

Stereochemical and Electronic Control of the Copper(II)/(I) Couple by N₂S₄-Donor Macrocycles

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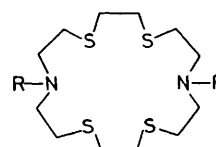
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The N₂S₄ donor complex [Cu(L¹)]²⁺ (L¹ = 1,4,10,13-tetrathia-7,16-diazacyclo-octadecane) shows a chemically reversible copper(II)/(I) couple at E₃ -0.31 V vs. Fc/Fc⁺ (ferrocene/ferrocenium), whereas the methylated analogue, [Cu(L²)]²⁺ (L² = 7,16-dimethyl-1,4,10,13-tetrathia-7,16-diazacyclo-octadecane) shows a more anodic copper(II)/(I) couple at E₃ +0.06 V vs. Fc/Fc⁺; these differences in redox potential can be related to the stereochemical features of the copper(II) complexes, the crystal structures of which have been determined for [Cu(L¹)]²⁺ and [Cu₂(L²)(NCMe)₂]²⁺.

The co-ordination chemistry of the mixed N₂S₄ donor macrocycles L¹ (L¹ = 1,4,10,13-tetrathia-7,16-diazacyclo-octadecane) and L² (L² = 7,16-dimethyl-1,4,10,13-tetrathia-7,16-diazacyclo-octadecane) are of particular interest since these ligands incorporate both hard and soft donor atoms in a co-ordinatively restricted environment.¹ Very little has been reported on the stereochemical characteristics of transition metal complexes of these ligands¹⁻³, although Black and co-workers have defined¹ the possibilities of *meso* and *rac* isomers for octahedral complexes of the type [M(L¹)]^{x+}. We were interested in the stereochemical preferences of d⁹ Cu^{II} with these N₂S₄ donor ligands, and report herein structural and redox data for these Cu^{II} species.

Reaction of Cu(ClO₄)₂ with one equivalent of L (L = L¹ or L²) in refluxing EtOH for 3 h afforded green solutions from

which the complexes [Cu(L)](ClO₄)₂ could be isolated as green products. Crystals of [Cu(L¹)](ClO₄)₂·H₂O were grown from aqueous solution. The single crystal X-ray structure of



L¹ : R = H

L² : R = Me

the complex shows† the Cu^{II} ion to have a tetragonally compressed stereochemistry with all six donor atoms of the macrocycle bound to the metal ion to give the *rac* isomer (Figure 1). This contrasts with the crystal structure of [Cu([18]aneS₆)]²⁺ ([18]aneS₆ = 1,4,7,10,13,16-hexathiacyclo-octadecane) which shows a tetragonally elongated stereochemistry with a *meso* configuration.⁴ The tetragonal compression in [Cu(L¹)]²⁺ occurs along the N–Cu–N axis [Cu–N(7) 2.007(13), Cu–N(16) 2.036(12) Å]; the conformational rigidity of the hexadentate macrocycle results in the equatorial S-donors being pushed away from the metal centre to give unusually long Cu–S distances [Cu–S(1) 2.577(5), Cu–S(4) 2.487(5), Cu–S(10) 2.528(5), Cu–S(13) 2.578(5) Å]. Importantly, related thioether crown complexes show shorter Cu–S distances: *e.g.* [Cu([18]aneS₆)]²⁺ [2.323(1), 2.402(1) Å for equatorial donors, 2.635(1) Å for apical donors],⁴ [Cu([15]aneS₅)]²⁺ [2.289(2)–2.398(2) Å],⁵ [Cu([9]aneS₃)₂]²⁺ [2.419(2)–2.459(3) Å].⁶ The two H atoms bonded to the N-donors in [Cu(L¹)]²⁺ are both hydrogen-bonded, HN(16) to the water molecule (N...O 2.87 Å) and HN(7) to a perchlorate oxygen O(6) atom (N...O 3.02 Å). There is a further hydrogen bond between the second perchlorate and the water molecule [O(100)...O(2) 3.02 Å].

