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Partial Hydrolysis of a Schiff-base Tripodal Ligand Induced by Copper(II) Salts: Crystal Structure of the Product from Reaction with Copper(II) Perchlorate

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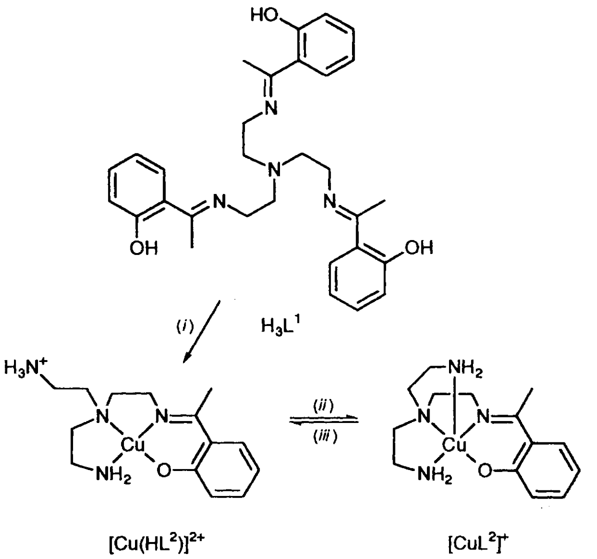
The reaction of $Cu(ClO_4)_2$ or $Cu(NO_3)_2$ with a potentially heptadentate Schiff-base tripod derived from tris(2-aminoethyl)amine and 2-hydroxyacetophenone occurs with accompanying hydrolysis of the ligand; single-crystal X-ray structure analysis of the product involving $Cu(ClO_4)_2$ shows the ligand to exist in a zwitterionic form and provide a near square-planar environment for the copper(II) cation.

Potentially heptadentate tripodal Schiff-base ligands, derived from the condensation of tris(2-aminoethyl)amine (tren) and various ring-substituted salicylaldehydes, have been synthesised and their co-ordination chemistry with a number of trivalent transition metals and lanthanides has provoked much attention.[1-6] In particular, the complexation of lanthanides by the ligand H_3L^1 derived from the condensation of tren and 2-hydroxyacetophenone in ethanol solution has been investigated[7] and the integrity of the ligand has been retained throughout; the structures of several of the complexes have been confirmed by X-ray crystallography.

We have found that in the reaction of the tripodal ligand H_3L^1 with copper(II) salts, partial hydrolysis of the ligand accompanies its co-ordination to copper(II) (see Scheme 1). The mixing of equimolar quantities of copper(II) perchlorate and H_3L^1 in refluxing ethanol affords an intensely coloured green solution from which the product deposits as red crystals on cooling.† The highest molecular weight peak in the positive ion FAB mass spectrum is found at *m/z* 326, well below the mass of the intact H_3L^1, and corresponds to a copper(II) complex of a new tripod ligand HL^2 formed by removal of two of the three 2-hydroxyacetophenone pendants. This has been confirmed by X-ray crystallography,‡ which revealed the copper(II) complex, $[Cu(HL^2)][ClO_4]_2{\cdot}H_2O$ featuring the unusual, near square-planar metal co-ordination geometry illustrated in Fig. 1.

In $[Cu(HL^2)]^{2+}$, the ligand is a zwitterion with the amine nitrogen atom of one tripod arm being protonated instead of the phenol oxygen atom; the protonated tripod arm is orientated away from the metal environment, presumably as a result of charge repulsion. The slightly distorted square-planar geometry



Scheme 1 Reactions of Schiff-base functionalised tripod ligands with Cu^{II}; complexation with hydrolysis and 'on-off' tripod arm equilibrium: (*i*) CuX_2 ($X = NO_3^-$ or ClO_4^-), EtOH, reflux; (*ii*) NEt_3, EtOH; (*iii*) concentrated HCl, $NaClO_4$, EtOH

