

# Interlocked Macrocyclic Ligands: A Kinetic Catenand Effect in Copper(I) Complexes

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**Abstract:** Copper(I) complexes of chelates and cyclic ligands containing 1,10-phenanthroline coordinating units have been prepared. Kinetic studies have been carried out in order to gain insight into the particular properties of the recently synthesized catenates. In the presence of the decomplexing agent  $\text{CN}^-$ , two dissociation mechanisms are involved: a bimolecular attack of  $\text{CN}^-$  on the copper(I) center and a monomolecular demetallation pathway. The rate law has been obtained and is in good agreement with the two dissociation pathways for each complex studied. The decomplexation rate depends strongly on both the topography and the topology of the molecules. For bis(2,9-diphenyl-1,10-phenanthroline)copper(I),  $\text{Cu}(\text{dpp})_2^+$ , accessibility of the metal by  $\text{CN}^-$  is hindered as compared to less substituted complexes, making the bimolecular dissociation process much slower. Such an effect is due to the particular shape of the molecule, two dpp's, fitting in together while encaging the copper atom. A pronounced cyclic effect has also been demonstrated, even for mixed complexes containing only one ring surrounding the chelated metal. A marked catenand effect, of topological origin, has been found: when the ligand is composed of two interlocked rings, the unravelling of the two cycles (necessary to demetallation) renders the latter reaction several orders of magnitude slower than for the acyclic analogue of the catenate.

Recently, a new class of ligands has been reported: the catenands.<sup>1</sup> They contain interlocked macrocycles, and for this reason they display novel topological properties characteristic of a catenane.<sup>2</sup> The interlocking of the two rings is performed by a template synthesis around a copper(I) ion, leading in a first step to a cuprocatenate.<sup>3</sup> The two highly rigid coordinating subunits, built on 2,9-diphenyl-1,10-phenanthroline (dpp) units, fit in together while encaging the metal atoms, providing a special topography to the complex. Cu(I) being the templating moiety, because of its preferred tetrahedral geometry, seems to be extremely well adapted to the ligand. Therefore, we undertook a kinetic study of the decomplexation by  $\text{CN}^-$  of the cuprocatenate and of other related complexes, in order to demonstrate a catenand effect. In addition, separation of the effects of topology (interlocked rings) from those of topography (two entwined dpp units) is expected to demonstrate the relative importance of these different geometrical contributions in decomplexation kinetics.

In particular, it should be possible to evaluate the size of various factors such as the catenane nature of the ligand, the rigidity and cage-like character of the system formed by the two intercrossed dpp's (as recently shown for acyclic complexes of copper(I)<sup>4</sup>), and the stacking between phenyl rings borne by one phenanthroline and the other phenanthroline nucleus within a given complex. Kinetic studies of monocyclic complexes (crown ethers<sup>5</sup> and azacrown<sup>6-8</sup>) and of cryptates<sup>9-11</sup> have previously demonstrated kinetic stabilization due to the cyclic structure of the ligand. For this reason we wished to investigate the kinetic properties of cyclic complexes such as the cuprocatenate and other related molecules. For the purposes of comparison with acyclic compounds, the copper(I) complex of 2,9-dimethyl-1,10-phenanthroline was also studied. This complex was previously shown to be highly stable in water<sup>12</sup> but only moderately stable in acetonitrile.<sup>13</sup> Kinetic studies of unsubstituted phenanthroline complexes of copper(I) in aqueous solution have previously been reported.<sup>14</sup>

The ligands used and their corresponding complexes are represented Figure 1.

## Experimental Section

**Materials and Methods.** Acetonitrile was dried and purified by distillation (normal pressure) over  $\text{CaH}_2$ .  $\text{Cu}(\text{CH}_3\text{CN})_4\cdot\text{BF}_4$  was prepared by the literature method.<sup>15</sup> All other chemicals were of the best commercially available grade and were used without further purification.

<sup>1</sup>H NMR spectra were recorded with a Bruker WP 200 SY spectrometer.

**Preparation of the Ligands.** Except for dmp which is commercially available (Fluka no. 72080), all ligands were prepared as previously reported<sup>16</sup>

**Preparation of the Copper(I) Complexes.**  $\text{Cu}(\text{dmp})_2^+$ ,  $\text{Cu}(\text{dpp})_2^+$ ,  $\text{Cu}(\text{dap})_2^+$ , and  $\text{Cu}(\text{cat-30})^+$  were prepared by literature methods.<sup>3,4,17</sup> For the preparation of  $\text{Cu}(\text{m-30,dap})^+$  the following experimental procedure was used: By the double-ended needle transfer technique, 0.25 mmol of  $[\text{Cu}(\text{CH}_3\text{CN})_4]^+\cdot\text{BF}_4^-$  in acetonitrile (10 mL) is added under argon and at room temperature to a stirred solution of m-30 (0.25 mmol)

