Structural Evidence for Carbonyl-oxygen Protonation in the Copper(II) Complex of 1,4,8,11-Tetraaza-5-oxocyclotetradecane

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Comparison between the structures of the two copper(II) complexes of 1,4,8,11-tetraaza-5-oxocyclotetradecane with a deprotonated and protonated amide group shows that the carbonyl oxygen is the protonation site and enables discussion of the detailed mechanism of acid dissociation.

Whereas complexes of tetraazacycloalkanes with Cu^{2+} and Ni^{2+} are kinetically inert towards acid dissociation,[1] the analogous complexes with macrocycles having amide donor functions are labile, their dissociation already starting at pH < 4.[2,3]

Studies of such complexes in solution indicate that, besides the species with a deprotonated amide group, others with a protonated amide function can be observed by potentiometric[3,4] or spectrophotometric[3] equilibrium measurements or by the kinetics of their acid dissociation.[3]

Protonation of such complexes can occur in two ways: (*i*) the proton can add to the amide group at the negatively charged nitrogen and the metal–nitrogen bond interconverts to a metal–oxygen bond, or (*ii*) the protonation takes place at the carbonyl oxygen without breaking the metal–nitrogen bond (Fig. 1). Mechanism (*i*) has been observed in many open-chain ligand complexes with labile metal ions,[5] whereas mechanism (*ii*) has only been described for kinetically inert cobalt(III) complexes.[6]

Since macrocyclic metal complexes very often are relatively similar to inert species, it was of interest to look more closely into the structural properties of such derivatives. For the copper(II) complex with 1,4,8,11-tetraaza-5-oxocyclotetradecane L, we were able to obtain crystals of both the deprotonated and the protonated complex and thus gain insight into the structural features of the protonation site.

The crystals were obtained by slow evaporation of an equimolar (0.5 mmol dm^{-3}) solution of $Cu(ClO_4)_2$ and L in water (5 cm^3) adjusted to pH 3.3. This pH was chosen since equilibria measurements had previously shown that under these conditions both $[Cu(LH_{-1})]^+$ and $[CuL]^{2+}$ are present.[3] In a first crystallization over two weeks intensely blue-violet crystals of $[Cu(LH_{-1})(H_2O)(ClO_4)]\cdot H_2O$ 1† were obtained, which were then followed by the formation of red needles of $[CuL(ClO_4)_2]\cdot H_2O$ 2. The IR spectra in KBr-pellets show a strong band at 1562 and 1688 cm^{-1} for 1 and 2, respectively, indicating the different nature of the coordinated amide group. Similarly visible spectra obtained as Nujol dispersions[7]
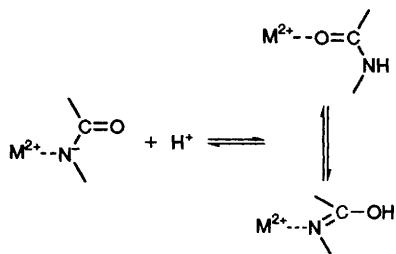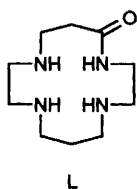
gave absorption maxima at 526 and 493 nm for 1 and 2, respectively.

