

Unique cationic, neutral and anionic copper(II) nitrite species in a single compound

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Crystallisation from an aqueous/acetonitrile solution of copper(II) nitrite containing bdmppy {bdmppy = 2,6-bis[(3,5-dimethyl)pyrazol-1-yl]pyridine} affords a compound with a unique arrangement of cationic $[\{\text{Cu}(\text{bdmppy})(\text{NO}_2)_2(\mu\text{-NO}_2\text{-}\kappa\text{O}:\kappa\text{N})\}]^+$, neutral $[\text{Cu}(\text{bdmppy})(\text{NO}_2)_2]$ and anionic $[\text{Cu}(\text{NO}_2)_4]^{2-}$ copper(II) nitrite species, which feature diverse copper–nitrite coordination modes.

Copper nitrite complexes with ancillary *N*-donor ligands are of current interest^{1–4} following the elucidation of the structures of several copper-containing nitrite reductase enzymes, such as *Achromobacter Cycloclastes*⁵ or *Alicylogenes Xylooxidans*.⁶ The nitrite anion is a versatile ligand to copper(II)^{7,8} exhibiting nitro (*via* the nitrogen),⁹ nitrito (*via* an oxygen),¹⁰ chelating (*via* both oxygens),⁸ or bridging (*via* the nitrogen and an oxygen)¹¹ coordination modes. This versatility is displayed in the complex $[\text{Cu}(\text{L})(\text{NO}_2)][\text{PF}_6]$ {L = tris[(2-pyridyl)methyl]amine}, where two structural isomers have been determined, differing only in nitro or nitrito co-ordination.^{2b} In nitrite reductases the site of nitrite binding has been shown to involve three histidine donors;^{5,6} the mode of nitrite coordination, although still to be confirmed, is thought to be asymmetric bidentate (*cis*-monodentate).⁶

Using the tridentate *N*-donor ligands 2,6-bis(pyrazol-1-yl)pyridine (bppy) and its tetramethyl analogue 2,6-bis[(3,5-dimethyl)pyrazol-1-yl]pyridine (bdmppy) to mimic the three histidine donors of the enzymes, we have investigated the chemistry of Cu(bppy) and Cu(bdmppy) moieties with the nitrite anion. As part of this work we have synthesised and structurally characterised the unique complex $[\{\text{Cu}(\text{bdmppy})(\text{NO}_2)_2(\mu\text{-NO}_2\text{-}\kappa\text{O}:\kappa\text{N})\}]_2[\text{Cu}(\text{bdmppy})(\text{NO}_2)_2]_2[\text{Cu}(\text{NO}_2)_4] \cdot \text{MeCN}$ **1**, which we describe herein.

The stoichiometric addition of an aqueous solution of 'copper nitrite' [prepared by the addition of an aqueous solution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ to a stoichiometric amount of $\text{Ba}(\text{NO}_2)_2$] to a solution of bdmppy resulted in a green solution, slow evaporation of which in air gave a green crystalline product **1**. Single crystal IR spectroscopy confirmed the presence of ligand and nitrite **1**.‡

The structure of complex **1** (Fig. 1) was determined by single crystal X-ray diffraction.§ Its unit cell consists of seven copper centres; two dimeric cationic $[\{\text{Cu}(\text{bdmppy})(\text{NO}_2)_2(\mu\text{-NO}_2\text{-}\kappa\text{O}:\kappa\text{N})\}]^+$ units, two neutral $[\text{Cu}(\text{bdmppy})(\text{NO}_2)_2]$ units, a $[\text{Cu}(\text{NO}_2)_4]^{2-}$ anion and an acetonitrile solvent molecule. Three distinct copper–nitrite coordination modes occur (Scheme 1). Following precedence⁷ these are defined as (i) *cis*-monodentate, (ii) *trans*-monodentate and (iii) bridging. For all *cis*-monodentate nitrites, the second oxygen atom is remotely located (>2.50 Å) in an axial coordination position. This contact is ignored, however, in describing the nitrite coordination mode and the copper(II) coordination geometry owing to the fact that it is a consequence of constraints imposed by the anion geometry.⁷

