Copper-induced N-N bond cleavage results in an octanuclear expanded-core grid-like complex

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Electronic Supplementary Information

Synthetic details

Adpt and Hdpt were prepared according to the procedure reported by Geldard and Lions (Scheme S1). All other materials were bought commercially and used as received. Methanol and acetonitrile were HPLC-grade, diethyl ether was laboratory reagent grade. IR spectra were recorded as pressed KBr discs on a Perkin Elmer Spectrum BX FT-IR spectrophotometer between 400 and 4000 cm⁻¹. ESI mass spectra were recorded at the University of Waikato on a Bruker MicrOTOFQ spectrometer in methanol. UV/Vis/NIR spectra were recorded on a Varian CARY 500 Scan UV/Vis/NIR spectrophotometer between 200 and 1600 nm in methanol. Microanalyses were measured at the Campbell Microanalytical Laboratory, University of Otago, New Zealand.

[Cu₈(dpt)₄(OH)₄(OAc)₈]
Anhydrous copper(I) acetate (61 mg, 0.50 mmol) and adpt (60 mg, 0.25 mmol) were combined, and methanol (40 mL) was added. The mixture was stirred at room temperature, open to the air for two hours, during which time it turned from a murky green-brown suspension to a clear dark green solution. This solution was subjected to diethyl ether vapour diffusion, resulting in the formation of blue-green crystals, which were isolated by filtration and dried thoroughly in vacuo. Yield: 69 mg (56%). Elemental analysis, found: C 40.23, H 3.35, N 13.87; calc. for Cu₈C₆₄H₆₀N₂₀O₂₀·0.5(C₂H₅)₂O: C 40.14, H 3.32, N 14.19; calc. for Cu₈C₆₄H₆₀N₂₀O₂₀: C 39.67, H 3.12, N 14.46%. IR (inter alia): 3435 (br, vs), 3096, 3054, 2975, 2926, 1614 (vs), 1565, 1468, 1419, 1396, 1332, 1278, 1254, 1187, 1040, 1024, 801, 755, 725, 648, 617, 554. UV/Vis/NIR (CH₃OH): λmax/nm: 675 (ε = 410 L mol⁻¹ cm⁻¹).

Several repeats of this synthesis consistently give elemental analysis consistent with the (1) contaminated with small amounts of solvent (methanol or diethyl ether). A typical example is shown above. When removed from solvent, the crystals are observed to lose their lustre – presumably due to disintegration of the crystal lattice. We suggest that at this point, small amounts of solvent are trapped by the complex, leading to the observed elemental analyses. The reported percentage yield refers to (1)·0.5(C₂H₅)₂O.
[Cu₄(dpt)₂(OH)(OMe)(OAc)₄]·H₂O

Hdpt (50 mg, 0.22 mmol) was dissolved in methanol (20 mL). To this clear colourless solution was added dropwise with stirring a suspension of copper(II) acetate hydrate (89 mg, 0.44 mmol) in methanol (10 mL). The resulting blue solution was stirred at room temperature, open to the air for one hour before a drop of triethylamine was added. This afforded no discernable colour change. The blue solution was subjected to diethyl ether vapour diffusion, resulting in the formation of blue powder and a few blue single crystals (removed for X-ray crystal structure determination), which were isolated by filtration and dried in vacuo. Yield: 82 mg (73%). Elemental analysis, found: C 39.61, H 3.39, N 14.04; calc. for Cu₄C₃₃H₃₂N₁₀O₁₀·H₂O: C 39.60, H 3.42, N 13.99%. IR (inter alia): 3417 (br, vs), 3095, 2927, 1614 (vs), 1509, 1468, 1419, 1397, 1332, 1279, 1255, 1188, 1041, 1024, 801, 755, 749, 725, 705, 660, 647, 617, 555.

Scheme S1. Synthesis of adpt and Hdpt. Reagents and conditions: (a) N₂H₄·H₂O, reflux (6 hrs); (b) 1 M HCl (aq), reflux (0.5 hr); (c) HNO₃(aq), NaNO₂(aq) 5 °C – reflux, 10 mins, then NH₄OH(aq).

Crystallography

Complex 1: All non-hydrogen atoms except disordered methyl group of one acetate moiety were refined anisotropically. One of the acetate groups is disordered, due to the terminal methyl group rocking backwards and forwards; this was modelled by having two equal occupancy sites for C(34) and the three hydrogen atoms attached to it H(34a-c) (alternative sites C(35) and H(35a-c). Figures 2, 3 and S1 show only the C(34) position of this group. Hydrogen atoms were placed at calculated positions and refined using a riding model except for those of the hydroxide groups which were located from difference maps, their bond lengths idealised, and then the atom positions fixed (using AFIX 01).
**Complex 2:** All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at calculated positions and refined using a riding model except for OH protons on the hydroxide and interstitial methanol molecules which were located from difference maps and fixed in place (using AFIX 01).

**Asymmetric Unit of 1:**

![Perspective view of asymmetric unit of \([\text{Cu}_8(\text{dpt})_4(\text{OAc})_8(\text{OH})_4]\) (1). Hydrogen atoms, except hydroxide protons, and minor site of disordered methyl group are omitted for clarity. Symmetry generated atoms are shown as dotted bonds; symmetry operations: a) \(x, 3/2-y, 3/2-z\); b) \(3/2-x, y, 3/2-z\).](image-url)
Fig. S2. Hydrogen-bonding interactions in central square of [Cu₈(dpt)₄(OAc)₈(OH)₄] 1. Only copper ions and bridging hydroxide moieties are shown. O…O = 2.689(9) Å, O…H = 1.84 Å, <O(1)-H(1x)…O(1a) = 169.4°. Symmetry operations used to generate equivalent atoms: a) x, 3/2-y, 1/2-z; b) 3/2-x, y, 1/2-z; c) 3/2-x, 3/2-y, z.
**Literature Mechanisms**

![Chemical structure diagram]

**Fig. S3.** Previously reported oxidative additions of compounds similar to adpt.\(^2\)\(^-\)\(^3\)

![Chemical structure diagram]

**Fig. S4.** Synthesis of 1,1′-azobis(tetrazole) and subsequent decomposition in solution with release of nitrogen gas.\(^4\)

![Chemical structure diagram]

**Fig. S5.** Synthesis of 1,4-bis-[1-methyltetrazol-5-yl]-1,4-dimethyl-2-tetrazene and subsequent decomposition upon pyrolysis with release of nitrogen gas.\(^5\)

![Chemical structure diagram]

**Fig. S6.** Zhang and Jiao’s proposed mechanism of copper-catalysed oxidative addition of aryl amines.\(^6\)
References