The results of the X-ray diffraction study of the two species show that in both the Cu^{2+} is coordinated by the four nitrogen atoms of the macrocycle and that the axial positions are occupied by two oxygen atoms: two perchlorates in 2, a
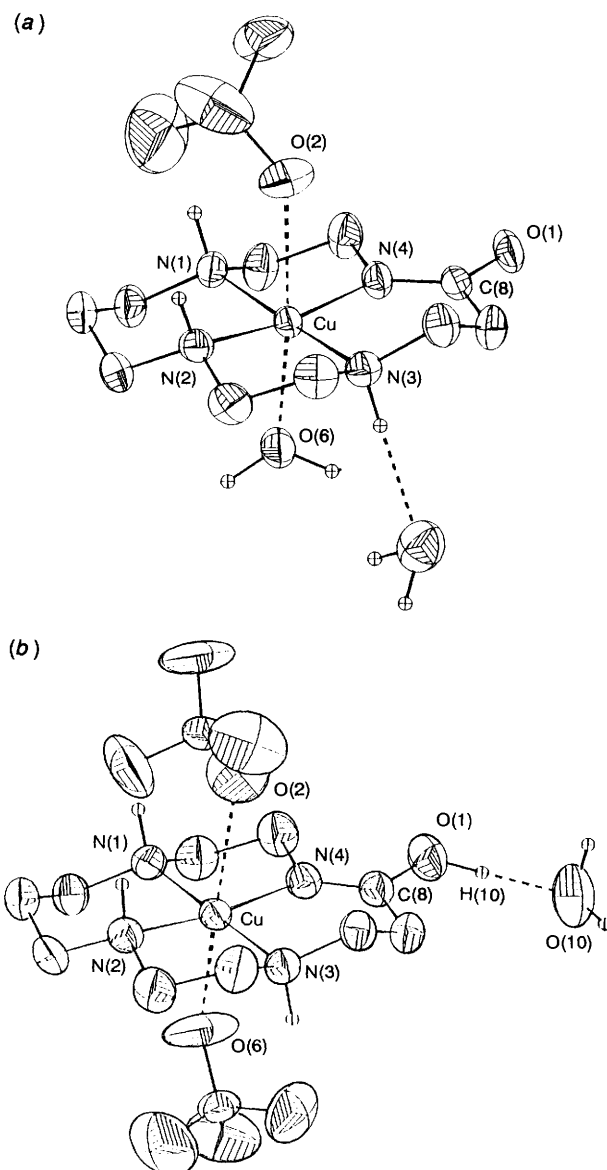
(*a*)

(*b*)

Fig. 2 ORTEP views of complexes 1 (top) and 2 (bottom). Selected bond lengths (Å) and angles (°) for 1[2]: Cu–N(1) 2.020(2) [2.005(2)], Cu–N(2) 2.022(2) [2.016(2)], Cu–N(3) 2.008(2) [2.001(2)], Cu–N(4) 1.960(2) [1.974(2)], Cu–O(2) 2.338(2) [2.568(6)], Cu–O(6) 2.841(2) [2.692(7)], N(4)–C(8) 1.299(3) [1.273(5)], C(8)–O(1) 1.286(3) [1.326(3)], C(8)–C(7) 1.512(3) [1.491(4)], N(1)–Cu–N(2) 93.74(8) [94.24(9)], N(2)–Cu–N(3) 85.74(8) [86.18(9)], N(3)–Cu–N(4) 94.55(8), [94.43(9)], N(4)–Cu–N(1) 85.44(8) [85.18(9)], N(4)–C(8)–O(1) 124.1(2) [119.2(3)], N(4)–C(8)–C(7) 119.1(2) [122.9(2)], O(1)–C(8)–C(7) 116.7(2) [117.9(2)].

$$M^{2+}\text{-}\text{-}O=C\diagup_{NH}$$

$$M^{2+}\text{-}\text{-}N\diagup^{C=O} + H^+ \rightleftharpoons$$

$$M^{2+}\text{-}\text{-}\text{-}N\diagup^{C-OH}$$

Fig. 1 Different possibilities in the protonation of metal–amide complexes

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perchlorate and a water in **1**, to complete tetragonally distorted coordination spheres (Fig. 2).

The four nitrogen atoms roughly form a plane with deviations of ± 0.067 and ± 0.070 Å for **1** and **2**, respectively, from which the Cu^{2+} is displaced by 0.116 (**1**) and 0.067 Å (**2**). The apical ligands form relatively long bonds [2.338(2) Å (H_2O), 2.841(2) Å (ClO_4^-) in **1**; 2.568(6), 2.693(7) Å (ClO_4^-) in **2**].

The most pronounced difference in the two structures is found in the Cu^{2+} amide group, whereas the other bonds and angles are relatively similar and have normal values. The additional H-atom could be localized in **2** at the carbonyl oxygen O(1) [bond length O(1)–H(10) 1.00(9) Å].§ A water molecule is hydrogen bonded to this H atom with a bond distance H(10)$\cdots$O(10) of 1.636(18). The bond lengths Cu–N(4), N(4)–C(8) and C(8)–O(1) are 1.960(2), 1.299(3) and 1.286(3) Å for **1** compared to 1.974(2), 1.273(5) and 1.326(3) Å for **2**. Thus, upon protonation the Cu–N and the C–O bonds become, as expected, somewhat longer, whereas the N–C bond shortens. It is also important to note that the angles around C(8) show smaller changes, but that its sp^2 hybridisation is retained, with angles close to 120°. Although the changes in bond lengths upon protonation or deprotonation are consistent with the structures shown in Fig. 1, it must be clearly stated that the structural changes are relatively small, indicating that resonance stabilisation plays an important role in both structures.

