

Synthesis and structure of an asymmetric copper(I) dimer with two-coordinate and four-coordinate copper(I) sites†

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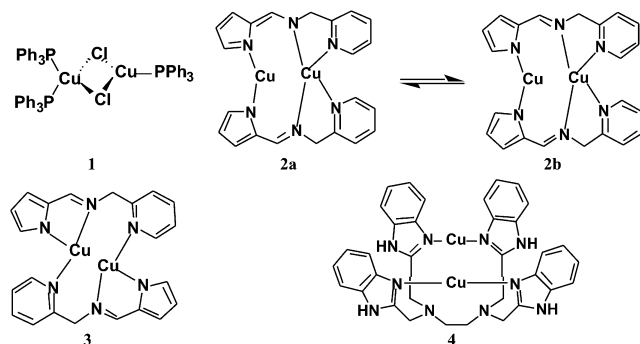
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An asymmetric copper(I) dimer $\text{Cu}_2(\text{pip})_2$ [pip = (2-picolyliminomethyl)pyrrole anion] with both two-coordinate and four-coordinate copper(I) sites was synthesized and studied by X-ray diffraction and DFT calculations.

Copper(I) coordination compounds have been studied intensively due to their biological relevance, catalytic properties, and theoretical interests.¹ Numerous mononuclear and polynuclear copper(I) complexes with different coordination numbers have been prepared and characterized. Recently the possible d^{10} – d^{10} interactions in copper(I) dimers have been the subjects of many experimental and theoretical studies.² Among the dimers and even polynuclear complexes, asymmetric ones are rare, especially when the compounds are synthesized from a single copper(I) source. Because of their potential of being selective catalysts and biomimetic models, asymmetric polynuclear complexes are of great interest, and several examples have been reported.³ An example is $\text{Cu}_2\text{Cl}_2(\text{PPh}_3)_3$ (**1**), which has both three- and four-coordinate copper(I).⁴ Herein, we report an unusual asymmetric copper(I) dimer with both 2- and 4-coordinate copper(I) sites (**2a** and its most important resonance form **2b**). **2** is an unusual homobimetallic complex with two isolated donor sets of different coordinate numbers,^{3d} and more importantly it was prepared in a way to not enforce asymmetry, *i.e.*, it self assembles. Hence, asymmetric **2** appears to be more stable than symmetric **3**, while our calculations of those of others⁵ show that **3** is a possible stable structure.



The reaction of CuCl and (2-picolyliminomethyl)pyrrole (1 : 1) in the presence of excess NaOMe in a mixture of CH_2Cl_2 and MeCN lead to the isolation of **2**. X-Ray diffraction analysis[‡] reveals that it has two different copper sites, best described as **2a**, Fig. 1. One copper coordinates with two deprotonated pyrroles forming a nearly linear geometry, with Cu – N distances of 1.865 and 1.864 Å and a N – Cu – N angle of 168.47°. The other copper is bonded to four imino- and pyridinyl nitrogens with two short distances in the four-coordinate site (1.987, 1.969 Å) and two long (2.165, 2.160 Å) distances that clearly indicate that all the four nitrogen

coordinate to copper. The copper(I) dimer $[\text{Cu}_2(\text{EDTB})](\text{ClO}_4)_2$ [EDTB = *N,N,N,N'*-tetrakis(2-benzimidazolymethyl)-1,2-ethanediamine] (**4**) has a similar geometry about its Cu (I) sites.⁶ However, the long (2.774 Å) separation between copper sites and two of the nitrogens indicate that the two nitrogens do not coordinate and that this compound is a symmetric dimer with two two-coordinate copper(I) sites.

