Highly dissymmetric chelate coordination of 3,4,7,8-tetramethyl-1,10-phenanthroline to $\mathrm{Cu^I}$(SR)

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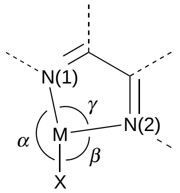
Not only $\mathrm{Au^I}$ and $\mathrm{Hg^{II}}$ species but also $\mathrm{Cu^I}$(SR) fragments can bind in a highly dissymmetrical fashion to symmetrical diimine chelate ligands; the 2 + 1 coordination arrangement observed for the metal in two complexes (tmphen)Cu(SR) (tmphen = 3,4,7,8-tetramethyl-1,10-phenanthroline) is characterised by obtuse angles α[N(1)–Cu–S] > 159° and by two very different distances Cu–N(1) and Cu–N(2).

The copper(I) state is characterised by the lack of a clear preference for specific coordination numbers (CN) or coordination geometries, the most common arrangements being close to tetrahedral (CN 4) or trigonal planar (CN 3).[1,2] Higher and lower coordination numbers, in particular CN 2, have also been documented.[2]

In probing copper–thiolate–N-chelate ligand chemistry to mimic the $\mathrm{Cu_A}$ dinuclear electron transfer center of enzymes[3] we reacted the α-diimine ligand 3,4,7,8-tetramethyl-1,10-phenanthroline (tmphen)[4] with electrolytically[5] obtained 2,4,6-trimethyl- and 2,6-diphenyl-thiophenolatocopper(I), Cu(SMes) and Cu(SDpp). The result† was not a di- or tetra-nuclear arrangement[3c,d] but mononuclear copper(I) complexes which could be crystallised for structural characterisation (Figs. 1 and 2).‡

Copper(I) does not normally display the same strong preference for a coordination number of two with linear coordination geometry as do gold(I) or mercury(II) centres, yet the list in Table 1 illustrates that the complexes (tmphen)Cu(SR) exhibit unusually distorted geometries as evident from very obtuse angles α and large differences between the distances Cu–N(1) and Cu–N(2), despite the formal equivalence of both nitrogen donor sites and the symmetry of the aryl groups, R (Table 1).



Gold(I) or mercury(II) centres which strongly prefer the linear geometry can be forced to accept a third donor atom *via* chelate coordination. Structurally characterised examples related to the neutral species (tmphen)Cu(SR) include the ionic systems [(bpy)Au(PPh$_3$)]PF$_6$[6a] and [(bpy)HgMe]NO$_3$ (Table 1; bpy = 2,2′-bipyridine).[6b] Ligands, especially thiolates, with steric bulk may cause a similar distortion from the trigonal geometry of d^{10} metal centres as has been realized in the T-shaped (Et$_2$O)Zn$^{\mathrm{II}}$(SC$_6$H$_2$Bu$^t_3$-2,4,6)$_2$[7b] and, in attenuated form, with the compound (phen)Cu[SSi(OBu^t)$_3$] (phen = 1,10-phenanthroline).[7b]

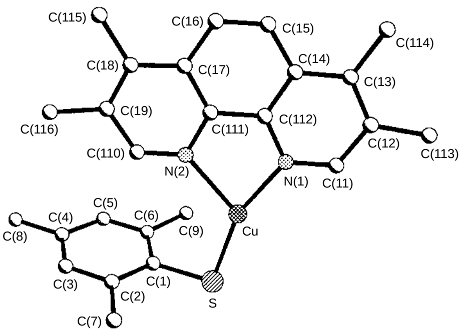


Fig. 1 Molecular structure of the metal complex in (tmphen)Cu(SMes)·0.5C$_3$H$_6$O with atom numbering. Selected bond lengths (Å) and angles (°): Cu–N(1) 1.976(2), Cu–N(2) 2.159(2), Cu–S 2.1470(8), S–C(1) 1.787(3); N(1)–Cu–N(2) 80.4(1), N(1)–Cu–S 159.13(8), S–Cu–N(2) 120.48(7), C(1)–S–Cu 98.7(1). Cu lies in the S–N(1)–N(2) plane; torsional angles (°): N(1)–Cu–S–C(1) −166.96(2), N(2)–Cu–S–C(1) 13.1(1).