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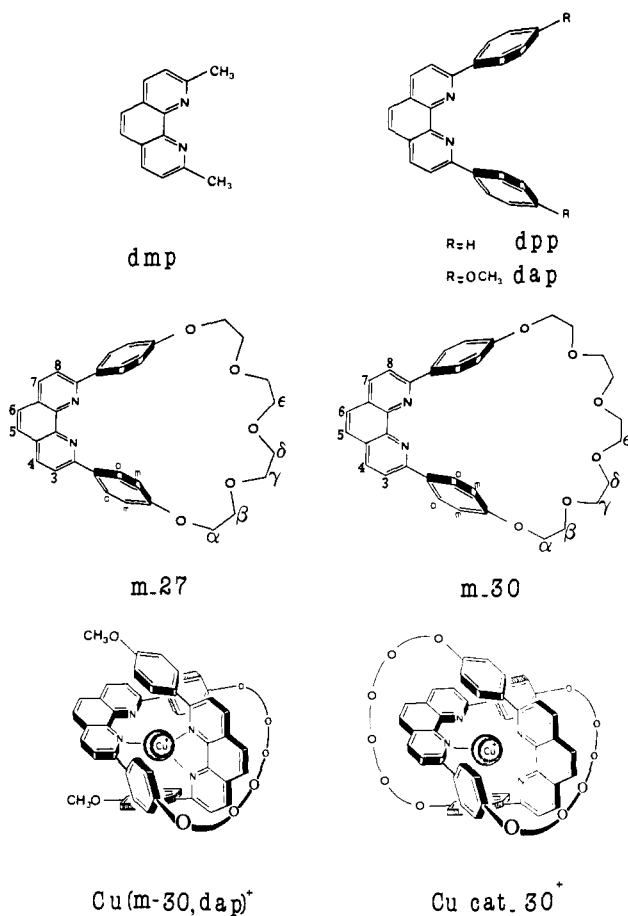
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**Table I.**  $^1\text{H}$  NMR Spectra of  $\text{Cu}(\text{m-27,dap})^+$  and  $\text{Cu}(\text{m-30,dap})^+$ :  $\delta$  (ppm) in  $\text{CD}_2\text{Cl}_2$  (Internal Reference  $\text{CDHCl}_2$  at 5.32 ppm)

compound	aromatic region <sup>a</sup>					polyoxyethylene chain and methoxy groups
	$\text{H}_{4,7}$ (2 H) $\text{H}_{4,7}$ (2 H)	$\text{H}_{5,6}$ (2 H) $\text{H}_{5,6}$ (2 H)	$\text{H}_{3,8}$ (2 H) $\text{H}_{3,8}$ (2 H)	$\text{H}_{6'}$ (4 H) $\text{H}_{6'}$ (4 H)	$\text{H}_{m'}$ (4 H) $\text{H}_m$ (4 H)	
$\text{Cu}(\text{m-30,dap})^+$	8.63	8.25	7.89	7.52	6.08	$\text{H}_e$ : 3.84 (4 H) s $\text{H}_{\alpha,\beta,\gamma,\delta}$ : 3.52 < m < 3.76 (16 H) $\text{OCH}_3$ : 3.49 (6 H) s
	8.48	8.04	7.85	7.31	5.99	
$\text{Cu}(\text{m-27,dap})^{\dagger b}$	8.80	8.26	7.92	7.43	6.06	$\text{H}_{\gamma,\delta}$ : 3.88 and 3.80 (8 H) m $\text{H}_e$ : 3.46 (4 H) m $\text{H}_\beta$ : 3.12 (4 H) t (5.3 Hz) $\text{OCH}_3$ : 3.51 (6 H) s
	8.51	8.06	7.86	6.86	5.77	

<sup>a</sup> Apart from  $\text{H}_{5,6}$  and  $\text{H}_{5,6'}$  (singlets), all other aromatic protons show an AB pattern with the same coupling constant ( $\sim 8.5$  Hz). <sup>b</sup> In  $\text{CD}_2\text{Cl}_2$  after addition of a small amount of ascorbic acid in order to avoid formation of paramagnetic copper(II).