The structural characterization **1** in the solid state strongly suggests that the analogous species observed in solution by spectrophotometry[3] and in the kinetics of acid dissociation through stopped-flow measurements with a photodiode array[3] have the same structure. This allows us to clearly define a dissociation mechanism for macrocyclic amide complexes, since the basic site for proton attack is clearly the carbonyl oxygen of the amide group. The protonated complex so formed in a pre-equilibrium is the reactive species, which can then undergo Cu–N bond rupture.

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Footnotes

† *Crystal data* for **1** $C_{10}H_{21}ClCuN_4O_4 \cdot 2H_2O$, $M = 396.325$, monoclinic, space group $P2_1/n$, $a = 7.620(1)$, $b = 13.760(2)$, $c = 16.433$ Å, $\beta = 95.676(8)°$, $V = 1714.7(3)$ Å^3, $Z = 4$, $D_c = 1.535$ g cm^{-3}, crystal dimensions $0.3 \times 0.35 \times 0.42$ mm, $\theta_{max} = 28°$, λ (Mo-Kα) $= 0.71069$ Å, $\omega/2\theta$ scan technique, 4108 independent reflections, 3082 reflections used in refinement, final $R_w = 0.0395$, weighting scheme $[1 - (\Delta F/6\sigma F)^2]^2$. Diffraction absorption correction was determined by ψ-scans.

‡ *Crystal data* for **2**: $C_{10}H_{22}Cl_2CuN_4O_8 \cdot H_2O$, $M = 494.777$, monoclinic, space group $P2_1/a$, $a = 8.334(1)$, $b = 27.312(2)$, $c = 9.093(1)$ Å, $\beta = 111.865(7)°$, $V = 1920.9(3)$ Å^3, $Z = 4$, $D_c = 1.711$ g cm^{-3}, crystal dimensions $0.1 \times 0.2 \times 0.25$ mm, $\theta_{max} = 77.5°$, λ (Cu-Kα) $= 1.54178$ Å, $\omega/2\theta$ scan technique 4030 independent reflections, 3184 reflections used in refinement, final $R_w = 0.0521$, weighting scheme $[1 - (\Delta F/6\sigma F)^2]^2$. Diffraction absorption correction was determined by ψ-scans.

Atomic coordinates, thermal parameters, bond lengths and angles for both structures have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ The hydrogen atoms of the amine nitrogens N(1)–N(3) as well as those of the amide oxygen O(1) and water oxygen O(10) were refined restraining the distance to 1 Å. The other protons are in calculated positions.

References

1 D. K. Cabiness and D. W. Margerum, *J. Am. Chem. Soc.*, 1970, **92**, 2151; C. C. Chang and C. S. Chung, *J. Chem. Soc., Dalton Trans.*, 1991, 1965 and references cited therein; L. Hertli and Th. A. Kaden, *Helv. Chim. Acta*, 1974, **57**, 1328.

2 R. W. Hay, M. P. Pujari and F. McLaren, *Inorg. Chem.*, 1984, **23**, 3033.

3 L. Siegfried and Th. A. Kaden, *J. Phys. Org. Chem.*, 1992, **5**, 549.

4 R. W. Hay, M. P. Pujari and A. Perotti, *Transition Met. Chem.*, 1985, **10**, 396.

5 D. W. Margerum and G. R. Dukes, in *Transition Metal Ions in Biological Systems*, ed. H. Sigel, Marcel Dekker, New York, 1974, vol. 1, p. 1 and references cited therein.

6 D. A. Buckingham, D. M. Forster and A. N. M. Sargeson, *J. Am. Chem. Soc.*, 1969, **91**, 3451; M. T. Barnet, H. C. Freeman, D. A. Buckingham and I. N. Hsu, *Chem. Commun.*, 1970, 367.

7 R. H. Lee, E. Griswold and J. Kleinberg, *Inorg. Chem.*, 1964, **3**, 1278.