

# One- and three-dimensional infinite arrays of Cu(I) ions exhibited by [Cu(NH<sub>3</sub>)<sub>2</sub>]Br and [Cu(NH<sub>3</sub>)Cl] in the solid state

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In the solid state, [Cu(NH<sub>3</sub>)Cl] forms a three-dimensional network with each Cu<sup>I</sup> ion being surrounded by three other Cu<sup>I</sup> centres in a trigonal-planar fashion [Cu...Cu = 2.979(1) Å; cubic space group *I*2<sub>3</sub>], whereas in [Cu(NH<sub>3</sub>)<sub>2</sub>]Br the cations establish infinite linear (Cu...Cu)<sub>∞</sub> chains spanning the crystal lattice [Cu...Cu = 2.931(1) Å; monoclinic space group *C*2/*c*].

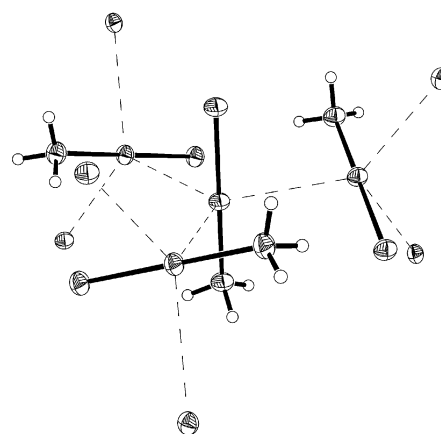
Two-coordinate linear complexes [AuL<sub>2</sub>] of gold(I) tend to aggregate in the solid state in such a manner that the Au–Au contacts approximate to those distances found in the bulk metal.<sup>1,2</sup> The term “aurophilicity” has been coined for this phenomenon, which is to be attributed to relativistic effects and hybridisation of 5d and 6s orbitals on the gold centres.<sup>3</sup> The question whether similar bonding interactions exist for the lighter elements (*e.g.* copper) is still heavily under debate. The problem is aggravated by the fact that most of the few structurally characterized copper complexes<sup>3–7</sup> featuring short Cu<sup>I</sup>–Cu<sup>I</sup> contacts either possess bridging ligands (*e.g.* tris[1,5-ditolyl]pentaazadienocopper(I)<sup>8</sup>) or are made up between monomeric units of different charge (*e.g.* [CuL<sub>2</sub>]<sup>+</sup>[CuL'<sub>2</sub>]<sup>–9,10</sup>). In many of these cases, aggregation may thus be merely ligand-enforced<sup>11</sup> or due to ion pairing, and it is difficult to decide whether weak d<sup>10</sup>–d<sup>10</sup> closed shell interactions do play a significant additional role. However, two examples of compounds have been published recently providing evidence for attractive Cu<sup>I</sup>–Cu<sup>I</sup> interactions between uncharged trinuclear complexes<sup>12</sup> and even between negatively charged cuprate molecules<sup>13</sup> in the absence of any bridging ligation. Similar conclusions can be drawn from theoretical studies on model dimers of the type [H<sub>3</sub>CCuX]<sub>2</sub> (X = *e.g.* NH<sub>3</sub>, CO, CNLi)<sup>14</sup> and [H<sub>3</sub>NCuCl]<sub>2</sub>.<sup>15</sup> We present in this paper the X-ray crystal structure determinations of the textbook compounds [Cu(NH<sub>3</sub>)Cl] **1** and [Cu(NH<sub>3</sub>)<sub>2</sub>]Br **2** as a contribution to the current discussion (Scheme 1).