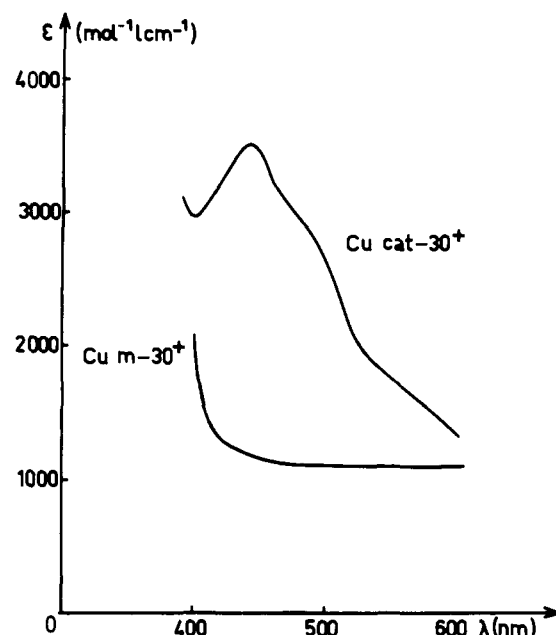
**Figure 1.**

in methylene chloride (10 mL). The mixture turns dark yellow instantaneously, indicating the formation of  $[\text{Cu}(\text{m-30,2CH}_3\text{CN})]^+\text{BF}_4^-$ . After 0.5 h at room temperature, a solution of 0.25 mmol of dap in methylene chloride (10 mL) is added to the latter complex. The solution turns dark red immediately. After the solution was stirred for 1 h under argon at room temperature, the solvents are evaporated to dryness: dark red needles of crude  $\text{Cu}(\text{m-30,dap})^+$  are obtained in quantitative yield.  $\text{Cu}(\text{m-27,dap})^+$  was prepared by an analogous experimental procedure.

Compounds  $\text{Cu}(\text{m-30,dap})^+$  and  $\text{Cu}(\text{m-27,dap})^+$  were characterized by  $^1\text{H}$  NMR in  $\text{CD}_2\text{Cl}_2$  (Table I). As shown by  $^1\text{H}$  NMR spectroscopy, both compounds were formed quantitatively and were not further analyzed by other techniques.

**Kinetic Measurements.** The solvent used in this study was a mixed solvent, acetonitrile (Merck, Uvasol)/water 90/10 by weight; it was chosen in order to solubilize both the reactants and the products of the demetallation reaction. The temperature was maintained constant at  $25.0 \pm 0.1$  °C. The ionic strength was adjusted to 0.1 with tetrabutylammonium perchlorate (Fluka, purum). The potassium cyanide (Pro-labo, Normapur) concentrations were always in large excess compared to the concentrations of the copper(I) complexes ( $10^{-5}$  mol  $\text{L}^{-1}$ ) and were varied over a wide range (from  $5 \times 10^{-4}$  to  $2 \times 10^{-2}$  mol  $\text{L}^{-1}$ ).

The preliminary spectrophotometric study was carried out with a Cary 17 spectrophotometer. The visible electronic spectra of  $\text{Cu}(\text{dmp})_2^+$  and

**Figure 2.** Visible spectra of  $\text{Cu}(\text{m-30})^+$  and  $\text{Cu}(\text{cat-30})^+$ : solvent, acetonitrile/water (90/10 by weight);  $l = 0.1$ ; temperature =  $25.0$  °C.

$\text{Cu}(\text{dpp})_2^+$  in methylene chloride<sup>18</sup> and of  $\text{Cu}(\text{dap})_2^+$  in ethanol<sup>4</sup> have already been reported. The determinations in our experimental conditions are in good agreement with these data:  $\epsilon_{454} = 7200$  mol $^{-1}$  L cm $^{-1}$  for  $\text{Cu}(\text{dmp})_2^+$ ;  $\epsilon_{440} = 3440$  mol $^{-1}$  L cm $^{-1}$  for  $\text{Cu}(\text{dpp})_2^+$ ; and  $\epsilon_{440} = 2600$  mol $^{-1}$  L cm $^{-1}$  for  $\text{Cu}(\text{dap})_2^+$ . The visible electronic spectra of the copper(I) complexes,  $\text{Cu}(\text{cat-30})^+$  and  $\text{Cu}(\text{m-30})^+$  ( $\text{CH}_3\text{CN}$  molecules probably being coordinated to  $\text{Cu}^+$ ), are presented in Figure 2. It is noteworthy to observe the similarity between the measured spectrum of  $\text{Cu}(\text{m-30})^+$  and that calculated for the monochelated species  $\text{Cu}(\text{dmp})^+$  by McMillin et al.<sup>13</sup> Both complexes are formed with a single phenanthroline and show the same drastic decrease of the absorption peak at 440 nm. The wavelength chosen for the kinetic study was 454 nm for  $\text{Cu}(\text{dmp})_2^+$  and 440 nm for all the other complexes considered.

