First example of a copper(I)–water bond. Synthesis and structure of polymeric poly-μ-2,3-diphenylquinoxaline–(aqua)copper(I) cation

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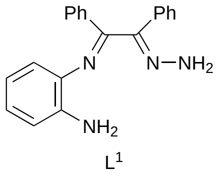
The perchlorate salt of the poly-μ-2,3-diphenylquinoxaline(aqua)copper(I) cation containing a discrete $Cu^+–OH_2$ bond is synthesised and characterised structurally.

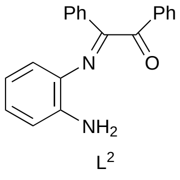
In terms of Pearson's hard–soft classification of Lewis acids and bases, Cu^+ is generally accepted as 'soft' while H_2O is 'hard'.[1] Consequently, according to the hard–soft acid–base (HSAB) principle of Pearson,[1–3] there is an inherent incompatibility between the Cu^+ ion and H_2O. This statement is supported by the experimental observation that the Cu^+ ion disproportionates in water ($\log K = 6.00$) into metallic copper and Cu^{2+} [eqn. (1)].[4] Hence while water is a very common ligand in the chemistry of the 'borderline' Cu^{2+} ion, ligation of water to a copper(I) center is hitherto unknown.[5] However, the HSAB principle only considers relative stability and does not preclude the possibility of a bond between Cu^+ and H_2O altogether. Herein for the first time we report a copper(I) complex having a discrete $Cu^+–OH_2$ bond.

$$2\mathrm{Cu}^+ \overset{K}{\rightleftharpoons} \mathrm{Cu}^{2+} + \mathrm{Cu}^0(\mathrm{s}) \qquad (1)$$

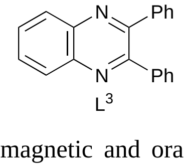
The novel copper(I) complex has been obtained during attempts to develop the copper(II) chemistry of the Schiff base L^1 of 1,2-phenylenediamine (opda) and benzilmonohydrazone (bmh). When copper(II) perchlorate hexahydrate is reacted with an equimolar quantity of L^1, generated *in situ* in ethanol, the C=N bonds are hydrolysed giving rise to L^2 and free hydrazine, opda and benzil. Subsequently L^2 cyclises with the elimination of a water molecule resulting in formation of 2,3-diphenylquinoxaline L^3. Reaction of opda with benzil also yields L^3.[6] The hydrazine formed *in situ* reduces Cu^{2+} to Cu^+. One of the products isolated from this reaction mixture is the perchlorate salt of the polymeric cationic copper(I) complex of L^3 and water, $\{[CuL^3(H_2O)]ClO_4\cdot0.5C_2H_5OH\}_n$ **1**. Subsequent investigation demonstrates that compound **1** is formed in good yield by reaction of copper(II) perchlorate hexahydrate with L^3 in the presence of excess hydrazine hydrate.†



L^1



L^2



L^3

Compound **1** is diamagnetic and orange–red [λ_{max} (Nujol mull): 390 nm]. It is indefinitely stable in air in the solid state. However, in solution, it is almost immediately oxidised to give a faint green solution. Its structure, as revealed by X-ray crystallography,‡ consists of an infinite polymeric chain cation (Fig. 1), where adjacent copper(I) centers are bridged by the aromatic nitrogens of L^3, and perchlorate anions which are not coordinated to the copper. Each copper atom is coordinated through nitrogen to two molecules of L^3 and a water molecule completes the coordination sphere (Fig. 2). The coordination of the copper is best described as distorted linear CuN_2 with a weak interaction with water. Alternatively the coordination might be viewed as distorted trigonal planar. The three angles around copper vary considerably from those expected in a regular environment [N(1)–Cu(1)–N(2) 152.5(2)°, N(1)–Cu(1)–O(1) 107.6(2)°, N(2)–Cu(1)–O(1) 99.8(2)°]. There is no precedent for a $Cu^+–OH_2$ bond in the literature with which the Cu(1)–O(1) bond length [2.154(6) Å] observed here can be compared. However, from the bond valence sum models,[7,8] in a symmetric CuO_3^+ chromophore, the ideal $Cu^+–O$ bond length is calculated to be 1.99 Å. Thus the Cu(1)–O(1) bond in **1** is longer than expected. On the other hand, the $Cu^+–N$ bonds [Cu(1)–N(1) 1.952(4) Å, Cu(1)–N(2) 1.968(5) Å] in **1** are slightly shorter than that expected (1.98 Å) for a symmetric CuN_3^+ moiety.

