

Cu(II) Ion Catalytic Oxidation of *o*-Phenylenediamine and Diaminomaleonitrile and the Crystal Structure of the Final Products (C₁₂N₄H₁₁)(ClO₄)·H₂O and [Cu₅(CN)₆(dmf)₄]

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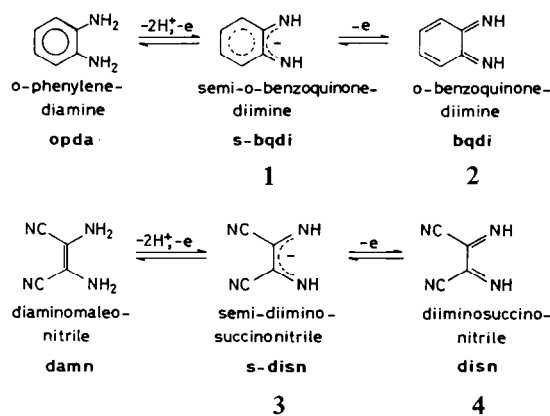
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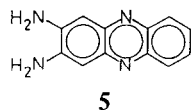
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Transition metal complexes with highly delocalized, unsaturated, electron-rich ligands are of considerable interest, owing to their unusual properties. As a result of works on the first row transition metal complexes of *s*-bqdi, bqdi, *s*-disn and disn ligands [1-4], we report the reactions of Cu(II) ion with opda and damn, and the crystal structures of the final products, (C₁₂N₄H₁₁)(ClO₄)H₂O and [Cu₅(CN)₆(dmf)₄].



Reaction of the cupric chloride with opda in ammoniacal solution led to the isolation of the grey compound, 2,3-diaminophenazine, 5.



The violet crystalline compound [Cu(opda)₂](ClO₄)₂ was dissolved in CH₃CN and oxidized by air immediately to give a dark green solution, which

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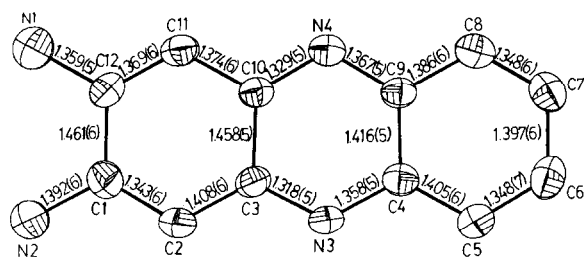
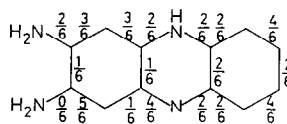


Fig. 1. ORTEP plot of the (C₁₂N₄H₁₁)⁺ cation. *P*2₁/*n*, *a* = 11.087(2), *b* = 4.923(1), *c* = 25.533(3) Å, β = 99.23(1)°. *Z* = 4. 1534 reflections with *I* > 2σ(*I*), 265 parameters, *R* = 0.056, *R*_w = 0.054.

gradually became dark orange after a few days, when orange crystals suitable for single crystal X-ray analysis were deposited. The structure of the orange crystal, shown in Fig. 1, consists of a protonated 2,3-diaminophenazine cation, a perchlorate anion and a water molecule; the proton of the cation was found to be on the N4 atom. According to the contribution of six possible resonance forms of the cation, the π bond strengths are as follows, if each resonance form is equally weighted. The observed bond pattern agrees very well with above π bond strength.



It has been reported [5] that [Ni(*s*-bqdi)₂]⁺ undergoes a disproportionation reaction to form 2,3-diaminophenazine, 5. It is believed that the dark green species initially formed by air oxidation of [Cu(opda)₂](ClO₄)₂ in CH₃CN is [Cu(*s*-bqdi)₂] or a similar complex. Due to the high electron affinity of the Cu(II) ion, the Cu(II) ion might attract one electron from the *s*-bqdi ligand; this would initiate the disproportionation reaction. Because the solution is neutral or slightly acidic, the final product is protonated 2,3-diaminophenazine, 5.

Yellow crystals were formed by reaction of the cupric acetate with damn in dmf solution for a few days. It was found later to have the composition of Cu₅(CN)₆(dmf)₄ and the characteristic IR frequencies of ν_{C-H}: 2960; ν_{C≡N}: 2156, 2122; ν_{C=O}: 1652 cm⁻¹.

The crystal structure of [Cu₅(CN)₆(dmf)₄] has a number of unusual and interesting features. Firstly, it is obviously a mixed valence metal complex which contains both Cu(I) and Cu(II) ions: two Cu(I) ions with linear coordination, [Cu(CN)₂] (see Fig. 2a), the other two Cu(I) ions with distorted tetrahedral coordination [Cu(μ-CN)(NC)₂]₂ (Fig. 2b), and one

