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π−π Stacking-Induced Cooperativity in Copper(I) Complexes with Phenanthroline Ligands

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The formation constants of mono- and bischelate copper(I) complexes with four phenanthroline derivatives have been determined by absorption spectrophotometry in acetonitrile and in a ternary acetonitrile/dichloromethane/water 80/15/5 (v/v) mixture. The influence of electron-donating methyl and anisyl substituents in positions 2 and 9 of the phenanthroline core has been investigated using both symmetrical (dmp = 2,9-dimethyl-1,10-phenanthroline; dap = 2,9-di(*p*-anisyl)-1,10-phenanthroline) and unsymmetrical (map = 2-(*p*-anisyl)-1,10-phenanthroline; Memap = 2-(*p*-anisyl)-9-methyl-1,10-phenanthroline) ligands. The equilibrium constants show no significant dependence upon the solvent composition. The binding affinity of α,α′-diimine ligands and their methyl-substituted derivatives is governed by the σ-donation of the nitrogen atoms. In contrast, anisyl substituents exert a destabilizing effect on the monochelate complexes likely due to steric hindrance, but favor the formation of the bischelate species. The resulting positive cooperativity was rationalized in terms of intramolecular $\pi-\pi$ stacking interactions between the electron rich anisyl groups and the electron accepting phenanthroline moieties. Cyanide-assisted demetalation kinetic studies were carried out in order to gain further insight into the structural properties of the four bischelate complexes examined. The rate constants, which reflect subtle geometrical variations, span over more than 5 orders of magnitude and reveal an unexpected high accessibility of the copper(I) center in the unsymmetrical complexes $Cu(map)_2^+$ and $Cu(Memap)_2^+$.

Introduction

One hundred years after the publication of the first synthetic procedure by Blau,[1] 1,10-phenanthroline (phen) is still of major interest to a large and diverse scientific community.[2] This rigid planar heterocycle is the parent of an important class of chelating agents belonging to the family of α,α′-diimine ligands which encompasses the bipyridine (bipy) and biquinoline (biq) frameworks (Figure 1). Of particular significance, are the 2,9-disubstituted phenanthroline derivatives obtained by nucleophilic addition with the corresponding alkyl- or aryllithium reagent followed by the rearomatization in the presence of an excess of manganese dioxide.[3,4] The steric hindrance introduced by noncoordinating groups adjacent to the nitrogen donor atoms has a strong influence on the stereochemistry of first-row transition metal complexes as it destabilizes the square planar, square-pyramidal, trigonal-bipyramidal, and octahedral coordination geometries in favor of pseudotetrahedral environments.[4−6]

The presence of 14 π electrons distributed in 7 low-energy orbitals delocalized over the aromatic ring confers peculiar spectroscopic, photochemical, and electrochemical properties to phenanthroline-based transition metal complexes. Following the discovery of phenanthroline, analytical chemists have taken advantage of the intriguing deep red color developed by the copper(I) and iron(II) adducts and designed numerous colorimetric analytical protocols.[7] However, it is only recently that a detailed understanding of the metal-to-ligand charge-transfer (MLCT) absorption and luminescence features has been achieved.[8,9] The impetus for the photophysical studies stems from the discovery by McMillin and co-workers of the photoluminescence at room-temperature of $Cu(dmp)_2^+$ (dmp = 2,9-dimethyl-1,10-phenanthroline, Figure 1).[10−13] Long-lived luminescent excited states have been achieved with 2,9-aryl-substituted 1,10-phenanthroline bischelate copper(I) complexes as a result of their more rigid and protecting entwined topography.[14,15] Due to the reducing character of the excited states, these and related copper(I) phenanthroline systems offer new possibilities in solar light harvesting and energy conversion by photocatalytic reduction processes.[16−19] With the recent

