Co-ordinated Ether Formation in the Metal-directed Condensation and Macrocyclization of Formaldehyde, Ethanolamine, and a Polyamine

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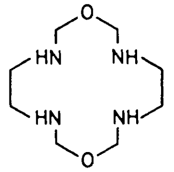
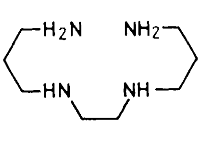
Reaction of formaldehyde, ethanolamine, and 1,10-diamino-4,7-diazadecane in the presence of Cu^{II} leads to the ready formation of the (1-oxa-1,6,8,12,15-penta-azatricyclo[13,3,1,$1^{8,12}$]icosane)copper(II) ion with the Cu^{II} bound by an ether oxygen and three amine donors, characterized by a crystal structure analysis.

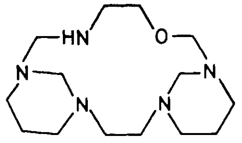
Reactions between co-ordinated molecules and formaldehyde alone have received only modest attention compared with some other metal-directed reactions.[1] Nevertheless, it is known that *cis*-disposed amines may react to form diaminomethylene (>N–CH_2–N<) links in several cobalt(III) polyamine compounds and in compounds of co-ordinated dihydrazines.[2,3] Further, $[Co(en)_2(gly)]^{2+}$ (en = ethane-1,2-diamine; gly = glycine anion) reacts with formaldehyde to form the co-ordinated macrocycle 1,8-dioxa-3,6,10,13-tetra-azacyclotetradecane (L^1) with two unco-ordinated ether units.[4] Here we report the first example, around a Cu^{II} template, of facile co-ordinated ether formation in a saturated macrocycle formed from reaction of formaldehyde, ethanolamine and the polyamine 1,10-diamino-4,7-diazadecane (L^2).

Reaction† yielded only one detectable product, the (3-oxa-1,6,8,12,15-penta-azatricyclo[13,3,1,$1^{8,12}$]icosane)copper(II) ion, $[Cu(L^3)]^{2+}$, in addition to unchanged $[Cu(L^2)]^{2+}$. The product crystallized readily following chromatographic separation and concentration of the solution by rotary evaporation. The reaction has not been optimized, but the macrocyclic complex may represent up to 20% of complexed copper following chromatography. The electronic absorption maximum in the visible (λ_{max} 600 nm, ε 120 $dm^3 mol^{-1} cm^{-1}$) is at lower energy than maxima reported for $Cu^{II}N_4$ chromophores with a range of macrocycles of variable ring size (for 13- to 15-membered systems, λ_{max} is in the range 530—570 nm),[5] and very similar to that of a structurally characterized $Cu^{II}N_3O$ chromophore with a multidentate amine ligand and one water molecule co-ordinated (λ_{max} 608 nm).[6] Unlike $Cu^{II}N_4$ systems of comparable ring size, the product in this case dissociates relatively rapidly in aqueous acid, as expected for a molecule with an O-ether donor. Microanalysis was consistent with a Cu : N : C ratio of 1 : 5 : 14, which could arise from incorporation of one molecule of L^2 and one molecule of ethanolamine in the product, with four additional carbons also introduced. The i.r. spectrum was indicative of a saturated ligand without primary amines present. Crystallography was necessary to clarify the structure.

The $[Cu(L^3)](ClO_4)_2\cdot\frac{1}{2}H_2O$ complex was characterized by an *X*-ray crystal structure analysis.‡ An ORTEP drawing of the cation appears in Figure 1. It is clear from the structure that condensation involving four formaldehyde units has


L^1


L^2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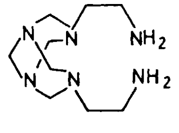
L^4

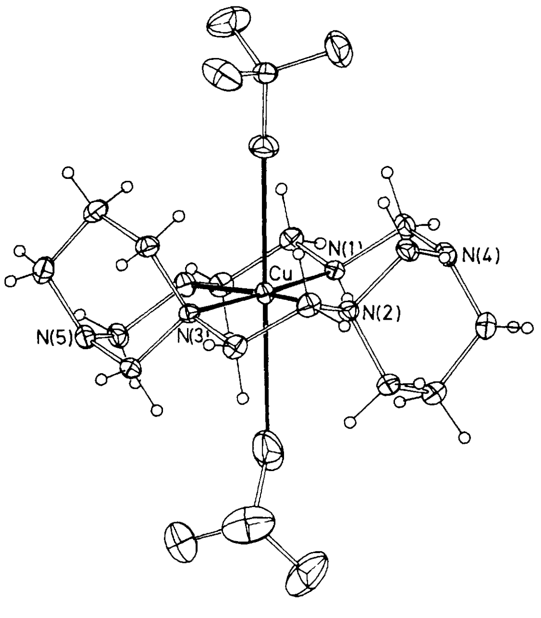

Figure 1. ORTEP drawing of the $[Cu(L^3)](ClO_4)_2$ compound. Selected bond lengths and angles are Cu–N(1) 1.976(4), Cu–N(2) 2.012(4), Cu–N(3) 2.020(3), Cu–O 2.008(3) Å, O–Cu–N(1) 83.7(1), N(2)–Cu–N(3) 88.6(1), O–Cu–N(2) 174.5, N(1)–Cu–N(3) 176.9°.