Compound **1** provides a rare example of a copper(I) complex with a neutral oxygen donor coordinated to the metal. There are, to the best of our knowledge, only two other examples[9,10] and in these the O donor atom belongs to acetone, which is much

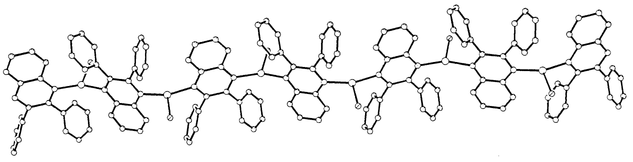


Fig. 1 The polymeric cation in **1**; H atoms are omitted for clarity

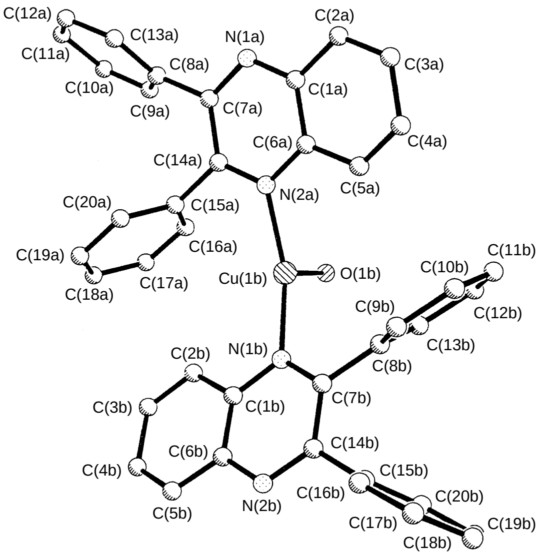


Fig. 2 The coordination sphere of the copper(I) ion in **1**; H atoms are omitted for clarity

'softer' than water. It may be noted in passing that the Cu^+ ion does not disproportionate in acetone to any significant extent ($\log K - 1.50$).[4]

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Footnotes

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[†] A 5 ml ethanolic solution of 0.370 g (1 mmol) of $Cu(ClO_4)_2{\cdot}6H_2O$ was added to a 20 ml ethanolic solution of 0.282 g of L^3 (1 mmol). The resulting bluish green solution was heated to boiling. To this hot solution, 0.05 ml of hydrazine hydrate (4 mmol) diluted in 5 ml of ethanol was added dropwise with constant stirring. The resulting deep orange reaction mixture was stirred for 5 min and then left in the air. (Initially a small amount of white precipitate appeared which dissolved during stirring.) After 30 min, the deep orange–red crystalline compound precipitated was filtered, washed with 2 ml of ethanol and dried *in vacuo* over fused $CaCl_2$. Yield, 0.290 g (60%). Satisfactory analytical data was obtained.

[‡] *Crystal data* for $C_{21}H_{19}ClCuN_2O_{5.5}$ **1**: $M_w = 486.37$, orthorhombic, space group $P2_12_12$, $a = 12.996(3)$, $b = 17.392(3)$, $c = 9.183(2)$ Å, $U = 2075.6(7)$ Å^3, $Z = 4$, $D_c = 1.56$ g cm^{-3}, $\mu = 1.22$ mm^{-1}. 2685 reflections collected on an automated four-circle diffractometer (Nicolet R3mV; Mo-Kα, $\lambda = 0.710\,73$ Å, 2θ 5–55° at 20 °C) and were corrected for Lorentz and polarisation effects, and empirically for absorption. The structure was solved by Patterson methods (SHELXS-86[11]) and refined using alternating least-squares and difference-Fourier techniques (SHELXL-93,[12] refinement based on F^2). In the latter stages a disordered solvent molecule (ethanol) was observed to lie about the twofold axis at (1.0, 0.5, z). The best refinement was obtained with a net occupancy of 0.5 for this molecule. The non-hydrogen atoms (except those of the ethanol) were refined anisotropically while the hydrogens of the organic ligand were placed in idealised positions. The final cycle of least-squares refinement included 268 parameters and did not shift any parameter by more than 0.01 times its standard deviation. The final residuals were $R = 0.0564$ and $wR_2 = 0.1538$, observed data [$I \geqslant 2\sigma(I)$] and $R = 0.0675$ and $wR_2 = 0.1742$, for all data. The absolute structure was determined using SHELXL-93 procedures [absolute structure parameter $-0.02(3)$]. CCDC 182/520.

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