

Kinetic Stabilisation of Catenates by Increased Rigidity of the Interlocked Ring System

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Owing to its topography, the catenand (**3**) forms highly inert copper(I) or proton catenates; the dissociation rate law indicates that, in contrast with complexes of (**2**), no important geometrical change takes place during decomplexation.

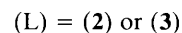
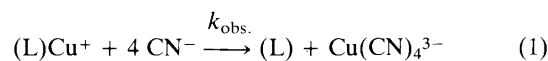
We have recently reported that the copper(I) complex of a ligand consisting of two interlocked rings (catenand) is highly stabilized with respect to acyclic complexes of analogous geometry.¹ For instance, although $\text{Cu}(\mathbf{1})_2^+$ is already a relatively inert complex, owing to the entwining of the two co-ordinating subunits, its dissociation rate is several orders of magnitude faster than that of $(\mathbf{2})\text{Cu}^+$.

We have now shown that the catenate $(\mathbf{2})\text{Cu}^+$ can be made drastically more inert by preventing the two rings of the ligand from gliding freely within each other. Such a situation is reached in $(\mathbf{3})^2$ and its complexes, the two phenyl rings located in the back of one phenanthroline precluding (**3**) from undergoing large conformational changes, (see Figure 1). Its topography is not very different from that of the catenate $(\mathbf{3})\text{Cu}^+$, the two 2,9-diphenyl-1,10-phenanthroline (dpp) fragments being still entwined in the free ligand.

Crystallographic and n.m.r. studies have shown that the monoprotonated form of (**2**) is a proton catenate;³ the same is true for $(\mathbf{3})\text{H}^+$, as demonstrated by its n.m.r. spectrum, characteristics of a molecular system containing two entwined dpp chelates.

The important geometrical effects of the two 'back' phenyl rings is reflected in the very different kinetic behaviour of the

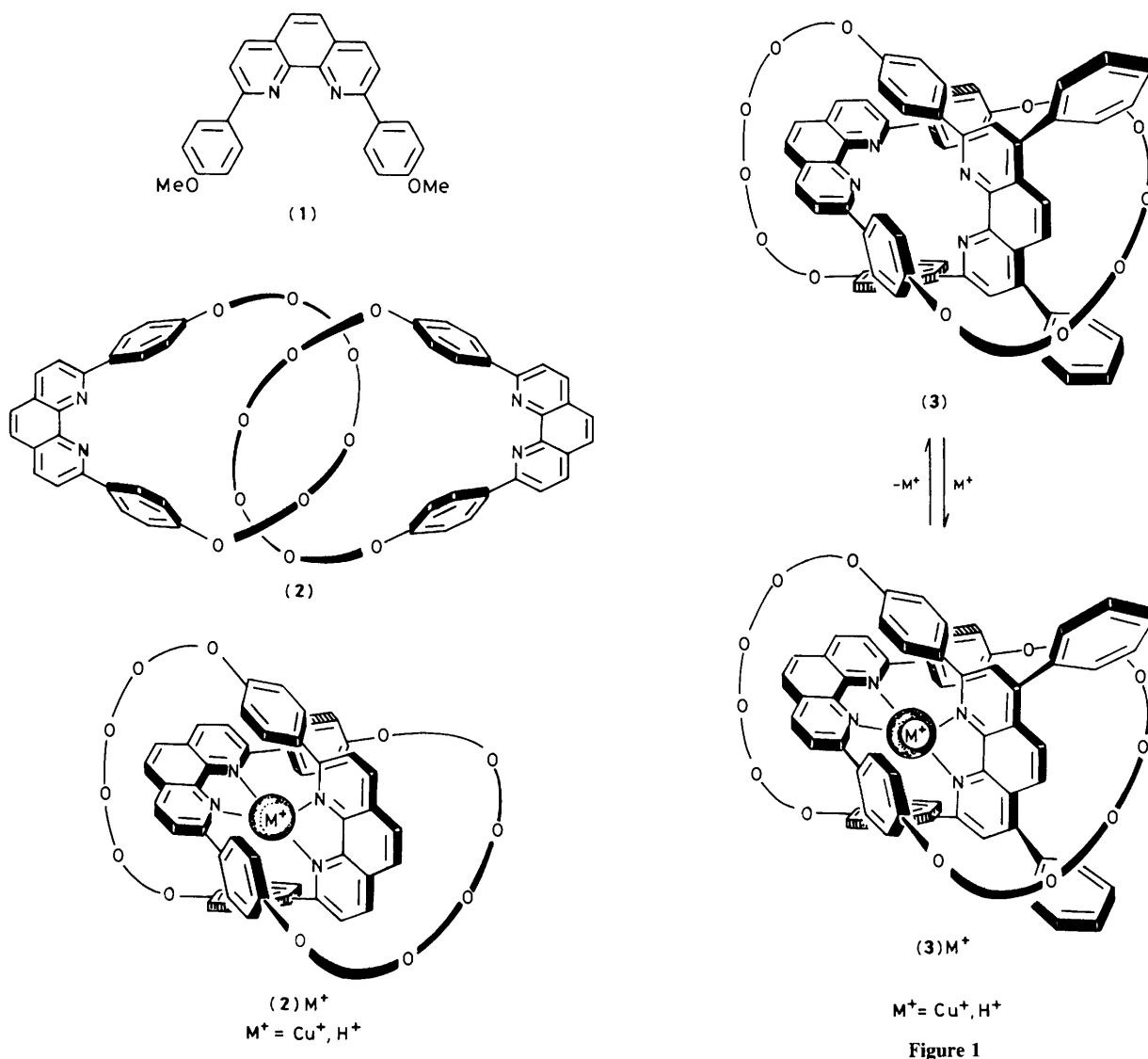
two systems, (**2**) and (**3**). The demetallation reaction, equation (1), corresponded to the rate law in equation (2) where k_D (s^{-1}) is the direct demetallation rate constant and k_{CN} ($\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$) is the cyanide-assisted demetallation rate constant.[†]