Low temperature NMR of **2** in CD_2Cl_2 at high-concentration (-25°C , 20 mg mL^{-1}) were identical to the room-temperature spectrum of a low-concentration solution (26°C , 5 mg mL^{-1}) in terms of splitting pattern and the ratio of the peaks. The splitting patterns of all the peaks are similar to that of the pure pip anion, and only changes in the chemical shifts occur. Hence, together with the calculations discussed below, the NMR data show that the asymmetric dimeric structure is stable in both solution and as a solid. Furthermore, an equilibrium between the dimer and the monomer was not observed. The NMR spectra are given in the ESI.[†] To exclude the possibility that **2** is a kinetic product arising from the low solubility of CuCl and NaOMe , $[\text{Cu}(\text{NCMe})_4][\text{PF}_6]$ was reacted with NPr_3 and pip and only forms **2a**. In contrast, pyrrole diimine copper(I) complexes⁵ have three-coordinate Cu (I) sites for both the monomers and dimers. Hence, it is intriguing as to why the asymmetric **2a** is favored over the symmetric **3**.

The relative stability of **2** and **3** was estimated by theoretical *ab initio* methods using B3LYP density functional theory.⁷ The non-valence electrons were described using the effective core potentials of Wadt and Hay,⁸ and the LANL2DZ basis set for the valence electrons.⁹ As the structure of **3** is unknown, it was fully optimized starting from the optimum B3LYP/LANL2DZ structure of **2**. A vibrational analysis of the B3LYP/LANL2DZ

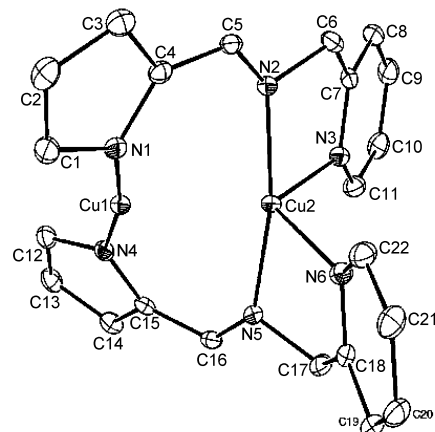


Fig. 1 ORTEP (50%) labeling of **2**. Cu1 – Cu2 2.6126(3), Cu1 – N1 1.8648(17), Cu1 – N4 1.8641(17), Cu2 – N2 1.9689(16), Cu2 – N3 2.1604(17), Cu2 – N5 1.9868(16), Cu2 – N6 2.1650(17) N1 – Cu1 – N4 168.48(7), N4 – Cu1 – Cu2 96.94(5), N1 – Cu1 – Cu2 , 94.31(5), N2 – Cu2 – N3 82.73(7), N2 – Cu2 – N6 , 106.79(7), N2 – Cu2 – N5 168.71(7), N2 – Cu2 – Cu1 86.19(5), N3 – Cu2 – Cu1 132.24(5), N3 – Cu2 – N6 111.89(6), N3 – Cu2 – N5 101.56(6), N6 – Cu2 – Cu1 115.80(5), N6 – Cu2 – N5 81.49(6), N5 – Cu2 – Cu1 83.23(5).

[†] Electronic supplementary information (ESI) available: synthesis, NMR, computational details. See <http://www.rsc.org/suppdata/cc/b2/b208865g/>

optimized structures of **2** and **3**, showed that both structures are true minimum energy structures (all frequencies are positive, the smallest one being equal to 15 cm⁻¹ in **2** and 13 cm⁻¹ in **3**).

The optimized structure of **2** is similar to that observed, with a two-coordinate Cu with Cu–N distances of 1.900 Å, and a N–Cu–N angle of 171.8°, and a four-coordinate Cu with the N atoms disposed in a butterfly form. The latter has two short Cu–N distances of 2.056 Å and the remaining two of 2.174 Å with a N–Cu–N angle between the largest two distances of 166.1°, between the shortest two distances of 122.9°, and between the short and large distances of 80.8 and 106.0°, depending on the pair selected. Also, the N atoms are disposed in a distorted tetrahedral form with a Cu–Cu distance of 2.705 Å. The structure of **3** is similar to that of **2**, also presenting both two- and four-coordinate Cu atoms. The Cu–N distances to the dicoordinated Cu are 1.879 Å (pyrrolic N) and 1.947 Å (pyridinic N), with a N–Cu–N angle of 166.1°. The tetra-coordinated Cu again has the N atom placed in a distorted tetrahedral disposition, with Cu–N distances of 2.010, 2.020, 2.114, and 2.210 Å. The angle between the shortest two Cu–N bonds is 143.3°, while that between the largest Cu–N bonds is 118.4°. Here the Cu–Cu distance is 3.225 Å. The main difference between **2** and **3** is the geometry of the ligands as **2** has the five and six-membered rings of each ligand nearly coplanar, whereas in **3** the five and six-membered rings are nearly perpendicular to each other. The relative stabilities of **2** and **3** obtained from the B3LYP/LANL2DZ calculations indicate that **2** is more stable than **3** by 17.2 kcal mol⁻¹. Thus, there is a clear thermodynamic preference for **2**, even at 0 K.