The complex cation [Cu(L¹)]²⁺ shows, by cyclic voltammetry, a reversible Cu^{II/I} couple in MeCN at $E_{1/2} = -0.31$ V vs. Fc/Fc⁺ (ferrocene/ferrocenium). By contrast, the di-methyl-

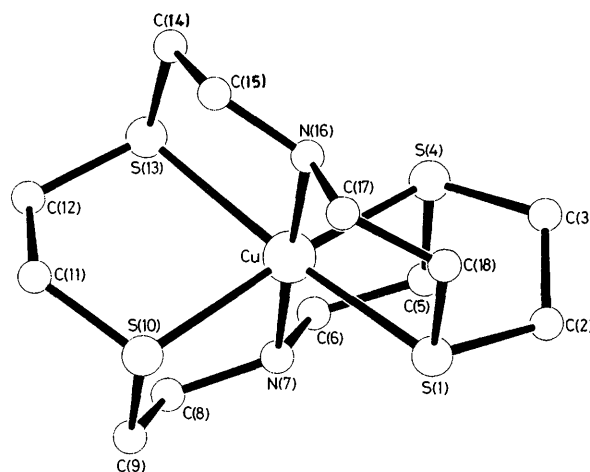


Figure 1. Structure of the complex cation [Cu(L¹)]²⁺ with numbering scheme adopted.

† Crystal data for [Cu(L¹)]₂(ClO₄)₂·H₂O, C₁₂H₂₆·CuN₂S₄·2ClO₄·H₂O. A crystal (0.3 × 0.3 × 0.3 mm) was set up to rotate about the *a* axis on a Stöe STADI2 diffractometer. Orthorhombic, space group *Pcab* with *a* = 12.020(8), *b* = 17.733(17), *c* = 21.999(23) Å, *U* = 4689 Å³, *Z* = 8, *D_m* = 1.68, *D_c* = 1.72 g cm⁻³, *F*(000) = 2504, μ(Mo-K_α) = 15.81 cm⁻¹. Data were collected using Mo-K_α radiation ($\lambda = 0.71073$ Å) and variable-width ω scans. 4390 Independent reflections were measured of which 1646 with *F* > 5 σ (*F*) were used in subsequent refinement. The structure was determined by the heavy atom method. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms bonded to carbon and nitrogen were included in calculated positions and their thermal parameters refined, with those of atoms bonded to the same carbon atom constrained to be equivalent.⁸ The hydrogen atoms on the water molecule could not be located. The final values for *R* and *R_w* were 0.085 and 0.091 respectively, with the final Fourier difference map showing no significant peaks.

Crystal data for [Cu₂(L²)(NCMe)₂](PF₆)₂, C₁₈H₃₆·Cu₂N₄S₄·2PF₆. A pale green crystal (1.35 × 0.12 × 0.08 mm) was mounted on a Stöe STADI4 four-circle diffractometer. Triclinic, space group *P1*, *a* = 7.3435(18), *b* = 11.0562(26), *c* = 11.824(3) Å, $\alpha = 62.298(10)^\circ$, $\beta = 81.904(15)^\circ$, $\gamma = 82.764(16)^\circ$, *U* = 839.5 Å³ [from 2 θ values of 22 reflections measured at $\pm\omega$ (22 < 2 θ < 24°, $\lambda = 0.71073$ Å)], *Z* = 1, *D_c* = 1.526 g cm⁻³, μ(Mo-K_α) = 10.17 cm⁻¹. Data collection used Mo-K_α radiation ($\lambda = 0.71073$ Å), $\omega/2\theta$ scans giving 2187 unique reflections (2 $\theta_{\max} = 45^\circ$, *h* -7 → 7, *k* -10 → 11, *l* 0 → 12) of which 1208 with *F* > 4 σ (*F*) were used in all calculations. A Patterson synthesis located the Cu position. Some disorder of the C atoms adjacent to the aza-functions of the macrocycle was identified. This was modelled successfully by refining the C–C–N units as rigid groups with idealised bond lengths and angles around each of these atoms; this showed two equally occupied sites for C adjacent to N. The PF₆⁻ counter-ions also exhibited some disorder which was modelled using partially occupied F atoms. Macrocylic H atoms were included in fixed, calculated positions while the methyl group in MeCN was refined as a rigid group.⁸ Anisotropic thermal parameters were refined for all atoms except H and disordered C. At final convergence, *R* = 0.0616, *R_w* = 0.0839, *S* = 1.105 for 218 parameters and the final difference map showed no feature above +0.88 e Å⁻³ or below -0.45 e Å⁻³.