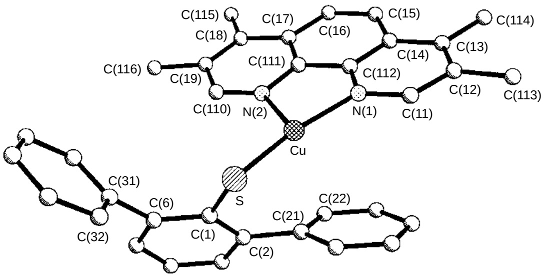


Fig. 2 Molecular structure of (tmphen)Cu(SDpp) with atom numbering. Selected bond lengths (Å) and angles (°): Cu–N(1) 1.972(4), Cu–N(2) 2.172(4), Cu–S 2.1687(14), S–C(1) 1.775(5), C(21)–C(22) 1.388(7); N(1)–Cu–N(2) 79.9(2), N(1)–Cu–S 164.37(12), S–Cu–N(2) 115.68(12), C(1)–S–Cu 97.8(2). Cu lies 0.026(2) Å over the S–N(1)–N(2) plane; torsional angles (°): N(1)–Cu–S–C(1) −136.1(5), N(2)–Cu–S–C(1) 50.2(2).

Table 1 Geometrical parameters for complexes with 2 + 1 coordination arrangement

Complex	α/°	β/°	γ/°	M–N(1)/Å	M–N(2)/Å	Ref.
(tmphen)Cu(SDpp)	164.4	115.7	79.9	1.972	2.172	This work
(tmphen)Cu(SMes)	159.1	120.5	80.4	1.976	2.158	This work
(phen)Cu[SSi(OBu^t)$_3$]	144.6	133.5	80.9	2.031	2.108	7(*b*)
[(bpy)Au(PPh$_3$)]$^+$	157.4	130.4	71.4	2.166	2.406	6(*a*)
[(bpy)HgMe]$^+$	164.0	126.0	69.4	2.236	2.421	6(*b*)
(Et$_2$O)Zn(SC$_6$H$_2$Bu$^t_3$)$_2$	159.6[a]	—	—	—	—	7(*a*)

[a] Angle S(1)–Zn–S(2).

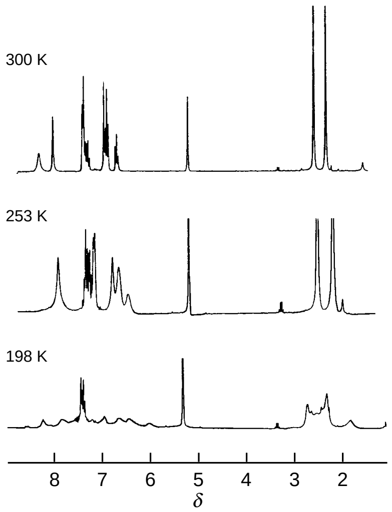


Fig. 3 Temperature-dependent ^{1}H NMR spectra of (tmphen)Cu(SDpp) in CD_2Cl_2 (300, 253 and 198 K, from top to bottom; 250 MHz)

The unsymmetrical coordination of the chelate ligand to the Cu^I center as observed in the solid state is probably responsible for the selective broadening in the ^{1}H NMR spectrum of (tmphen)Cu(SDpp) (Fig. 3).

These observations suggest a low but non-negligible barrier for the 'movement' of Cu between two equivalent energy minimum sites, separated by *ca.* 0.28 Å. No intermolecular interactions were recognised in the crystal structures which can be made responsible for this unusual copper(I)–thiolate[3c,d,8] coordination arrangement. To rationalise the observed dissymmetry we thus invoke the strong σ and π donor effect of thiolate groups SR and the donor substitution of the α-diimine tmphen.[4] There appears to be no need then for full coordination of a third donor atom to the electron-rich copper(I) centres, leaving the inevitably close second nitrogen atom N(2) of the chelate ligand as a lesser coordinated donor centre to result in the observed coordination number 2 + 1.

Notes and References

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† *Synthesis*: Arylcopper(I) precursors were obtained by electrolysing[5] solutions of the thiophenols[9,10] in acetonitrile–2 mmol dm^{-3} NBu_4ClO_4 in a cell containing a copper anode.