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† An ethanolic solution (15 cm^3) of the copper(II) salt (perchlorate or nitrate) (1 mmol) was added to a solution of the Schiff base H_3L^1 (1 mmol) (prepared by the method of Smith *et al.*[7]) in ethanol (40 cm^3). The deep green solution was warmed gently for 2 h, filtered and allowed to cool. The products were filtered off, washed and dried. **CAUTION**: Perchlorates may be explosive and should be treated with extreme care. Red crystals of $[Cu(HL^2)][ClO_4]_2$. Yield 62%; IR (KBr disc): ν_{NH} 3350, $\nu_{C=N}$ 1605, ν_{Cl-O} 1090, 625 cm^{-1}; MS (positive FAB): *m/z* 326 $[CuL^2]^+$ [Found (calc.) for $C_{14}H_{24}Cl_2CuN_4O_9{\cdot}H_2O$: C, 31.20 (30.85); H, 5.05 (4.80); Cl, 12.30 (13.00); N, 10.15 (10.30)%]. Red crystals of $[Cu(HL^2)][NO_3]_2$. Yield 59%; m.p. 192–194 °C; IR (KBr disc): ν_{NH} 3360, $\nu_{C=N}$ 1605, ν_{NO} 1380 cm^{-1}; MS (positive FAB): *m/z* 326 $[CuL^2]^+$ [Found (calc.) for $C_{14}H_{24}CuN_6O_7{\cdot}H_2O$: C, 35.75 (35.80); H, 5.50 (5.60); N, 17.85 (17.90)%].

‡ Crystal data for $[Cu(HL^2)][ClO_4]_2{\cdot}H_2O$. $C_{14}H_{26}Cl_2CuN_4O_{10}$, $M = 544.83$, monoclinic, space group $P2_1/n$ (alternative setting of $P2_1/c$), $a = 14.193(3)$, $b = 14.268(4)$, $c = 10.744(3)$ Å, $\beta = 97.06(3)°$, $U = 2159.23$ Å^3, $Z = 4$, $D_c = 1.676$ g cm^{-3}, $F(000) = 1124$, λ(Mo-Kα) = 0.710 69 Å, μ(Mo-Kα) = 1.29 mm^{-1}. Data were collected on a Philips PW1100 diffractometer using a red crystal (0.46 × 0.16 × 0.12 mm) mounted on a quartz fibre. Of 1263 data collected, 1063 were unique with $I/\sigma(I) \geqslant 3$. The structure was solved with Patterson and Fourier difference syntheses.[8] After refinement with isotropic thermal parameters, an empirical absorption correction[9] was applied (max. 1.126, min. 0.739). In the final cycles of full-matrix least squares, the metal and the oxygen atoms of the perchlorate counter ions were assigned anisotropic thermal parameters and refinement converged at $R = 0.0609$, $R' = 0.0577$ and $R_g = 0.0617$ for 172 parameters [$w = 1/\sigma^2(F)$]. Residual electron density is in the range + 0.41 to −0.41 e Å^{-3}. Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