The $[\{\text{Cu}(\text{bdmppy})(\text{NO}_2)_2(\mu\text{-NO}_2\text{-}\kappa\text{O}:\kappa\text{N})\}]^+$ units [Fig. 1(a)] are dimeric [Cu...Cu 5.304(1) Å] and represent the first fully structurally characterised example of the $\kappa\text{O}:\kappa\text{N}$ bridging motif in copper(II) chemistry. Previously, a disordered example has been described in $[\{\text{Cu}(\text{dien})\}_2(\mu\text{-bimpydz})][\text{NO}_2]$

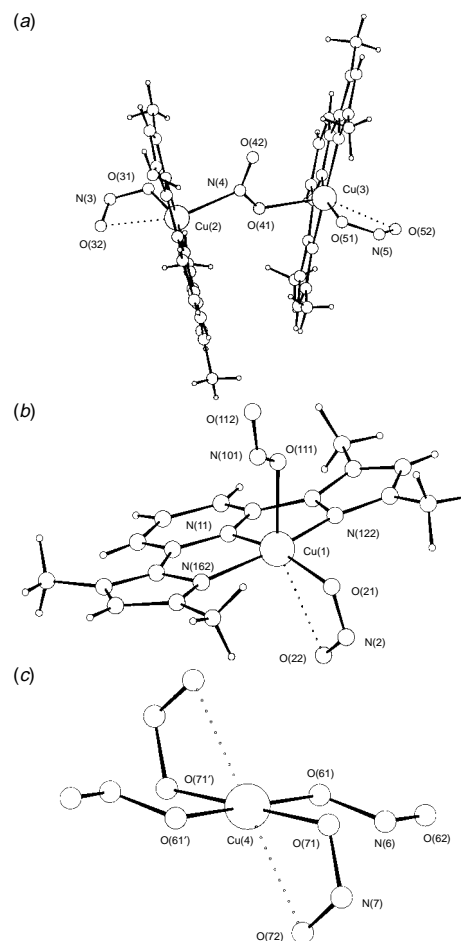
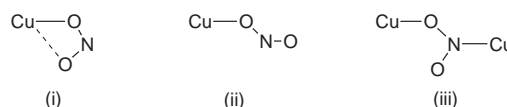


Fig. 1 The molecular structures of the three unique copper nitrite species in **1**: (a) the dinuclear $[\{\text{Cu}(\text{bdmppy})(\text{NO}_2)_2(\mu\text{-NO}_2\text{-}\kappa\text{O}:\kappa\text{N})\}]^+$ cation, (b) the neutral $[\text{Cu}(\text{bdmppy})(\text{NO}_2)_2]$ species and (c) the $[\text{Cu}(\text{NO}_2)_4]^{2-}$ anion

$[\text{BF}_4]_3 \cdot \text{MeCN}$ [dien = diethylenetriamine; bimpdz = 3,6-bis(imidazol-1-yl)pyridazine].¹¹ Each of the two independent copper atoms has all three nitrogen atoms from the bdmppy ligand and an oxygen atom from a *cis*-monodentate nitrite in the basal positions of a square pyramidal geometry [Cu(2)–N 1.964(3), 1.997(3), 2.010(3); Cu(2)–O(31) 1.962(3); Cu(3)–N 1.968(3), 2.006(4), 2.011(4); Cu(3)–O(51) 1.957(3) Å]. The bridging nitrite occupies the apical position of both copper coordination spheres [Cu(2)–N(4) 2.307(4), Cu(3)–O(41) 2.267(3) Å]. The second oxygen atoms of each of the *cis*-



Scheme 1 Copper–nitrite coordination modes: (i) *cis*-monodentate (asymmetric bidentate); (ii) *trans*-monodentate; (iii) bridging

monodentate nitrites are weakly bound in axial positions [Cu(2)–O(32) 2.577(3), Cu(3)–O(52) 2.576(3) Å].

