Formation of a μ-η^2 : η^2-Disulfide Dinuclear Copper(II) Complex by Thermal Decomposition of a Thiolate Complex *via* C–S Bond Cleavage

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Thermal decomposition of a thiolatocopper(II) complex Cu(SCPh$_3$)(HB(3,5-Pr$^i_2$pz)$_3$) **1** yields a novel μ-η^2 : η^2-disulfide dinuclear copper(II) complex {Cu[HB(3,5-Pr$^i_2$pz)$_3$]}$_2$(S$_2$) **2** whose crystal structure was determined by X-ray crystallography.

While a wide variety of transition metal disulfide complexes are known, the disulfide copper(II) complex has not been reported so far to our knowledge.[1–7] We now found that spontaneous thermal decomposition of a thiolatocopper(II) complex Cu(SCPh$_3$)[HB(3,5-Pr$^i_2$pz)$_3$] **1**† results in formation of a novel μ-η^2 : η^2-disulfide dinuclear copper(II) complex {Cu[HB(3,5-Pr$^i_2$pz)$_3$]}$_2$(S$_2$) **2**.

Previously, we have reported the synthesis and structure of **1** as an accurate synthetic model for the active sites of blue copper proteins.[8] Complex **1** is thermally unstable; when **1** was allowed to stand in *n*-octane under argon at room temp., the intense blue solution turned reddish brown within 1 h. Removal of the solvent followed by recrystallisation of the resultant solid from CH$_2$Cl$_2$ afforded analytically pure deep reddish brown crystals of **2** in *ca.* 35% isolated yield.‡ The FD-MS spectrum and analytical data suggested the formulation of **2** as a dinuclear complex solely bridged with a disulfide. Complex **2** exhibits characteristic visible bands at 479 (ε, 3500 dm^3 mol^{-1} cm^{-1}) and 660 (190) nm. The former band is attributable to a $S_2^{2-} \rightarrow Cu^{II}$ LMCT transition,[1,9] whereas the latter one is assigned to a d–d band, which is diagnostic of copper in the 2+ oxidation state with a tetragonal coordination environment. As presented in Fig. 1, the dinuclear structure of **2** was confirmed by X-ray crystallography.§

Each copper atom in **2** is five-coordinate, being surrounded with three nitrogen atoms from the tris(pyrazolyl)borate ligand and two sulfur atoms of the bridging disulfide. The S–S′ distance [2.073(4) Å] is close to the values reported for other disulfide complexes (2.00–2.06 Å).[1–6] Since the molecule sits on a crystallographically imposed centre of symmetry, the disulfide and two copper atoms sit on a plane. The Cu–S and Cu–S′ distances, 2.274(2) and 2.256(3) Å, are almost identical within experimental error. Thus, the coordination mode of the disulfide is referred to as planar-μ-η^2 : η^2. It is notable that the S–S′ distance is significantly shorter than that found in the other planar-μ-η^2 : η^2-disulfide nickel complex (2.21 Å).[7] The unusually elongated distance of disulfide in the nickel complex may be associated with its mixed valence state [Ni^{I,II}]. With the same tris(pyrazolyl)borate, a structurally analogous μ-η^2 : η^2-peroxo copper(II) complex {Cu[HB(3,5-Pr$^i_2$pz)$_3$]}$_2$(O$_2$) has been synthesised.[10] We suggest that the strong peculiarity of copper(II) ion to favor a five-coordination over tetrahedral structure is the predominant driving force to substantiate the unique μ-η^2 : η^2 coordination mode of disulfide or peroxide, with this hindered facial capping ligand.

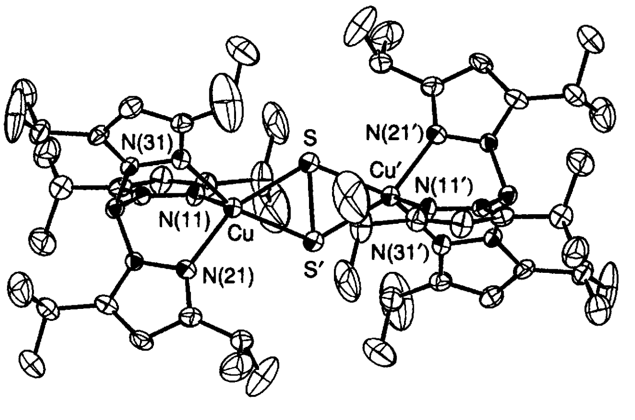
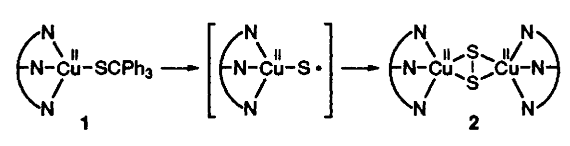


