Reaction of Copper(I) Phenoxide with PhNCS: Formation and *X*-Ray Structure of a Novel Copper(I) Hexameric Complex

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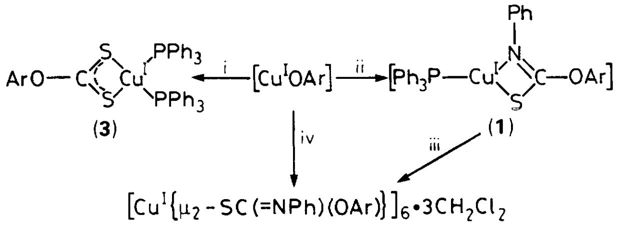
In the presence of phosphites, PhNCS inserts into the Cu^{I}–OPh bond; the complex formed loses the phosphite and oligomerises to form a unique copper(I) hexamer hexakis[μ-{*N*-phenylimino(*p*-tolyloxy)methanethiolato}copper(I)] (**2**), as evidenced from an *X*-ray crystallographic study.

The current interest in modelling activation of O_2 by copper enzymes has led to the identification of novel structures and geometries for copper(I).[1] However, similar studies involving heteroallenes like CO_2, PhNCS, *etc.*, have attracted less attention.[2] Recently, interesting transformations of copper(I) phenoxide in the presence of a variety of donors, such as CO, PR_3, and isocyanides, have been reported.[3] As part of our study[4] on the reactions of copper(I) phenoxide with heteroallenes, we report the isolation of a novel product formed by its reaction with PhNCS. Surprisingly, the use of two different potential tertiary phosphorus donor ligands culminated in different products. In the presence of PPh_3 the reaction with PhNCS led to the formation of a monomeric complex (**1**) with the phosphine co-ordinated to copper(I).† In marked contrast, the use of $P(OMe)_3$ as a ligand resulted in compound (**2**) with no $P(OMe)_3$ in the molecule. Interesting features of (**1**) are the lability of PPh_3 and its ready conversion to (**2**) during an attempted recrystallisation from MeCN.

The red–orange compound (**2**) was prepared under an atmosphere of dry nitrogen. Cu^{I}–OPh was generated by the metathetical reaction between PhONa (3 mmol) and $Cu^{I}Cl$ (3 mmol) in dry degassed dichloromethane. The resulting yellow precipitate was treated with $P(OMe)_3$ (3 mmol). A stoicheiometric amount of neat PhNCS was added to this mixture, giving an initially yellow and ultimately red–orange solution.‡ On diffusion of n-hexane and standing the solution overnight, air-stable red–orange crystals were obtained which were identified as the novel hexameric, *N*-phenylimino(*p*-tolyloxy)methanethiolato copper(I) complex (**2**)§ by *X*-ray structural analysis.¶



Ar = 4-MeC_6H_4

Scheme 1. *Reagents and conditions:* i, PPh_3, CS_2, CH_2Cl_2; ii, PPh_3, PhNCS, CH_2Cl_2; iii, MeCN, room temp.; iv, $P(OMe)_3$, PhNCS, CH_2Cl_2.

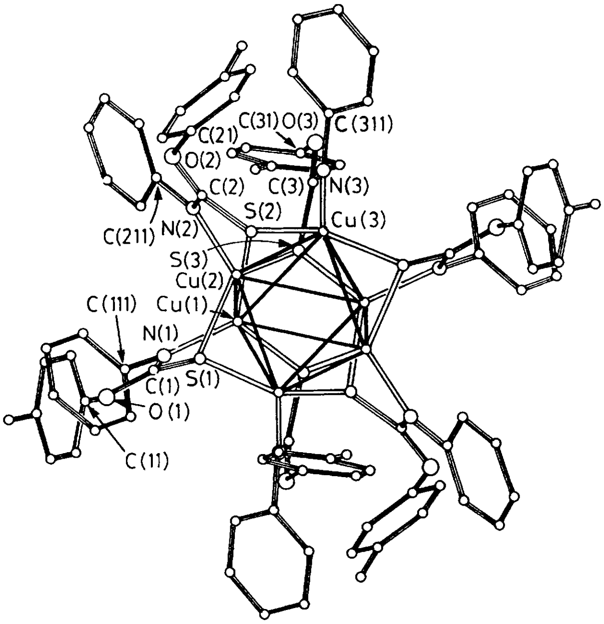


Figure 1. Molecular structure of $[Cu^{I}\{\mu_2\text{-}SC(=NPh)(OC_6H_4Me\text{-}4)\}]_6$ (**2**). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and bond angles (°): Cu(1)–Cu(2) 2.823(1), Cu(2)–Cu(3) 2.811(1), Cu(1)–Cu(3) 3.236(1), Cu(1)–Cu(2′) 3.253(1), Cu(1)–Cu(3′) 2.874(1), Cu(2)–Cu(3′) 3.062(1); the Cu–Cu–Cu angles range from 54.2(1) to 70.1(1); Cu–S 2.245(1), Cu–N 2.027(4), S–Cu–S 114.9(1), N–Cu–S 119.1(1) (mean values); Cu–N–C–S torsional angles vary from 0.8(8) to 3.3(8).