In the neutral [Cu(bdmppy)(NO₂)₂] species [Fig. 1(b)], the copper atom has a coordination geometry based on a square pyramid, with the three nitrogen atoms of the bdmppy ligand occupying three of the basal positions [Cu(1)–N(11) 1.978(4), Cu(1)–N(122) 1.990(5), Cu(1)–N(162) 1.984(4) Å]. The remaining basal site is occupied by a *cis*-monodentate nitrite [Cu(1)–O(21) 1.958(4) Å]. The apical position is occupied by a weakly bound disordered nitrite which adopts either a *trans*-monodentate [67%; Cu(1)–O(111) 2.168(8) Å] or *cis*-monodentate [33%; Cu(1)–O(121) 2.15(3), Cu(1)–O(122) 2.90(3) Å] co-ordination mode. Overall the copper atom adopts an N₃O₂ donor set. Again the second oxygen atom of the basally located *cis*-monodentate nitrite is weakly bound in the remaining axial position [Cu(1)–O(22) 2.655(4) Å].

The [Cu(NO₂)₄]²⁻ anion [Fig. 1(c)] is situated on a centre of inversion, and comprises two symmetry related *cis*-monodentate [Cu(4)–O(71) 2.039(5) Å] and two symmetry related *trans*-monodentate nitrites [Cu(4)–O(61) 1.955(4) Å], resulting in a square planar CuO₄ coordination sphere. The second oxygen atoms of the *cis*-monodentate nitrites are weakly bound in the two remaining axial positions [Cu(4)–O(72) 2.518(5) Å]. Although the anions [Cu(NO₂)₅]³⁻ and [Cu(NO₂)₆]⁴⁻ are well documented in the literature as salts of the form M^I₃[Cu(NO₂)₅] (M^I = K, Cs),¹² and M^I₂M^{II}[Cu(NO₂)₆] (M^I = Tl, K, Rb, Cs; M^{II} = Ca, Sr, Ba, Pb)¹³ or M^I₅M^{III}[Cu(NO₂)₆]₂ (M^I = Tl, K, Rb, Cs; M^{III} = Ce)¹⁴ there is only one previous report of the [Cu(NO₂)₄]²⁻ anion, as the structurally uncharacterised 1,2-xylylenebis(triphenylphosphonium) salt.¹⁵ Hence this is the first reported structure containing the tetranitritocuprate(II) anion.

The only other copper(II) nitrite in the literature containing a *mer*-directed tridentate N-donor ligand is [Cu(terpy)(NO₂)(H₂O)] [NO₂]·H₂O, **2** (terpy = 2,2':6',2''-terpyridyl). Despite the similarity of the tridentate ligands, the two complexes show very different formulations. Complex **2** has a square based pyramidal geometry and is ligated by the three N-donors of the terpy ligand, a monodentate nitrite anion and an axially located water molecule.⁹

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Notes and References

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‡ Single crystal IR spectroscopy for **1**: v/cm⁻¹ (unassigned bands are presumed to be associated with the various modes of coordinated nitrite):

3125m (bdmppy), 1616s (bdmppy), 1596s (bdmppy), 1569s (bdmppy), 1488s (bdmppy), 1476s, 1455s (bdmppy), 1432s, 1396br, 1365s (bdmppy), 1318br, 1301br, 1182m, 1144m, 1057m (bdmppy), 1040m (bdmppy), 1014m (bdmppy), 999m (bdmppy), 827m, 809m, 798m (bdmppy).
§ *Crystal data*: C₉₀H₁₀₂Cu₇N₄₄O₂₈·2CH₃CN, *M* = 2775.02, triclinic, space group *P*1 (no. 2), *a* = 10.785(3), *b* = 15.192(3), *c* = 18.917(4) Å, *α* = 101.83(2)°, *β* = 96.63(3)°, *γ* = 107.81(2)°, *U* = 2834.97 Å³, *Z* = 1, *μ* = 1.38 mm⁻¹, 9375 unique data. *T* = 150.0(2) K. Refinement converged to give conventional *R* = 0.0762, *R'* = 0.0847 for all data and 0.0668, 0.0789 for 8212 data with *I* ≥ 2σ(*I*). CCDC 182/912.

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