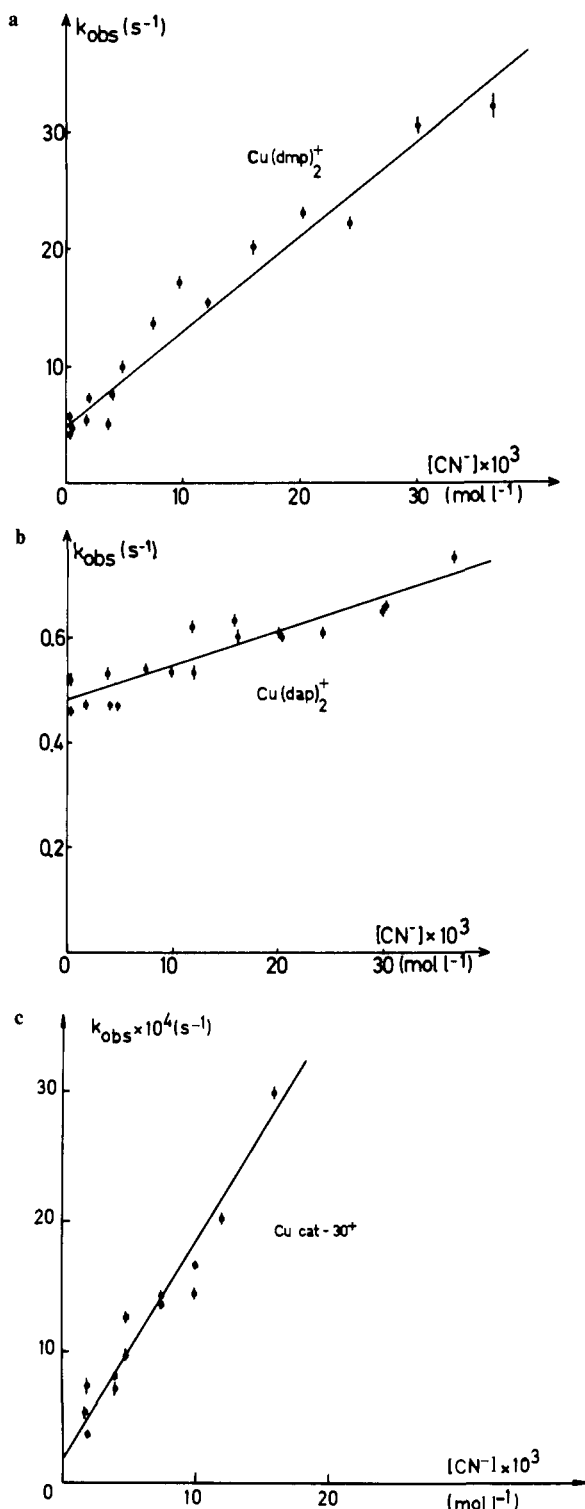
A fast mixing technique (stopped-flow spectrophotometer Durrum-Gibson D-110) was necessary for measuring the rates of demetallation by  $\text{CN}^-$  of  $\text{Cu}(\text{dmp})_2^+$ ,  $\text{Cu}(\text{dpp})_2^+$ , and  $\text{Cu}(\text{dap})_2^+$ . The kinetic data were recorded by a Datalab transient recorder and treated on-line with a Apple II microcomputer and a first-order kinetics program.<sup>19</sup> The slow dissociation rate of the other complexes,  $\text{Cu}(\text{m-30,dap})^+$ ,  $\text{Cu}(\text{m-27,dap})^+$  and  $\text{Cu}(\text{cat-30})^+$ , was determined by classical spectrophotometry (Cary 17). The copper(I) complexes and cyanide solutions were first brought to temperature equilibrium in a bath kept at  $25.0 \pm 0.1$  °C and then directly mixed in the optical cell. The transmittance at 440 nm of the reaction was recorded as a function of time.

## Results and Discussion

Because  $\text{CN}^-$  is known to form very stable complexes with copper(I)<sup>20</sup> ( $\log \beta_4 = 28$ ), this decomplexing agent, previously

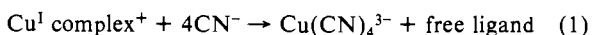
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**Figure 3.** Plots of  $k_{\text{obsd}}$  as a function of cyanide concentration for  $\text{Cu}(\text{dmp})_2^+$ ,  $\text{Cu}(\text{dap})_2^+$ , and  $\text{Cu}(\text{cat-30})^+$ . Same experimental conditions as in Figure 2.

used for preparative purposes,<sup>1</sup> was chosen for the present study. The same reagent was used throughout the study in order to allow direct comparison between complexes. In each case, the overall reaction is given by eq 1.



$$v = -\frac{d[\text{Cu}^{\text{I}} \text{ complex}^+]}{dt} = k_{\text{obsd}}[\text{Cu}^{\text{I}} \text{ complex}^+] \quad (2)$$

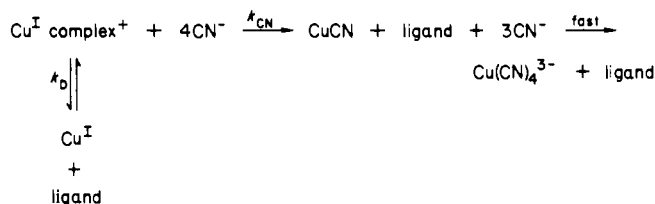
$k_{\text{obsd}}$  ( $\text{s}^{-1}$ ) = observed first-order rate constant

The following rate law has been obtained by spectrophotometric measurements in the presence of an excess of cyanide. This rate law applies to all complexes studied, from  $\text{Cu}(\text{dmp})_2^+$  to  $\text{Cu}(\text{cat-30})^+$  (see Figure 1). The variations of  $k_{\text{obsd}}$  with concentrations of cyanide in excess are linear for all complexes considered:

$$k_{\text{obsd}} = k_{\text{D}} + k_{\text{CN}}[\text{CN}^-] \quad (3)$$

with  $k_{\text{D}}$  ( $\text{s}^{-1}$ ) = direct dissociation rate constant and  $k_{\text{CN}}$  ( $\text{mol}^{-1} \text{L s}^{-1}$ ) =  $\text{CN}^-$  assisted dissociation rate constant. Typical experimental data are presented in Figure 3.