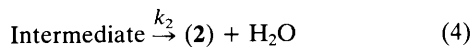
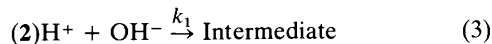
$$-\frac{d[(\text{L})\text{Cu}^+]}{dt} = k_{\text{obs.}} [(\text{L})\text{Cu}^+] = \{k_D + k_{\text{CN}} [\text{CN}^-]\} [(\text{L})\text{Cu}^+] \quad (2)$$

The deprotonation reaction takes place in two successive steps for $(\mathbf{2})\text{H}^+$, equations (3) and (4), where k_1 ($\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$) is the hydroxide-assisted deprotonation rate constant and k_2 (s^{-1}) is the rate constant, independent of $[\text{OH}^-]$ and concerning the rearrangement of the intermediate species. Equations (5) and (6) are the corresponding rate expressions.

[†] Kinetic data were obtained by classical spectrophotometry for the slow demetallation of the Cu^{I} complexes or by a stopped-flow technique for the deprotonation reactions.

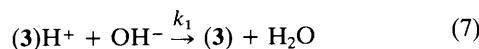


In contrast, deprotonation of (3)H⁺ is a one step second order reaction, equations (7) and (8). The values of the various rate constants are shown in Table 1.



$$-\frac{d[(2)H^+]}{dt} = k_1[OH^-][(2)H^+] \quad (5)$$

$$\frac{d[(2)]}{dt} = k_2[\text{Intermediate}] \quad (6)$$



$$-\frac{d[(3)H^+]}{dt} = k_1[OH^-][(3)H^+] \quad (8)$$

The copper(I) catenate (3)Cu⁺ is remarkably inert, being more than 10² times slower to demetallate than (2)Cu⁺ by

either pathway. This effect is due to the particular topography of (3) and its complexes: the two phenyl rings located in the rear of one dpp unit confine the pentaoxyethylene link connected to the other dpp fragment to a certain region of space.

The deprotonation process is surprisingly slow for both proton catenates; in contrast, deprotonation of (1)H⁺ is too fast to be studied by stopped-flow techniques, whereas deprotonation of (3)H⁺ requires minutes. Previous studies have shown that protonation-deprotonation reactions of various substituted pyridines⁴ or 1,10-phenanthroline⁵ are very fast.

Interestingly, the two dissociation mechanisms found for (2)H⁺ and (3)H⁺ are different. Whereas the latter undergoes a classical one step second order deprotonation reaction, deprotonation of (2)H⁺ occurs in two distinct steps. This may be related to the catenane topology of the organic skeleton. The fast bimolecular reaction arises from attack of the bound proton by OH⁻. The slow unimolecular process could correspond to the rearrangement of the molecular system and the simultaneous release of the water molecule formed. In (2), the two dpp subunits are fully disentangled,⁶ implying that the two interlocking cycles have to glide within each other during

Table 1. Demetallation and deprotonation rate constants of (L)Cu⁺ and (L)H⁺.^a

| (L) | Demetallation | | Deprotonation | |
|-----|----------------------------------------|---------------------------------------------------------------|------------------------------------------------------------|--------------------------|
| | k_D (s ⁻¹) | k_{CN} (mol ⁻¹ dm ³ s ⁻¹) | k_1 (mol ⁻¹ dm ³ s ⁻¹) | k_2 (s ⁻¹) |
| (2) | 2×10^{-4b} $\sim 10^{-4c}$ | 1.6×10^{-1b} 5×10^{-2c} | 1.47×10^5 | 2.7×10^{-1} |
| (3) | $< 10^{-6}$ | $< 5 \times 10^{-5}$ | 1.16 | — ^d |

^a Solvent: MeCN-CH₂Cl₂-H₂O (v/v 80:10:10); $T = 25.0 \pm 0.1$ °C; ionic strength = 0.1 (tetrabutylammonium perchlorate). Demetallation: [(L)Cu⁺]₀ ≈ 10⁻⁵ M, [CN⁻]₀ = 3 to 20 × 10⁻³ M. Deprotonation: [(2)H⁺]₀ = 4 × 10⁻⁶ M, [OH⁻]₀ = 1 to 5 × 10⁻⁵ M; [(3)H⁺]₀ = 7 × 10⁻⁶ M; [OH⁻]₀ = 2 to 12 × 10⁻³ M. ^b Solvent MeCN-H₂O (90:10 by weight). ^c Inaccurate determination. ^d No unimolecular step detected.

deprotonation. By contrast, for (3), with its entwined rigid geometry like that of (3)H⁺, no unimolecular slow rearrangement step can be measured.

Finally, it is noteworthy that the bimolecular deprotonation step of (3)H⁺ is five orders of magnitude lower than that of (2)H⁺ (k_1 values in Table 1). Clearly, the rigidity of (3) accounts for this large factor, in agreement with the kinetic inertness of (3)Cu⁺.

Although deprotonation of (3)H⁺ is much faster than that of rigid protonated diaza cage compounds,⁷ it demonstrates that kinetic properties can be tuned by appropriate geometrical modifications remote from the binding site.

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