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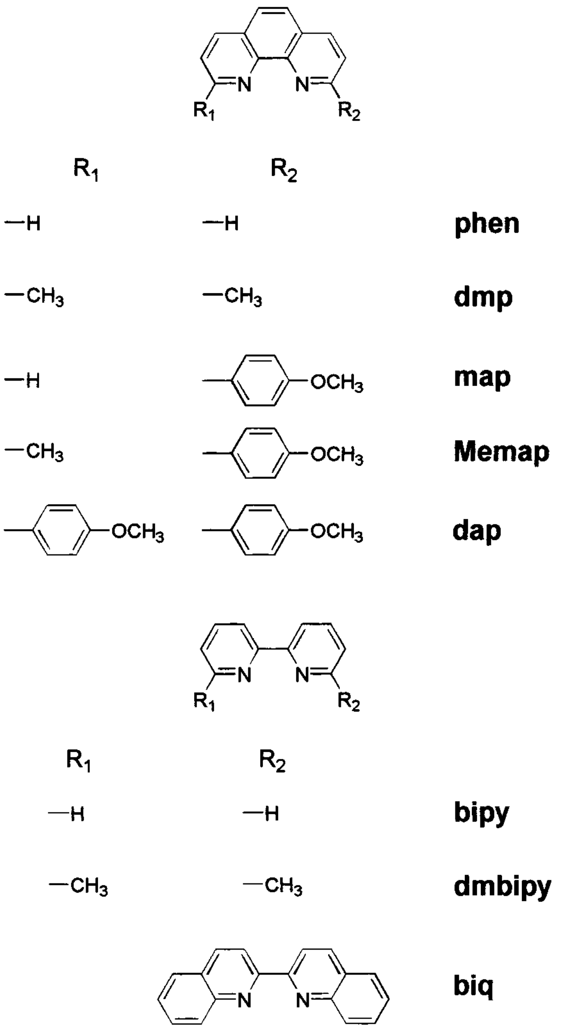

Figure 1. Molecular structure of the ligands considered in this study (bipy = 2,2′-bipyridine, dmbipy = 6,6′-dimethyl-2,2′-bipyridine, biq = 2,2′-biquinoline).

discovery of the efficient nuclease activity of $Cu(phen)_2^+$, new fields of applications have emerged which include biology and medicine.[2,20]

Phenanthroline-based copper(I) complexes have also found prominent uses in supramolecular chemistry as most useful building blocks in the construction of molecular tweezers,[21,22] pseudo-rotaxanes,[23] and rotaxanes,[24] including models of the bacterial photosynthetic reaction center,[25,26] and of double-stranded helices.[27−29] However, the most spectacular achievement which takes advantage of the tridimensional template effect induced by the pseudotetrahedral coordination geometry of copper(I), is the high-yield preparation of topological nontrivial architectures such as catenates and trefoil knots.[30−35] The success of the template strategy relies primarily on the high stability of the bischelate synthon which is the only species formed in solvents showing no binding affinity for cuprous ions such as water, alcohols, ketones, nitromethane, DMF, or halogenated hydrocarbons.[5,36] In contrast, Lewis bases such as acetonitrile or pyridine strongly stabilize the +1 oxidation state of copper which becomes much less sensitive to air oxidation. The drawbacks of the competition between coordinating solvent and ligand molecules are (i) the stabilization of the monochelate relative to the bischelate species[37,38] and (ii) the base catalysis of substitution reactions at the copper(I) center.[39,40]

Prompted by the importance of the bisphenanthroline copper(I) core in medicinal and supramolecular chemistry, we have investigated the formation equilibria of four systems including dmp, map (2-(*p*-anisyl)-1,10-phenanthroline), Memap (2-(*p*-anisyl)-9-methyl-1,10-phenanthroline), and dap (2,9-di(*p*-anisyl)-1,10-phenanthroline) (Figure 1) and related the thermodynamic and kinetic properties of the corresponding bischelate complexes to their structure. This sequence of ligands offers for the first time the opportunity to systematically explore the steric and electronic effects of alkyl and aryl substituents in α position to the nitrogen diimine atoms on the stability of the corresponding mono- and bischelate copper(I) complexes. Furthermore, the kinetic parameters related to the decomplexation by cyanide of the corresponding bisphenanthroline complexes were determined in order to gain structural information.[23,41,42]

Experimental Section

Except for 2,9-dimethyl-1,10-phenanthroline (dmp) which is commercially available (Neocuproine monohydrate, Aldrich), 2-(*p*-anisyl)-1,10-phenanthroline (map), (2-(*p*-anisyl)-9-methyl-1,10-phenanthroline (Memap), 2,9-di(*p*-anisyl)-1,10-phenanthroline (dap), their corresponding tetrafluoroborate bischelate copper(I) complexes, and crystalline copper(I) tetrakisacetonitrile tetrafluoroborate were prepared following previously described procedures, and their purity was checked by elemental analysis.[43−45] Spectrophotometric grade acetonitrile (Merck, Uvasol) and methylene chloride (Merck, Uvasol) were used as received. Distilled water was further purified by passing through a mixed bed of ion-exchanger (Millipore) and saturated with argon. The ionic strength of all solutions was adjusted to 0.1 with tetrabutylammonium trifluo-

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romethanesulfonate (Fluka, puriss. p.a. electrochemical grade). All stock solutions were prepared by careful weighing using an analytical balance (precision: 1/100 mg). Ion-pair formation has been neglected since the association constant in pure acetonitrile of the supporting electrolyte is 4.4 ± 2.1 M^{-1}.[46] The temperature was maintained constant at 25.0(1) °C.