The rate law found supports the following two possible pathways: a pathway related to the intrinsic inertness of the complex in the absence of  $\text{CN}^-$  ( $k_{\text{D}}$ ) and a second pathway corresponding to a first-order attack of  $\text{CN}^-$  on the complex ( $k_{\text{CN}}$ ).



The bimolecular dissociation step is depicted in Scheme I for  $\text{Cu}(\text{cat-30})^+$ .

It was verified that no intermediate complex with cyanide exists in the dissociation process. The experimental data are collected in Table II. A wide range of dissociation rate constants is found, requiring various techniques from fast mixing to classical measurements. In order to discuss our results it is more convenient to take into account two separate effects relating respectively to the nature of the substituents borne by the phenanthroline ligands [ $\text{Cu}(\text{dmp})_2^+$ ,  $\text{Cu}(\text{dpp})_2^+$ , and  $\text{Cu}(\text{dap})_2^+$ ] and to the presence and size of one or two macrocyclic coordinating subunits [ $\text{Cu}(\text{m-30,dap})^+$ ,  $\text{Cu}(\text{m-27,dap})^+$ , and  $\text{Cu}(\text{cat-30})^+$ ].

**Influence of Substituents.** Steric factors may be evaluated by comparing results for  $\text{Cu}(\text{dmp})_2^+$  and  $\text{Cu}(\text{dpp})_2^+$ . Whereas the intrinsic dissociation process does not strongly depend on the size of the substituents  $\alpha$  to the nitrogen atoms of phenanthroline ( $k_{\text{D}} = 4.8$  for  $\text{Cu}(\text{dmp})_2^+$  and  $k_{\text{D}} = 1.29$  for  $\text{Cu}(\text{dpp})_2^+$ ), the bimolecular reaction, involving  $\text{CN}^-$  attack, is highly disfavored as the hindering character of the substituents increases.  $\text{Cu}(\text{dpp})_2^+$  dissociates 60 times more slowly via a bimolecular process than  $\text{Cu}(\text{dmp})_2^+$ , and  $\text{Cu}(\text{dap})_2^+$  is even more resistant to dissociation (see Table II). This is not really surprising if one considers the special molecular shape of  $\text{Cu}(\text{dpp})_2^+$ : two dpp ligands are entwined around the metal, the two phenyl groups of one dpp being located one on either side of the phenanthroline plane of the other ligand. This arrangement gives the system a pronounced encaged character, making the copper(I) center noticeably more protected than for  $\text{Cu}(\text{dmp})_2^+$ <sup>21</sup> and thus rendering more difficult any nucleophilic attack on the copper atom.

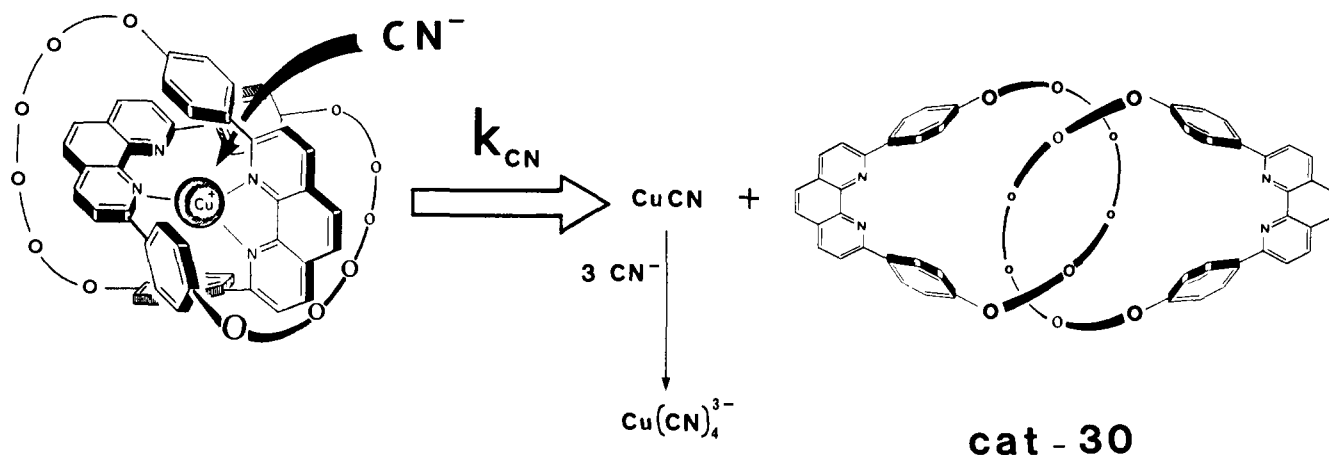
The special topography of  $\text{Cu}(\text{dpp})_2^+$  is responsible for interesting photochemical properties. A comparative photophysical study of  $\text{Cu}(\text{dmp})_2^+$  and  $\text{Cu}(\text{dpp})_2^+$  has recently been reported.<sup>18</sup> The kinetic data obtained in the present study correlate well with the photophysical properties, both sets of parameters being worthy of discussion (see Table III); in particular, they tend to indicate that the ground state and the excited state have analogous geometries.