Single crystals of **1** and **2** have been grown from the reaction mixtures of the appropriate copper(II) halide with two equivs. of lithium bis(trimethylsilyl)amide and 1,4-naphthohydroquinone (Scheme 1).<sup>†</sup> As byproducts, 1,4-naphthoquinone and 1,4-bis(trimethylsilyloxy)naphthalene could be isolated and identified using IR and NMR spectroscopy. It may thus be concluded that 1,4-naphthohydroquinone not only acts as a proton source, but is also involved in the reduction of the Cu(II) centres. The reaction of copper(II) chloride with lithium bis(trimethylsilyl)-

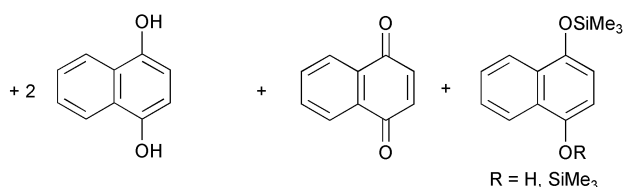
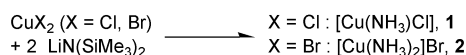
amide in the absence of 1,4-naphthohydroquinone is known to give the copper(I) amide [CuN(SiMe<sub>3</sub>)<sub>2</sub>].<sup>16</sup> It is thus uncertain whether 1,4-naphthohydroquinone is the only reducing agent in our case. However, we found no evidence for the formation of hydrazine derivatives or other products likely to be generated *via* amine radical species.

The crystals of [Cu(NH<sub>3</sub>)Cl] **1** are chiral (cubic space group *I*2<sub>3</sub>) with the three heavy atoms lying on a crystallographic three-fold axis (Fig. 1).<sup>‡</sup> The copper–nitrogen and copper–chlorine bond lengths possess values of 1.894(3) Å and 2.105(1) Å, respectively. Each copper atom is surrounded by three other [Cu(NH<sub>3</sub>)Cl] moieties which leads to a trigonal-bipyramidal coordination sphere (Fig. 1). Given the high symmetry of the crystal lattice, all three Cu...Cu distances are necessarily equal [Cu...Cu contacts between next neighbours = 2.979(1) Å; copper metal: 2.56 Å<sup>4</sup>]. All in all, an infinite three-dimensional network of Cu<sup>I</sup> ions featuring comparatively short Cu...Cu contacts is established in the solid state. In each trigonal-bipyramidal fragment three [Cu(NH<sub>3</sub>)Cl] molecules are grouped around the central unit in a propeller-like arrangement with their chloride ligands placed on the same side of the Cu<sub>4</sub> plane as the central ammine group [Cl–Cu...Cu#1 = 87.5(1)°; Cl–Cu...Cu#1–Cl#1 = 109.4(1)°]. The three equatorial [Cu(NH<sub>3</sub>)Cl] units are linked *via* N–H...Cl hydrogen bonds [N–H = 0.89(4) Å, H...Cl = 2.66(4) Å; N–H...Cl = 167(3)°].

[Cu(NH<sub>3</sub>)<sub>2</sub>]Br **2** crystallizes in the monoclinic space group *C*2/*c* (Fig. 2).<sup>‡</sup> The Cu–N bond lengths of 1.898(3) Å in the linear cation [Cu(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup> are identical to those found in the corresponding monoammine complex **1** [Cu–N = 1.894(3) Å].