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† Yellow crystals, m.p. 78—80 °C, IR (Nujol): ν(C=N) 1520s, ν_{as} (C–O–C) 1200s, ν_s (C–O–C) 1100 s cm^{-1}; ^1H NMR ($CDCl_3$, 298 K): δ 7.6—6.7 (m, 22H, PPh_3 and $-OC_6H_4-$), 2.25 (s, 3H, Me).

‡ The same procedure using PPh_3 instead of $P(OMe)_3$ yielded (**1**). Compound (**3**) was obtained from the reaction of CS_2 (an analogue of PhNCS) in the presence of PPh_3 and the structure was confirmed by a single crystal *X*-ray study.[5]

§ *Spectral data* for (**2**): satisfactory elemental analyses (Cu, N, C, H) were obtained. Yield 90%, m.p. 196—198 °C, IR (Nujol): ν(C=N) 1495s, ν_{as}(C–O–C) 1200s, ν_s(C–O–C) 1115 s cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): two Me singlets and two $-OC_6H_4-$ AB quartets in 1 : 2 intensity ratio at room temp.; at 60 °C the ratio changed to 1 : 1; at 293 K, δ 7.7—7.2 (5H, m, –NPh), 7.0—6.39 (4H, 2 × ABq, 1 : 2, $-OC_6H_4-$), 5.29 (0.5H, s, CH_2Cl_2), 2.26—2.29 (3H, s, 1 : 2, Me); at 333 K, δ 7.49—7.16 (5H, m, –NPh), 6.97—6.41 (4H, 2 × ABq, 1 : 1, $-OC_6H_4-$), 2.28—2.25 (3H, s, 1 : 1, Me).

¶ *Crystal data* for (**2**): $C_{84}H_{72}N_6O_6S_6Cu_6\cdot 3CH_2Cl_2$, triclinic, space group $P\bar{1}$, a = 13.089(1), b = 13.309(1), c = 13.554(1) Å, α = 97.37(1), β = 97.05(1), γ = 100.23(1)°, U = 2264(1) $Å^3$, Z = 1, D_c = 1.523, D_m = 1.52 g cm^{-3}, $F(000)$ = 1062, λ = 0.7107 Å, μ (Mo-K_α) = 18.1 cm^{-1}, T = 298 K. Intensity data were collected on an Enraf-Nonius CAD-4 diffractometer using the ω–2θ scan mode in the range 1.5 ≤ 2θ ≤ 50°. The structure was solved by direct methods (SHELX86) and refined by full-matrix least-squares procedures. The final residuals R and R_w are 0.060 and 0.059 for 4460 observed reflections with $I \leq 2.5\,\sigma(I)$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

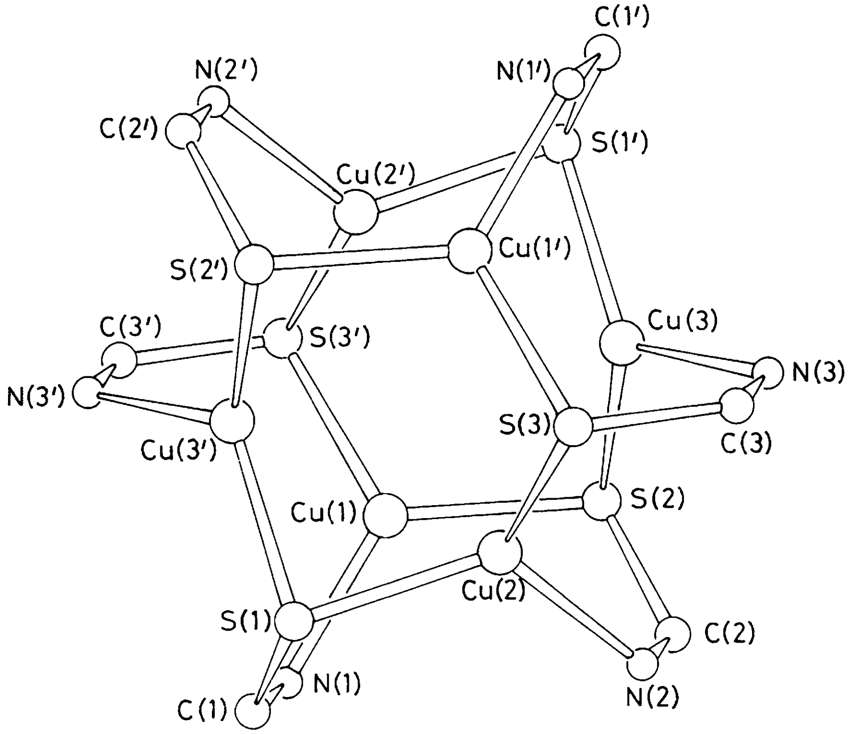

Figure 2. A view of the central core of the molecule illustrating the 'paddle-wheel' geometry.