(2,4,6-Trimethylthiophenolato)(3,4,7,8-tetramethyl-1,10-phenanthroline)copper(I) was prepared by adding 250 mg (1.18 mmol) of the thiolatocopper precursor to a suspension of 278 mg (1.18 mmol) tmphen in 20 ml toluene. After reflux for 2.5 h the clear brownish solution was filtered hot, cooling produced 352 mg (62%) of (tmphen)Cu(SMes)·C_7H_8. Single crystals suitable for X-ray diffraction were obtained from acetone as (tmphen)Cu(SMes)·$0.5C_3H_6O$ (correct C, H, N elemental analysis). ^{1}H NMR (CD_2Cl_2, 300 K): δ 2.16 (s, 6 H, Mes-4-CH_3), 2.41 (s, 24 H, tmphen-3,8-CH_3 and Mes-2,5-CH_3), 2.65 (s, 6 H, tmphen-4,7-CH_3), 6.66 (s, 4 H, Mes-3,5-H), 8.03 (s, 4 H, tmphen-5,6-H), 8.34 (s, 4 H, tmphen-2,9-H).

(2,6-Diphenylthiophenolato)(3,4,7,8-tetramethyl-1,10-phenanthroline)copper(I) was prepared by adding 120 mg (0.37 mmol) of the thiolatocopper precursor to a solution of 87 mg (0.37 mmol) tmphen in 25 ml toluene. After reflux for 1 h the clear brownish solution was filtered hot, and careful cooling produced 50 mg (24%) of the compound, partially as single crystals suitable for X-ray diffraction. Correct elemental analysis (C, H, N). ^{1}H NMR (CD_2Cl_2, 300 K): δ 2.45 (s, 6 H, 3,8-CH_3), 2.70 (s, 6 H, 4,7-CH_3), 6.79 (t, J 7.4 Hz, 2 H, aryl-H), 6.96–7.05 (m, 5 H, aryl-H), 7.35–7.50 (m, 6 H, aryl-H), 8.11 (s, 2 H, 5,6-H), 8.40 (br s, 2 H, 2,9-H). Selective broadening of the resonances was observed upon cooling to 198 K (Fig. 3).

‡ *Crystallography*: (tmphen)Cu(SMes)·$0.5C_3H_6O$: $C_{25}H_{27}CuN_2S\cdot 0.5C_3H_6O$, M = 480.16, crystal size 0.4 × 0.4 × 0.4 mm, monoclinic, space group $P2_1/n$ (no. 14), a = 8.1319(7), b = 14.8164(12), c = 19.6605(12) Å, β = 98.388(8)°, U = 2343.5(3) Å^3, D_c = 1.351 g cm^{-3}, μ(Mo-Kα) = 1.039 mm^{-1}, F(000) = 994, Wyckoff scans, 6561 measured reflections, 6156 independent reflections, 5830 reflections used for refinement, Lorentz polarisation, R = 0.0501 for 4244 reflections with $I > 2\sigma(I)$; 183 K, Siemens P4 diffractometer with graphite monochromator and Mo-Kα radiation (λ = 0.71073 Å). The structure was solved by direct methods (Siemens SHELXTL-PC) and refined (SHELXL-93) by full-matrix least squares on F^2 (362 parameters). One half equivalent of a solvent molecule had to be included. Hydrogen atoms were introduced at calculated positions and refined freely; (tmphen)Cu(SDpp): $C_{34}H_{29}CuN_2S$, M = 561.19, crystal dimensions 0.4 × 0.4 × 0.3 mm, monoclinic, space group $P2_1/n$ (no. 14), a = 11.949(2), b = 13.284(2), c = 17.636(2) Å, β = 104.56(1)°, U = 2709.5(6) Å^3, D_c = 1.376 g cm^{-3}, μ(Mo-Kα) = 0.909 mm^{-1}, F(000) = 1168, Wyckoff scans, 6188 measured reflections, 5971 independent reflections, 5499 reflections used for refinement, Lorentz polarisation, R = 0.0687 for 3490 reflections with $I > 2\sigma(I)$; 183 K, Siemens P4 diffractometer with graphite monochromator and Mo-Kα radiation (λ = 0.71073 Å). The structure was solved by direct methods (Siemens SHELXTL-PC) and refined (SHELXL-93) by full-matrix least squares on F^2 (430 parameters). Hydrogen atoms were introduced at calculated positions and refined freely. CCDC 182/737.

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