In a bimolecular attack of the copper center by a base ( $\text{CN}^-$  for  $k_{\text{CN}}$  in the ground state or  $\text{CH}_3\text{OH}$  for  $k_{\text{Q}}$  in the excited state),

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Scheme I

**Table II.** Decomplexation of Various Copper(I) Complexes by KCN: Kinetic Parameters<sup>a</sup>

rate constants	Cu(dmp) <sub>2</sub> <sup>+</sup>	Cu(dpp) <sub>2</sub> <sup>+</sup>	Cu(dap) <sub>2</sub> <sup>+</sup>	Cu(m-30,dap) <sup>+</sup>	Cu(m-27,dap) <sup>+</sup>	Cu(cat-30) <sup>+</sup>
<i>k<sub>D</sub></i> (s <sup>-1</sup> )	4.8 ± 0.6	1.29 ± 0.03	0.48 ± 0.01	(1.4 ± 0.5) × 10 <sup>-3</sup>	<4 × 10 <sup>-5</sup>	(1.8 ± 0.9) × 10 <sup>-4</sup>
<i>k<sub>CN</sub></i> (mol <sup>-1</sup> L s <sup>-1</sup> )	820 ± 43	14.6 ± 1.8	6.5 ± 0.7	1.7 ± 0.2	0.15 ± 0.02	0.16 ± 0.01

<sup>a</sup>Solvent, acetonitrile/water (90/10 by weight); *I* = 0.1; *T* = 25 °C; uncertainties 1 σ.

**Table III.** Comparison of Dissociation Rate Constants *k<sub>D</sub>* and *k<sub>CN</sub>* with Photophysical Data (Lifetime of the Charge Transfer Excited State  $\tau_0$  and Quenching Rate Constant *k<sub>Q</sub>*)

	Cu(dmp) <sub>2</sub> <sup>+</sup>	Cu(dpp) <sub>2</sub> <sup>+</sup>
intrinsic properties		
<i>k<sub>d</sub></i> (s <sup>-1</sup> )	4.8	1.3
1/ $\tau_0^a$ (s <sup>-1</sup> )	1.1 × 10 <sup>7</sup>	4 × 10 <sup>6</sup>
bimolecular reactions		
<i>k<sub>CN</sub></i> (mol <sup>-1</sup> L s <sup>-1</sup> )	820	15
<i>k<sub>Q</sub></i> <sup>b</sup> (mol <sup>-1</sup> L s <sup>-1</sup> )	2.2 × 10 <sup>7</sup>	5 × 10 <sup>4</sup>

<sup>a</sup>Excited state lifetime  $\tau_0$  in CH<sub>2</sub>Cl at room temperature.<sup>18</sup>

<sup>b</sup>CuL<sub>2</sub><sup>+</sup>  $\xrightarrow{k_d}$  CuL<sub>2</sub><sup>+</sup>, *k<sub>d</sub>* = 1/ $\tau$ . <sup>c</sup>Rate constant for quenching by CH<sub>3</sub>OH at room temperature in CH<sub>2</sub>Cl<sub>2</sub>.<sup>18</sup> <sup>d</sup>Cu<sub>2</sub>L<sub>2</sub><sup>+</sup> + CH<sub>3</sub>OH  $\xrightarrow{k_Q}$  CuL<sub>2</sub><sup>+</sup> + CH<sub>3</sub>OH.

the efficient shielding effect of the phenyl substituent which inhibits the approach of the additional ligand leads to much slower reactions with Cu(dpp)<sub>2</sub><sup>+</sup> (*k<sub>CN</sub>*) or \*Cu(dpp)<sub>2</sub><sup>+</sup> (*k<sub>Q</sub>*) than with their dmp analogues. Such photophysical properties have recently allowed the use of Cu(dpp)<sub>2</sub><sup>+</sup> as an efficient photosensitizer in a system for the photochemical reduction of water.<sup>22</sup>

Cu(dpp)<sub>2</sub><sup>+</sup> and Cu(dap)<sub>2</sub><sup>+</sup> differ only slightly in their kinetic properties (Table II). However, the study of Cu(dap)<sub>2</sub><sup>+</sup> was necessary in order to compare this acyclic complex with macrocycle containing compounds [(Cu(m-30),dap)<sup>+</sup> to Cu(cat-30)<sup>+</sup>], the electronic properties of the latter being identical with those of Cu(dap)<sub>2</sub><sup>+</sup>.

