that the reaction of **2** and CuI in dichloromethane at ambient temperature affords Cu_4I_4 cubane complex $\{Cu_4(\mu\text{-}I)_4[(CH_2NHCOC_2H_4PPh_2)_2]_2\}$ **3** in a good yield, however, the detailed mechanism of this reaction is not yet clear. Fig. 2 shows the labeling scheme for atoms in the molecule of **3**. The most relevant structural parameters are also reported. Four copper and four iodine atoms, taken alternatively, define a distorted cubane framework where each copper atom is tetrahedrally coordinated with three μ_3-iodides and a phosphorus atom of bis(ethylamidophosphine) ligand. Complex **3** is the first example of copper(I) iodide cubane complex bridging with a bidentate ligand. Both the Cu–I [range from 2.589(1) to 2.763(2) Å] and the Cu–P [2.252(3) and 2.266(3) Å] bond distances are

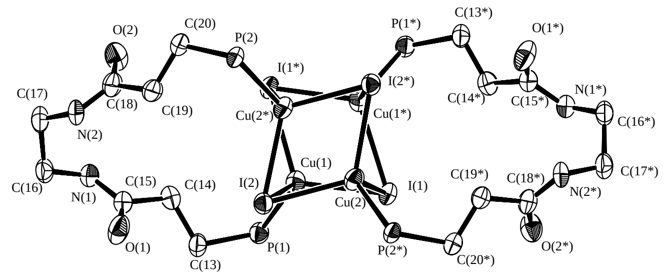

Fig. 2. The structure of $\{Cu_4(\mu\text{-}I)_4[(CH_2NHCOC_2H_4PPh_2)_2]_2\}$ **3**, with atom numbering scheme (phenyl rings and hydrogen are omitted for clarity). The 30% probability thermal ellipsoids are shown. Selected bond lengths (Å) an angles (°): Cu(1)—Cu(2) 2.88, Cu(1)—Cu(1*) 2.90, Cu(2)—Cu(2*) 2.81, Cu(1)—Cu(2*) 3.06, Cu(1)—I(1) 2.589(1), Cu(1)—I(1*) 2.763(2), Cu(1)—I(2) 2.709(2), Cu(2)—I(1) 2.705(2), Cu(2)—I(2) 2.619(2), Cu(2)—I(2*) 2.726(2), Cu(1)—P(1) 2.525(3), Cu(2)—P(2) 2.266(3), I(1)—I(2) 4.35, I(1)—I(2*) 4.33, I(1)—I(1*) 4.43, I(2)—I(2*) 4.48; Cu(1)—I(1)—Cu(1*) 65.51(6), Cu(1)—I(1)—Cu(2) 65.91(5), Cu(1*)—I(1)—Cu(2) 68.02(5), Cu(1)—I(1)—Cu(2*) 65.45(4), Cu(1*)—I(1)—Cu(2*) 68.50(5), Cu(2)—I(1)—Cu(2*) 63.28(5).

closely similar to the corresponding values observed in **1**. While the single ligand bridged Cu···Cu [3.06 Å] distances are slightly longer than those of non-bridging Cu···Cu bonds [2.81–2.90 Å], they are much shorter than the doubly bridged Cu···Cu bond observed in **1**. All the non-bonding Cu···Cu and I···I [4.33–4.48 Å] distances are within the expected range of values observed in other copper(I) iodide cubane systems with phosphine donors [15–18]. The Cu_4I_4 core shows significant distortions from regular cubane geometry, which is probably owing to the repulsion between the iodides. The distortion also leads to the small Cu–I–Cu angles, ranging from 63.28(5) to 68.50(5)°.

Supplementary material

For experimental details, please refer to the electronic supplement.

Acknowledgements

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