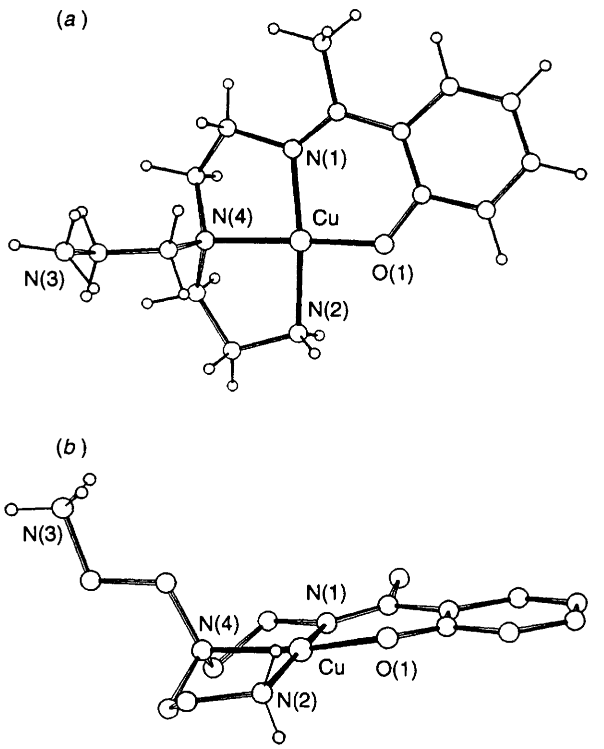

Fig. 1 Structure of the $[\mathrm{Cu(HL^2)}]^{2+}$ cation showing: (*a*) the disposition of the protonated tripod arm away from the metal environment and (*b*) the near square-planar copper(II) co-ordination geometry: Cu–N(1) 1.959(11), Cu–N(2) 2.021(12), Cu–N(4) 2.047(11), Cu–O(1) 1.868(9) Å; N(1)–Cu–N(2) 167.9(4), N(1)–Cu–N(4) 86.2(5), N(1)–Cu–O(1) 95.0(5), N(2)–Cu–N(4) 86.0(5), N(2)–Cu–O(1) 93.9(5), N(4)–Cu–O(1) 172.4(4)°

results from co-ordination of an N_3O donor set which produces angles at the metal in the range 86.0(5)–95.0(5)°. The shortest bond in the metal co-ordination sphere is to the phenolate oxygen [Cu–O(1) 1.868(9) Å] while the imine nitrogen donor [Cu–N(1) 1.959(11) Å] produces a substantially shorter Cu–N bond length than either amine [Cu–N(2) 2.021(12), Cu–N(4) 2.047(11) Å]. [There is a small but distinct tetrahedral distortion in the metal co-ordination sphere; the *trans* donor pairs in N(1), N(2) and N(4), O(1) respectively lie on opposite sides of the CuN_3O least-squares plane although the maximum deviation from the plane is less than 0.15 Å.] The closest non-bonded approach to the metal co-ordination sphere involves a Cu ··· O distance of 2.9 Å to a perchlorate counter ion. The solid-state structure features a complicated network of intermolecular hydrogen bonds involving both perchlorate anions, the water of crystallisation, the amine hydrogen and phenolate oxygen of the co-ordinated ligand.

In basic conditions the pendant arm of $[\mathrm{Cu(HL^2)}][\mathrm{ClO_4}]_2$ deprotonates to yield a green five-co-ordinate copper(II) complex* in which all the nitrogens of L^2 interact with the metal (Scheme 1). The deprotonation reaction is reversible and by addition of a molar equivalent of hydrochloric acid to an ethanolic solution of $[\mathrm{CuL^2}]\mathrm{ClO_4}$ in the presence of excess perchlorate anion, it is possible to regenerate the red crystals of $[\mathrm{Cu(HL^2)}][\mathrm{ClO_4}]_2$.

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* Reaction of $[\mathrm{Cu(HL^2)}][\mathrm{ClO_4}]_2$ with base. A solution of $[\mathrm{Cu(HL^2)}][\mathrm{ClO_4}]_2$ (0.39 g, 0.74 mmol) in absolute ethanol (75 cm^3) was stirred and an ethanolic solution (10 cm^3) of triethylamine (0.07 g, 0.74 mmol) added. After warming gently for a further 30 min the green solution was filtered and cooled. Long green needles of the product $[\mathrm{CuL^2}]\mathrm{ClO_4}$ were isolated, washed with ethanol and air-dried. Yield 65%; IR (KBr disc): ν_{NH} 3370, $\nu_{C=N}$ 1605, ν_{Cl-O} 1110, 625 cm^{-1}; MS (positive FAB): *m*/*z* 326 $[\mathrm{CuL^2}]^+$ [Found (calc.) for $C_{14}H_{23}ClCuN_4O_5 \cdot 0.5EtOH$: C, 39.85 (40.10); H, 5.55 (5.85); Cl, 7.90 (7.90); N, 12.10 (12.45)%].

Reaction of $[\mathrm{CuL^2}]\mathrm{ClO_4}$ with acid. The copper complex $[\mathrm{CuL^2}]\mathrm{ClO_4}$ (0.51 g, 1.2 mmol) was dissolved in absolute ethanol (15 cm^3). A saturated solution of sodium perchlorate in ethanol (5 cm^3) was added, followed by concentrated (37%) hydrochloric acid (0.1 cm^3, 1.2 mmol). The solution was stirred under reflux for 30 min and filtered. On cooling, red crystals of the product $[\mathrm{Cu(HL^2)}][\mathrm{ClO_4}]_2$ were deposited.