**Catenand Effect.** The presence of a polyoxyethylene chain drastically increases the kinetic inertness of the copper(I) complex considered. Although the electronic properties of Cu(dap)<sub>2</sub><sup>+</sup> and Cu(m-30,dap)<sup>+</sup> are virtually identical, the decomplexation process via the direct pathway is about 300 times slower for the ring-containing compound than for its acyclic analogue. This large factor is probably due to the difficulty encountered by the dap fragment in threading out of the ring during the decomplexation reaction. It shows that a chain, holding the "rear" of one of the coordinating fragments (dap), efficiently prevents the two ligands (m-30 and dap) of the complex from moving away from one another.

On the other hand, the bimolecular process is only slightly slowed down by introducing a monocyclic subunit. *k<sub>CN</sub>* is only 4 times higher for Cu(dap)<sub>2</sub><sup>+</sup> than for Cu(m-30,dap)<sup>+</sup>. This effect reflects the steric properties of the complexes: the accessibility

of the copper(I) center is not greatly modified by the presence of a pentaoxyethylene chain.

By comparing Cu(m-30,dap)<sup>+</sup> and Cu(m-27,dap)<sup>+</sup>, one can evaluate the influence of the ring size. Clearly, Cu(m-27,dap)<sup>+</sup> is much more inert than its higher analogue. The intrinsic dissociation rate constant *k<sub>d</sub>* is about two orders of magnitude smaller when the cycle contains 27 atoms than when it is a 30-membered ring. Only a 10% change in ring size, corresponding to the presence or absence of a CH<sub>2</sub>CH<sub>2</sub>O link, has a surprisingly large effect on the kinetic properties of the complexes. It is worth noting that the steric constraint due to the cyclic structure is not directly exerted on the copper(I) coordination sphere but on the other ligand. In other words, the two coordinating subunits m-27 and dap are firmly held together mainly because the dap ligand is tightly encompassed by the 27-membered macrocyclic ligand, whereas in Cu(m-30,dap)<sup>+</sup> the pentaethyleneoxy fragment of m-30 does not really compress the "back" (4, 5, 6, 7 positions) of the dap ligand. Indeed, a space-filling model of Cu(m-27,dap)<sup>+</sup> indicates that the system is so strained that the two phenanthrolines are not perpendicular to one another and that, more importantly, the tetraethyleneoxy link cannot run between the 5 and 6 positions but rather between 4 and 5 (or 6 and 7), making it easier to surround the dap ligand. The marked dissymmetry thus introduced to the molecular geometry is somewhat similar to that of a cuprocatenate consisting of two 27-membered interlocked rings around Cu<sup>I</sup> and is responsible for the very special properties of these complexes. The bimolecular dissociation process is about ten times slower for Cu(m-27,dap)<sup>+</sup> than for Cu(m-30,dap)<sup>+</sup>. This factor is probably not entirely due to a steric effect in the vicinity of the copper atom (the latter appearing to be at least as accessible in the highly distorted structure of Cu(m-27,dap)<sup>+</sup> as in its higher distorted structure of Cu(m-27,dap)<sup>+</sup> as in its higher homologue), reflecting also some of the large effects observed for the monomolecular pathway (*k<sub>D</sub>*). The short chain makes the separation of the two coordinating subunits dap and m-27 difficult, whatever the dissociation mechanism.

Finally, a comparison of Cu(dap)<sub>2</sub><sup>+</sup>, Cu(m-30,dap)<sup>+</sup>, and Cu(cat-30)<sup>+</sup> provides a direct measurement of the kinetic catenand effect.

The cuprocatenate Cu(cat-30)<sup>+</sup> is kinetically about ten times more stable than its monocyclic analogue, Cu(m-30,dap)<sup>+</sup>, via either the monomolecular pathway or the bimolecular reaction with CN<sup>-</sup>. Moreover, Cu(cat-30)<sup>+</sup> dissociates several orders of magnitude more slowly than the acyclic complexes Cu(dmp)<sub>2</sub><sup>+</sup> and Cu(dap)<sub>2</sub><sup>+</sup>. Clearly, this effect indicates great difficulty in disengaging the two interlocked rings. This is the catenand effect,

characteristic of the particular topology of the ligand cat-30. This very slow decomplexation process via either of the two possible paths is in good agreement with a recent crystallographic study of both  $\text{Cu}(\text{cat-30})^+$  and its free ligand cat-30.<sup>23</sup> The molecular structures of the two compounds are very different. In the catenate, the two diphenylphenanthroline subunits are held in close proximity by complexation to  $\text{Cu}(\text{I})$ , forming a relatively compact assembly due to the interlacing of the dpp fragments, whereas they are fully separate after decomplexation, being far apart one from the other. The kinetic catenand effect is thus directly related to the difficulty encountered by the two rings in disengaging from a given molecular arrangement, while remaining interlocked during the unravelling process. The molecular structure of  $\text{Cu}(\text{cat-30})^+$  shows that the coordination polyhedron of  $\text{Cu}^{\text{I}}$  is so distorted with respect to a tetrahedron that the metal center is relatively accessible to small ligands.<sup>23</sup> In fact, the steric hindrance around the copper atom is not significantly greater in  $\text{Cu}(\text{cat-30})^+$  than in  $\text{Cu}(\text{dap})_2^+$ . The observed kinetic stabilization of the cuprocatenate with respect to acyclic analogues is thus entirely due to the special topology of the ligand.