Fig. 1 ORTEP view of {Cu[HB(3,5-Pr$^i_2$pz)$_3$]}(S$_2$) **2**. The solvent molecules of crystallisation are omitted for clarity. Selected bond distances (Å) and angles (deg): Cu–S, 2.274(2); Cu–S′, 2.256(3); Cu–N(11), 2.215(5); Cu–N(21), 2.020(5); Cu–N31, 2.016(6); Cu··Cu′, 4.028(3); S–S′, 2.073(4); S–Cu–N(11), 107.3(1); S–Cu–N(21), 156.2(2); S–Cu–N(31), 103.3(2); S′–Cu–N(11), 108.3(2); S′–Cu–N(21), 104.6(2); S′–Cu–N(31), 153.9(2); N(11)–Cu–N(21), 89.3(2); N(11)–Cu–N(31), 90.4(2); N(21)–Cu–N(31), 93.3(2); Cu–S–Cu′, 125.5(1); Cu–S–S′, 62.3(1); Cu–S′–S, 63.2(1).

Because of its dinuclear structure, **2** exhibits an enormously strong antiferromagnetic property; **2** is EPR silent and gives rise to a very sharp ^{1}H NMR spectrum typical for diamagnetic complex.[10] The diamagnetic property was further confirmed by the magnetic susceptibility.[11] Thus, the μ-η^2 : η^2-disulfide can mediate a very strong magnetic coupling ($-2J > 600$ cm^{-1}) between the two copper(II) ions as does μ-η^2 : η^2-peroxide.[11]

The formation of **2** *via* thermal decomposition of **1** is explained by homolytic C–S bond cleavage illustrated in eqn. (1).



(1)

Homolysis of C–S bond of thiolate ligands coordinated to metal ions is known.[12] The resultant Cu^{II}–S· species are coupled together to afford the disulfide copper(II) complex **2**.

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Footnotes

† HB(3,5-Pr$^i_2$pz)$_3$ = hydrotris(3,5-diisopropyl-1-pyrazolyl)borate.

‡ FTIR(KBr, cm^{-1}): ν(BH) 2539. ^{1}H NMR(C$_6$D$_5$CD$_3$, 270 MHz, 27 °C) δ: 1.23 (d, J = 7 Hz, 36H, CH*Me*$_2$), 1.24 (d, J = 7 Hz, 36H, CH*Me*$_2$), 3.48 (m, J = 7 Hz, C*H*Me$_2$), 3.60 (m, J = 7 Hz, 6H, C*H*Me$_2$), 5.91 (s, 6H, pz). UV–VIS [CH$_2$Cl$_2$, λ_{max}, nm(ε, dm^3 mol^{-1} cm^{-1})] 355(31200), 479(3500), 660(190). FD-MS(m/z) 1121(M$^+$).

§ *Crystal data* for **2**·5(CH$_2$Cl$_2$)(C$_{59}$H$_{102}$N$_{12}$B$_2$Cu$_2$S$_2$Cl$_{10}$) M = 1546.9: Monoclinic space group $C2/c$, a = 22.379(12), b = 13.288(8), c = 28.358(12) Å, β = 110.18(6)°, V = 7915(7) Å^3 and Z = 4. The X-ray data collection was carried out at −80 °C. The initial structure was solved by the direct method and expanded using Fourier techniques. All non-hydrogen atoms except for one CH$_2$Cl$_2$ molecule which were calculated isotropically were refined anisotropically. Hydrogen atoms were included but not refined. The structure was refined by full-matrix least-squares method (TEXSAN) for 3817 observed reflections [$(I > 5\sigma(I)$] and 391 variable parameters. The current R (Rw) factor is 5.93 (5.61)%. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Centre. See Information for Authors, Issue No. 1.

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