We have also analyzed the electronic structure of the isomers **2** and **3** to get some extra information on the electronic structure of Cu atoms. A Mulliken population analysis indicates that both Cu in **2** have a similar effective charge (0.33 e⁻ on the di- and 0.37 e⁻ on the tetra-coordinated Cu). Thus their oxidation state is similar. All of the N atoms have small negative charges (-0.16, -0.16, -0.21, -0.21, -0.38, -0.38 a.u.), the C atoms have charge alternation (4 positive values around 0.30 a.u., 18 negative values with an averaged value of -0.28 a.u.). The same analysis for **3** indicates similar net electronic charges on the two Cu atoms (0.36 and 0.42 e⁻, larger in the tetra-coordinated Cu), all N atoms are again negatively charged (-0.16, -0.17, -0.26, -0.27, -0.33, and -0.42 a.u.). The C atoms again show an alternation on the signs, with similar values to those found for **2**. In both isomers the H atoms have net electronic charges (~0.20 a.u.). Given the well-known tendency of the Mulliken method of decreasing the charge on the metal atom in metal–ligand bonds, a second population analysis in which the charge is computed so that it reproduces the molecular electrostatic potential map was performed. Again, these results indicate that the effective charge on the two Cu atoms is similar (**2**: 0.53, 0.60 e⁻; **3**: 0.60 and 0.36 e⁻ on the di- and tetra-coordinated atom, respectively, computed using the Merz–Kollman method,¹⁰ taking as radii the values 1.50, 0.96, and 1.20 Å for C, Cu and H, respectively). This value is a more realistic indication of the effective oxidation state of the Cu, whose formal charge is +1 in each Cu.

Given the short 2.613 Å distance between the two copper atoms for **2** the question of the presence of a direct Cu...Cu interaction between the two d¹⁰ Cu(I) atoms arises. Previous studies on Cu...Cu interactions on neutral dimers, as occurs for **2** and **3**, reveals a stabilizing Cu...Cu interaction of ~2.5 kcal mol⁻¹. Such interactions can only be taken into account properly by methods that adequately describe the dispersion term. This is not the case for the B3LYP density functional method. Given the small magnitude of this term and the similar Cu...Cu distances found in both isomers, we do not expect that if the Cu...Cu interaction were properly taken into account

using more sophisticated methods this would change the relative stability of the two isomers.

In conclusion, the asymmetric copper(I) dimer **2** has been prepared and computationally shown to be more stable than its symmetric isomer by 17.2 kcal mol⁻¹. This is the first fully characterized copper(I) dimer with two-coordinate and four-coordinate copper sites.

Computational details: all calculations were carried out at the B3LYP/LANL2DZ level using the appropriate options in Gaussian-98.¹¹ The optimized geometries, energy, localized charges and vibrational frequencies for each isomer are given as ESL.†

Notes and references

† Crystal data for **2**: C₂₂H₂₀Cu₂N₆, *M* = 495.52, monoclinic, space group *P*2₁/*n*, *a* = 8.84000(10), *b* = 18.8747(3), *c* = 13.1348(2) Å, β 109.4323(8)°, *V* = 2066.73(5) Å³, *T* = 150 K, *Z* = 4, *D*_c = 1.593 Mg cm⁻³, μ(Mo-Kα) = 2.079 mm⁻¹, 8013 measured reflections, 4705 unique reflections, with *I* ≥ 2σ(*I*) used in the refinement, absorption correction (multi-scan), *R*₁ = 0.0280, *wR*₂ = 0.0662. CCDC reference number 191949. See <http://www.rsc.org/suppdata/cc/b2/b208865g/> for crystallographic data in CIF or other electronic format.

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