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In summary, the present results show that the decomplexation reaction rates of various copper(I) complexes span a wide range. Whereas the least hindered complex,  $\text{Cu}(\text{dmp})_2^+$ , dissociates rapidly under given conditions (in the order of 0.1 s), the entwining of two phenanthroline ligands bearing aromatic groups  $\alpha$  to the nitrogen atoms leads to a special molecular topography, greatly decreasing the rate of the demetalation process ( $\sim 1$  s). The introduction of rings to the molecules and, in particular, their interlocking around the copper atom induces an additional decrease in demetalation rate. The resulting catenand effect leads to kinetically inert complexes: the disentangling of two interlocked macrocyclic ligands during the decomplexation process requires a complete disengagement of the molecule while maintaining interlocking of the rings. Dissociation of the cuprocatenate or of strained monocyclic complexes is therefore a slow reaction ( $\sim 10^3$  s).

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**Registry No.**  $\text{Cu}(\text{dmp})_2^+$ , 21710-12-3;  $\text{Cu}(\text{dpp})_2^+$ , 85626-37-5;  $\text{Cu}(\text{dap})_2^+$ , 95246-98-3;  $\text{Cu}(\text{m-30,dap})^+$ , 95740-41-3;  $\text{Cu}(\text{m-27,dap})^+$ , 95740-42-4;  $\text{Cu}(\text{cat-30})^+$ , 95740-43-5;  $\text{CN}^-$ , 57-12-5.

## Ground-State Analogues of Transition States for Attack at Sulfonyl, Sulfinyl, and Sulfenyl Sulfur: A Sulfuranide Dioxide (10-S-5) Salt, a Sulfuranide Oxide (10-S-4) Salt, and a Sulfuranide (10-S-3) Salt<sup>1</sup>

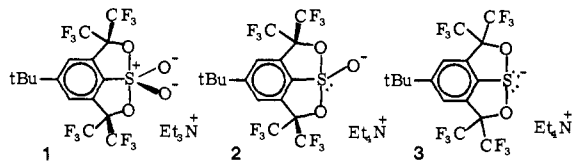
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**Abstract:** The preparation and properties of anionic 10-S-5, 10-S-4, and 10-S-3 species (**1**, **2**, and **3**) are described. The X-ray crystallographic structures show these species to be pseudotrigonal bipyramidal in geometry in the solid state. Data from  $\text{pK}_a$  measurements and low-temperature NMR spectra prove the importance of hypervalent bonding in the ground-state structures in solution as well. The anions of **1** and **2** are the first examples of sulfuranide dioxide and sulfuranide oxide anions. They are also shown to be hypervalent in the solution phase. The anions of **1**, **2**, and **3** are shown by measurements of  $\text{pK}_a$  values for their open-chain conjugate acids (7.2, 5.0, and 4.4, respectively) to be at least 2.6, 5.9, and 7.5 kcal/mol more stable than their open-chain isomers. The results of X-ray crystallographic studies of these anions are discussed, as well as the implications that the isolation and characterization of these salts have on the mechanisms of associative nucleophilic displacements at sulfur.

Anions of 10-S-5 salt **1**, 10-S-4 salt **2**, and 10-S-3 salt **3** are



analogues of high-energy intermediates or transition states that lie along the pathway of associative nucleophilic attack at sulfonyl, sulfinyl, and sulfenyl sulfur. We call them sulfuranide dioxides, sulfuranide oxides, and sulfuranides, respectively. (In the preliminary account<sup>1b</sup> of this research the three species were called

sulfurandioxides, sulfuranoxides, and sulfuranides.)

In associative nucleophilic displacements, bond making and bond breaking may occur stepwise (addition-elimination) or in synchrony (no intermediate). Researchers have studied nucleophilic displacements at sulfonyl,<sup>2</sup> sulfinyl<sup>3</sup> and sulfenyl<sup>4</sup> sulfur in

(1) (a) The *N-X-L* designation (e.g., 10-S-3) refers to a molecule in which *N* electrons are involved in bonding *L* ligands to the central atom, X: Perkins, C. W.; Martin, J. C.; Arduengo, A. J.; Lau, W.; Alegria, A.; Kochi, J. K. *J. Am. Chem. Soc.* 1980, 102, 7753. (b) For a preliminary account of this work, see: Perkins, C. W.; Martin, J. C. *Ibid.* 1983, 105, 1377.

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