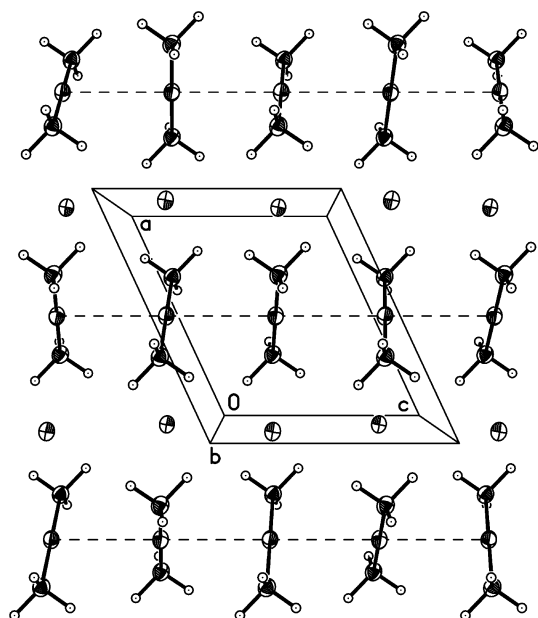
**Fig. 1** Crystal structure of compound **1**; thermal ellipsoids shown at the 50% probability level. Selected bond lengths [Å], atom–atom distances [Å], angles [°] and torsion angles [°]: Cu–N = 1.894(3), Cu–Cl = 2.105(1), Cu...Cu#1 = 2.979(1); N–Cu–Cl = 180.0, N–Cu...Cu#1 = 92.6(1), Cl–Cu...Cu#1 = 87.5(1), Cu#1...Cu...Cu#2 = 119.8(1), N–Cu...Cu#1–N#1 = 109.4(1), Cl–Cu...Cu#1–Cl#1 = 109.4(1), N–Cu...Cu#1–Cl#1 = –70.6(1), Cu#2...Cu...Cu#1...Cu#4 = 109.4(1), Cu#3...Cu...Cu#1...Cu#4 = –61.8(1), Cu#2...Cu...Cu#1...Cu#5 = –79.4(1); Hydrogen bonds: N–H = 0.89(4), H...Cl = 2.66(4); N–H...Cl = 167(3). Symmetry transformations used to generate equivalent atoms: *x*, –*y*, –*z* – 1/2; –*x*, –*y* – 1/2, *z*; –*x* – 1/2, *y*, –*z*.



**Scheme 1** Synthesis of **1** and **2**.

In contrast to **1**, which establishes a Cu–Cl bond, the bromide counterion of **2** does not coordinate to the copper centre [shortest distance Cu⋯Br = 3.446(1) Å]. Similar to **1**, comparatively short Cu⋯Cu contacts are also observed between the cationic [Cu(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup> fragments of **2** [Cu⋯Cu = 2.931(1) Å], even though this arrangement suffers from electrostatic repulsion (note: for the ligand-unsupported anionic dimer [tBuCuCN]<sub>2</sub><sup>2-</sup>, a Cu⋯Cu distance of 2.713(1) Å has been reported.<sup>13</sup> The fact that this value is 0.218 Å smaller than the one observed in **2** indicates a rather shallow potential energy surface related to the Cu⋯Cu stretching mode). Each Cu<sup>I</sup> ion of **2** is surrounded by two nitrogen atoms and two other Cu<sup>I</sup> centres in a planar fashion. This coordination sphere results in infinite linear (Cu⋯Cu)<sub>∞</sub> chains spanning the crystal lattice. Adjacent [Cu(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup> moieties adopt a staggered rather than an eclipsed conformation relative to each other [torsion angle N–Cu⋯Cu#1–N#1 = 68.2(4)°]. Each bromide ion is connected to six different ammonia molecules *via* hydrogen bonds. While the crystal structure of [Ag(NH<sub>3</sub>)<sub>2</sub>]Br is yet unknown, the corresponding gold complex has been investigated by X-ray diffraction.<sup>17</sup> Here, the asymmetric unit contains two crystallographically independent C<sub>s</sub>-symmetric [Au(NH<sub>3</sub>)<sub>2</sub>]Br molecules forming a dimer consisting of mutually orthogonal linear [Au(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup> cations [Au⋯Au = 3.414(1) Å]. DFT calculations will soon be published to provide information on the nature of the Cu⋯Cu interactions in **1** and **2** in the solid state.