The molecular structure of (**2**) is shown in Figure 1. The structure consists of six copper(I) ions and six organic groups, $(4\text{-MeC}_6\text{H}_4\text{O-})(\text{PhN=})\text{C-S}^-$ (formed *in situ*), with a centre of symmetry. The copper(I) ions define a distorted octahedron, which can be described in terms of two triangular faces consisting of Cu(1), Cu(2′), and Cu(3) and their centrosymmetric equivalents. The six ligand moieties link copper(I) ions of two triangles through donors S^- and N, resulting in a 'paddle-wheel' shaped core, with CuNCS fragments for blades, Figure 2. Cu(1) and Cu(2′) are bridged by S(3′) in a μ_2 fashion, while N(3′) of the same ligand co-ordinates Cu(3′) of the second triangle *via* a S–C–N bridge. Cu(1) is also co-ordinated to N(1) of ligand 1, whose S(1) bridges Cu(2) and Cu(3′). The same pattern holds for other copper(I) ions. Thus each copper(I) ion is linked to three ligands and each ligand to three copper(I) ions. This results in an approximate trigonal geometry around each copper, with two S and one N. Cu(1), Cu(2), and Cu(3) deviate from the planes of the co-ordinating atoms by 0.21(1), 0.41(1), and 0.32(1) Å, respectively. The Cu–S and Cu–N distances are essentially identical. Within the ligand the C–S [mean 1.752(3) Å] and C–N [mean 1.295(4) Å] distances correspond to single and partial double bond character, respectively. The copper(I) ions are in two different environments. This asymmetry is also indicated by ^{1}H NMR. The longer Cu–Cu distances, 3.018(1) and 3.236(1) Å, are between Cu atoms bridged through sulphur, while shorter distances, 2.823(1) Å, are between copper atoms bonded through the S and N donors present at the two ends of the ligand. Thus each copper has two long and one short bonds to neighbouring copper atoms.

The structure and formation of this complex is interesting. This is the first example of a hexanuclear copper(I) complex with only S and N donors. The *in situ* formation of the ligand is noteworthy, and may not take place by a single-step insertion reaction but rather involve multiple steps, as has been shown to be the case with $\text{Mo}_2(\text{OR})_6$ and $\text{W}_2(\text{OR})_6$.[6] The stability and relatively high oxidation potential, as indicated by cyclic voltammetry,‖ are unusual and indicate the strong binding of 'soft' donors S and N.[7] Interestingly, there is evidence for a further change in the nuclearity at higher temperatures from the ^{1}H NMR. Such interconversions of multinuclear complexes have been reported in solution.[8]

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References

1 K. D. Karlin and Y. Gultneh, *Prog. Inorg. Chem.*, 1988, **35**, 219; K. D. Karlin, R. W. Cruse, Y. Gultneh, J. C. Hayes, and J. Zubieta, *J. Am. Chem. Soc.*, 1984, **106**, 3372; T. N. Sorrel and A. S. Borovik, *J. Chem. Soc., Chem. Commun.*, 1984, 1489.

2 T. Saegusa and T. Tsuda, in 'Fundamental Research in Organometallic Chemistry,' ed. M. Tsutsui, Van Nostrand Reinhold, New York, 1982, p. 227; T. Tsuda, S. Sanada, K. Ueda, and T. Saegusa, *Inorg. Chem.* 1976, **15**, 2329; M. E. Vol'pin, *Pure Appl. Chem.*, 1972, **30**, 607.

3 P. Fiaschi, C. Floriani, M. Pasquali, A. Chiesi-Villa, and C. Guastini, *Inorg. Chem.*, 1986, **25**, 462.

4 N. Narasimhamurthy and A. G. Samuelson, *Tetrahedron Lett.*, 1986, **27**, 991; N. Narasimhamurthy and A. G. Samuelson, *ibid.*, 1988, **29**, 827.

5 N. Narasimhamurthy, A. G. Samuelson, and H. Manohar, unpublished results.

6 M. H. Chisholm, F. A. Cotton, K. Folting, J. C. Huffman, A. L. Ratermann, and E. S. Shamshoum, *Inorg. Chem.*, 1984, **23**, 4423; F. A. Cotton and E. S. Shamshoum, *Polyhedron*, 1985, **4**, 1727.

7 S. G. Murray and F. R. Hartley, *Chem. Rev.*, 1981, **81**, 365; M. A. Augustin, J. K. Yandell, A. W. Addison, and K. D. Karlin, *Inorg. Chim. Acta*, 1981, **55**, L35.

8 G. Van Koten and J. G. Noltes, in 'Comprehensive Organometallic Chemistry,' eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon, Oxford, 1982, vol. 2, ch. 14, pp. 709—763; S. Gamarotta, C. Floriani, A. Chiesi-Villa, and C. Guastini, *J. Chem. Soc., Chem. Commun.*, 1983, 1156.

‖ Performed under an inert atmosphere; two oxidation waves corresponding to E_{pa} values of +0.67 and +1.07 V.