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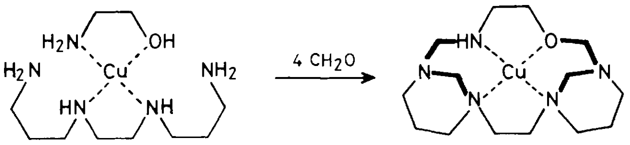
† In a typical experiment, $Cu(NO_3)_2\cdot3H_2O$ (4 g), L^2 (3 g), 37% aqueous H_2CO (10 cm^3) and ethanolamine (3 g) were heated in methanol (300 cm^3) for 2 h. The solution was diluted with water and sorbed onto a column of SP-Sephadex C-25 (Na^+-form) resin (28 × 4 cm) and eluted with 0.2 mol dm^{-3} $NaClO_4$. A deep blue band of the product preceded a purple band identified (microanalysis, comparison with authentic sample) of $[Cu(L^2)]^{2+}$. On concentration, $[Cu(L^3)](ClO_4)_2$ crystallized (1 g). (Found: C, 30.4; H, 5.9; N, 12.7. Calc. for $C_{14}H_{30}Cl_2CuN_5O_{9.5}$: C, 30.3; H, 5.5; N, 12.6%).

‡ *Crystal data:* $C_{14}H_{29}Cl_2CuN_5O_9\cdot\frac{1}{2}H_2O$, *M* = 554.9, monoclinic, space group *C*2/c, *a* = 32.777(8), *b* = 9.395(2), *c* = 14.914(6) Å, β = 111.97(2)°, *U* = 4259(3) $Å^3$, D_c (*Z* = 8) = 1.73 g cm^{-3}, *F*(000) = 2304, μ(Mo-K_α) = 12.6 cm^{-1}, λ(Mo-K_α) = 0.71069 Å. Reflections were measured with an ENRAF-Nonius CAD-4 four-circle diffractometer. The structure was solved by full-matrix least-squares and refined to *R* = 0.041 on for 3238 reflexions [$I > 3\sigma(I)$]. All H atoms were located and refined in (x, y, z, U_{iso}). 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.



Scheme 1

occurred as outlined in Scheme 1, with the inserted methylene groups identified by the heavy lines. In addition to three diaminomethylene linkages, an $-O-CH_2-N<$ linkage to form a co-ordinated ether has been formed. The Cu–O(ether) distance [2.008(3) Å] is not markedly different from Cu–N(tert.) distances [2.012(4), 2.020(3) Å] but longer than the Cu–N(sec.) bond [1.976(4) Å]. The Cu^{II} lies in the plane of the four donors. At each end of the new macrotricyclic ligand new 1,3-diazacyclohexane rings have been formed by insertion of a methylene between the adjacent primary and secondary nitrogens of L^2. Further methylenes link the original terminal nitrogens of L^2 to N and O donors of an ethanolamine residue, forming a 14-membered macrocycle. The 'caps' at the end of the molecule are somewhat reminiscent of the cap formed in the multidentate ligand L^4 from Ni^{II} directed condensation of ethane-1,2-diamine, formaldehyde, and ammonia, where fused 1,3,5-triazacyclohexane rings form.[7]

There are very few examples of co-ordinated ether formation reported. The bis[*N*-(2-bromoethyl)salicylideneaminato]nickel(II) ion self-condenses when treated with NaI in acetone to form a *trans*-N_2O_2 macrocycle with ether oxygens bound to Ni^{II}.[8] Reaction of 2,6-diacetylpyridine with 2-hydroxy-1,3-diaminopropane in the presence of Ba^{2+} leads to a tetraimine macrocycle with pendant OH-groups. However, in the presence of Pb^{2+}, a ring-contracted macrocycle forms where the OH groups are incorporated into two hinged oxazolidine rings, presumably by addition of the OH group across the adjacent C=N bond with consequential proton transfer.[9] In the present example, a like reaction of the OH group of the ethanolamine and an imine intermediate formed by condensation of the terminal amine of L^2 with a formaldehyde is presumed to operate. In this case the ether is not incorporated into a small ring, but forms part of the 14-membered macrocycle only. This appears to be the first example of this chemistry leading to a saturated macrocyclic product.

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