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**Fig. 2** Crystal structure of compound **2**; thermal ellipsoids shown at the 50% probability level. Selected bond lengths [Å], atom–atom distances [Å], angles [°] and torsion angles [°]: Cu–N = 1.898(3), Cu⋯Cu#1 = 2.931(1), Br⋯Br#2 = 4.497(1); N–Cu–N#3 = 180.0; N–Cu⋯Cu#1 = 92.4(1), N–Cu⋯Cu#4 = 87.6(1), Cu#1⋯Cu⋯Cu#4 = 180.0; N–Cu⋯Cu#1–N#1 = 68.2(4). Hydrogen bonds: N–H(1) = 0.78(6), N–H(2) = 1.01(7), N–H(3) = 0.92(8), H(1)⋯Br = 2.87(6), H(2)⋯Br#5 = 2.54(7), H(3)⋯Br#6 = 2.59(8); N–H(1)⋯Br = 159(4), N–H(2)⋯Br#5 = 162(5), N–H(3)⋯Br#6 = 175(6). Symmetry transformations used to generate equivalent atoms: #1: 1 – x, y, –1/2 – z; #2: 1 – x, –y, –z; #3: 1 – x, 1 – y, –z; #4: 1 – x, y, 1/2 – z; #5: 3/2 – x, 1/2 – y, 1 – z; #6: 3/2 – x, 1/2 – y, –z.

## Notes and references

† *Synthesis of [Cu(NH<sub>3</sub>)Cl] 1*: A solution of LiN(SiMe<sub>3</sub>)<sub>2</sub> (0.33 g, 2.00 mmol) in THF (2 mL) was added dropwise with stirring at –78 °C to a slurry of CuCl<sub>2</sub> (0.13 g, 1.00 mmol) in THF (10 mL), whereupon a deep blue solution formed. After the solution had been stirred at –78 °C for 1 h, 1,4-naphthoquinone (0.32 g, 2.00 mmol) in THF (15 mL) was added slowly. The resulting mixture was allowed to warm to ambient temperature and stored for 1 d to give colourless blocks of **1**. Yield: 0.04 g (35%). *Synthesis of [Cu(NH<sub>3</sub>)<sub>2</sub>]Br 2*: **2** was synthesized similar to **1** from CuBr<sub>2</sub> (0.22 g, 1.00 mmol), LiN(SiMe<sub>3</sub>)<sub>2</sub> (0.33 g, 2.00 mmol) and 1,4-naphthoquinone (0.32 g, 2.00 mmol) in THF. The product crystallized as colourless needles. The reaction was repeated ten times with yields ranging between 25–45%.

‡ *Crystal data of [Cu(NH<sub>3</sub>)Cl] 1*: H<sub>3</sub>ClCuN, *M* = 116.02 g mol<sup>–1</sup>, cubic, *a* = *b* = *c* = 8.4135(8) Å, *V* = 595.57(10) Å<sup>3</sup>, *T* = 146(2) K, space group *I*2<sub>3</sub>, *Z* = 8, μ(Mo–K<sub>α</sub>) = 7.898 mm<sup>–1</sup>, 6829 reflections measured, 505 unique (*R*<sub>int</sub> = 0.072) which were used in all calculations. The final *wR*(*F*<sup>2</sup>) was 0.042 (all data), min./max. residual electron density –0.36/0.46 e Å<sup>–3</sup>. The H atom position was taken from a difference Fourier synthesis. It was refined with an individual isotropic displacement parameter. The direction of the chiral axis was determined by the value of the Flack *x* parameter: *x* = –0.03(2). CCDC reference number 200580. *[Cu(NH<sub>3</sub>)<sub>2</sub>]Br 2*: H<sub>6</sub>BrCuN<sub>2</sub>, *M* = 177.52 g mol<sup>–1</sup>, monoclinic, *a* = 6.602(1), *b* = 12.879(2), *c* = 5.861(1) Å, β = 114.91(2)°, *V* = 451.98(14) Å<sup>3</sup>, *T* = 100(2) K, space group *C*2/*c*, *Z* = 4, μ(Mo–K<sub>α</sub>) = 13.472 mm<sup>–1</sup>, 4925 reflections measured, 641 unique (*R*<sub>int</sub> = 0.088) which were used in all calculations. The final *wR*(*F*<sup>2</sup>) was 0.071 (all data), min./max. residual electron density –0.87/1.02 e Å<sup>–3</sup>. Hydrogen atoms were refined isotropically. CCDC reference number 200581. See <http://www.rsc.org/suppdata/cc/b2/b212517/> for crystallographic data in CIF or other electronic format.

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