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.

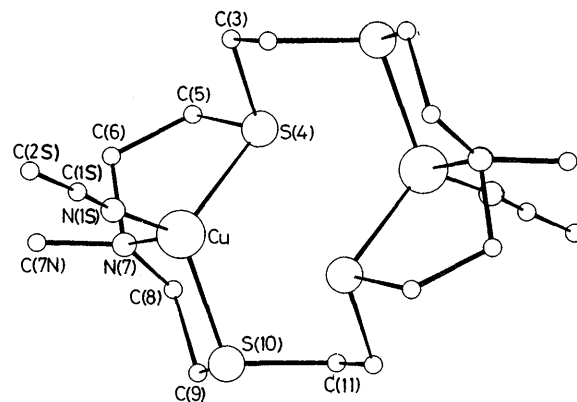


Figure 2. Structure of the complex cation [Cu₂(L²)(NCMe)₂]²⁺ with numbering scheme adopted.

ated Cu^{II} complex, [Cu(L²)]²⁺, shows a reversible Cu^{II/I} couple at +0.06 V vs. Fc/Fc⁺ under the same conditions. Coulometry confirms these reductions to be one-electron processes, with the resultant colourless Cu^I solutions being *e.s.r.* silent. The large difference in reduction potentials for these complexes is dramatic considering the only change in the macrocycle is methylation of the two NH groups. In addition, methylation of N-donors might be expected to stabilise higher oxidation state metal species rather than lower. We therefore reasoned that a substantial stereochemical change at the Cu^{II} centre was occurring on going to the di-methylated complex.

Molecular mechanics calculations on the complex cation [Cu(L²)]²⁺ were carried out by computer-simulated replacement of the NH protons by methyl groups in the structure obtained for [Cu(L¹)]²⁺. A number of unfavourable steric interactions were apparent at the co-ordinated N-donors, suggesting that methylation results in an elongation of the Cu–N distance. The strain in [Cu(L²)]²⁺ was partially relieved by an increase of the Cu–N distances to 2.12 Å; on the basis of these results and our recent studies³ on the complexation of

Pd^{II} with L^1 and L^2 , we propose that the cation $[\text{Cu}(\text{L}^2)]^{2+}$ would adopt a *meso* configuration. This would allow closer approach of the four soft thioether donors to the metal centre, and thus provide greater stability of the Cu^{I} species, as observed experimentally.

The net stabilisation of Cu^{I} by L^2 is reflected in the isolation of the stable binuclear species $[\text{Cu}_2(\text{L}^2)(\text{NCMe})_2]^{2+}$. The single crystal *X*-ray structure of $[\text{Cu}_2(\text{L}^2)(\text{NCMe})_2](\text{PF}_6)_2$ shows[†] (Figure 2) a centrosymmetric structure with each Cu^{I} centre bound tetrahedrally to two S-donors and one N-donor of L^2 [Cu-S(4) 2.317(4), Cu-S(10) 2.286(4), Cu-N(7) 2.165(7) Å], and one MeCN molecule [Cu-N(1S) 1.924(9) Å]. The Cu...Cu separation is 4.283(2) Å with each Cu^{I} ion bound by an N_2S_2 donor set similar to that found in the Type 1 copper proteins.⁷

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