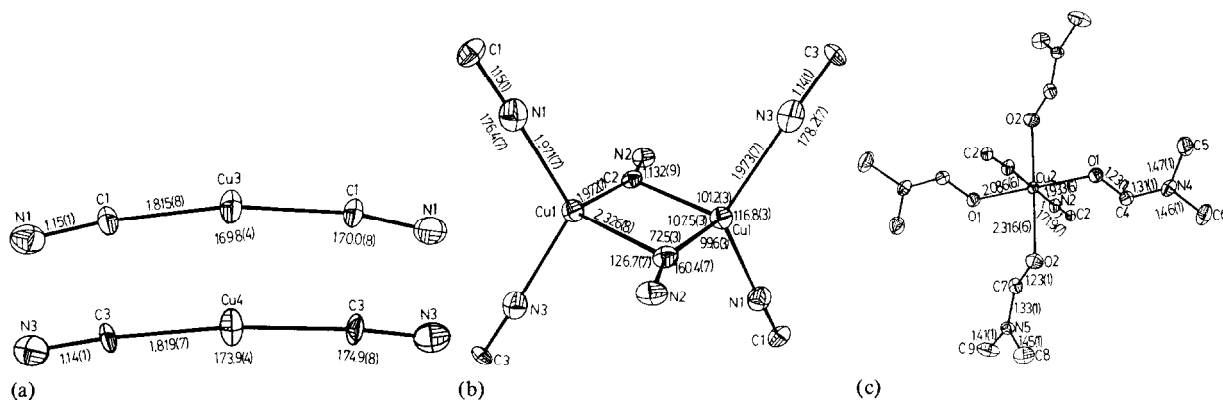


Fig. 2. ORTEP plot of the coordination sphere of the $[\text{Cu}_5(\text{CN})_6(\text{dmfd})_4]$ complex. $C2/c$, $a = 14.034(4)$, $b = 12.591(3)$, $c = 16.403(3)$ Å, $\beta = 91.99(2)^\circ$. $Z = 4$. 1270 reflections with $I > 3\sigma(I)$, 227 parameters, $R = 0.039$, $R_w = 0.041$. The structure is a three-dimensional network with bridge cyanides. Cu1 is at general position, Cu2 is at inversion center, and Cu3 and Cu4 are at 2-fold axis. (2a) Coordination sphere of linear Cu(I) ions. (2b) Coordination sphere of distorted tetrahedral Cu(I) ions. (2c) Coordination sphere of distorted octahedral Cu(II) ion.

Cu(II) ion with distorted octahedral geometry $[\text{Cu}(\text{NC})_2(\text{dmfd})_4]$ (Fig. 2c). Secondly, the structure can be described as a 3-dimensional network with bridging cyanides. There are two types of CN bridges; one is a bidentate bridge $[\text{C1}-\text{N1}, \text{C3}-\text{N3}]$ which connects the linear Cu(I)-Cu3, Cu4 and the tetrahedral Cu(I)-Cu1. The other is a tridentate bridge $[\text{C2}-\text{N2}]$, which coordinates asymmetrically to two tetrahedral Cu1 ions through a carbon atom and to the octahedral Cu2 ion through a nitrogen atom. As far as we know, the tridentate CN bridge has not been reported. Thirdly, the coexistence of the Cu(II) ion with the cyanide ion in this structure should be noted, since it is well known that the Cu(II) ion can oxidize the cyanide ion to form cyanogen [6]. The magnetic moment, 2.1 BM, and the g values of the Cu(II) ion, 2.308, 2.174, 2.051, are consistent with the distorted octahedral geometry of the Cu(II) ion [7].

It is clear that the cyanide ion originates from the oxidation of damn through S-disn, disn, cyanogen intermediates. Such oxidations have been reported in the synthesis of $[\text{Co}(\text{CN})(\text{s-disn})_2]$ by the air oxidation of damn and Co(II) ion [1]. On the other hand, the HCN can be added to cyanogen to form disn, which is readily reduced to damn [8, 9]. The reason why the $[\text{Cu}(\text{s-disn})_2]$ complex is unstable is attributed to the high electron affinity of Cu(II) ion, which will cause the further oxidation of the s-disn ligand.

The attempted isolation of reaction intermediates, Cu complexes of benzoquinonediimine or diiminosuccinonitrile, is currently being undertaken.

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References

- 1 S. M. Peng, Y. Wang, S. Wang, M. Chung, Y. Le Page and E. Gabe, *J. Chem. Soc., Chem. Commun.*, 329 (1981).
- 2 S. M. Peng, Y. Wang and C. K. Chiang, *Acta Crystallogr., Sect. C*, 40, 1541 (1984).
- 3 S. M. Peng, C. T. Chen, D. S. Liaw, C. I. Chen and Y. Wang, *Inorg. Chim. Acta*, 101, L31 (1985).
- 4 S. M. Peng, D. S. Liaw, Y. Wang and A. Simon, *Angew. Chem., Int. Ed. Engl.*, 24, 210 (1985).
- 5 M. G. Miles and J. D. Wilson, *Inorg. Chem.*, 14, 2357 (1975).
- 6 F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry', Wiley, New York, 1980.
- 7 A. Abragam and B. Bleaney, 'Electron Paramagnetic Resonance of Transition Ions', Clarendon, Oxford, 1970.
- 8 R. E. Moser, J. M. Fritsch, T. L. Westman, R. M. Kliss and C. N. Matthews, *J. Am. Chem. Soc.*, 89, 5673 (1967).
- 9 R. W. Begland, A. Cairncross, D. S. Donald, D. R. Hartter, W. A. Sheppard and O. W. Webster, *J. Am. Chem. Soc.*, 93, 4953 (1971).