Spectrophotometric Titrations. Formation constants were determined in both pure acetonitrile and in a freshly prepared homogeneous ternary solvent containing acetonitrile, methylene chloride and water (80/15/5 v/v). Copper(I) tetrakisacetonitrile tetrafluoroborate ($[Cu^+]_{tot} \sim (1-2) \times 10^{-4}$ M) and variable aliquots of a ligand stock solution ($0 \leq [Ligand]_{tot} \leq \sim 10^{-3}$ M) were mixed in 5 mL volumetric flasks using a precision piston microburet (Manostat). Although the formation kinetics are fast as evidenced by an instantaneous color change, the solutions were allowed to equilibrate for at least 1 h in the dark in a water bath maintained at 25.0(1) °C. Absorption spectra were recorded on an Uvikon 860 (Kontron) spectrophotometer equipped with 1 cm quartz cells (Hellma) thermostated at 25.0(1) °C. Typically, absorbance data recorded at 20 wavelengths spanning the 350−580 nm region for 15−20 solutions were refined with the nonlinear least-squares program Letagrop-Spefo employing a pit-mapping minimization method.[47−51] Alternatively, the entire multiwavelength data sets comprising absorbances measured in one nanometer steps were decomposed in their principal components by factor analysis, and subsequently the formation constants and extinction coefficients were adjusted to the reduced data sets by a nonlinear least-squares method based on the Marquardt algorithm with the commercial SPECFIT program.[52] In each case, both methods gave identical results and the formation constants are reported as the average of at least three independent titrations. Distribution curves were calculated with the help of the Haltafall program.[53]

Kinetic Measurements. The cyanide-assisted demetalation of $Cu(dmp)_2^+$, $Cu(map)_2^+$, $Cu(Memap)_2^+$, and $Cu(dap)_2^+$ was carried out in the ternary solvent mixture ($CH_3CN/CH_2Cl_2/H_2O$ 80/15/5 v/v) in an analogous way to that adopted for threaded and knotted dinuclear copper(I) complexes.[23,42] The tetraethylammonium cyanide (Fluka, purum) concentrations were always in large excess (at least 10 times) with respect to the concentrations of the copper(I) complexes ($\sim 10^{-5}$ M) in order to obtain pseudo-first-order conditions. The measurement of the decomplexation rates required a fast mixing device. Either a Durrum-Gibson D-110 or an Applied Photophysics DX17MV stopped-flow spectrophotometer interfaced to a microcomputer was used. The data sets averaged out of at least five replicates recorded at the absorption maximum of the MLCT band, were processed on-line with commercial software based on Marquardt[54] or Simplex[55] algorithms. The pseudo-first-order rate constants thus derived are included in the Supporting Information. The second-order rate constants were calculated by nonweighted linear regression and are given together with their corresponding standard deviation.

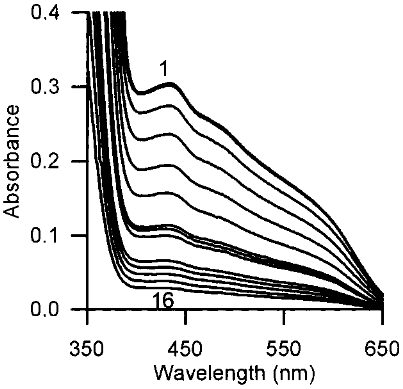

Figure 2. Spectrophotometric titration of $Cu(CH_3CN)_4^+$ by dap in $CH_3CN/CH_2Cl_2/H_2O$ 80/15/5 (v/v). $I = 0.1$ $(n\text{-}C_4H_9)_4NCF_3SO_3$; $T = 25$ °C; $l = 1$ cm; $[Cu^+] = 107$ μM and [dap] = 886, 590, 295, 236, 207, 177, 148, 118, 89, 81, 75 μM (spectra 1−11); $[Cu^+] = 214.7$ μM and [dap] = 118, 103, 89, 74, 59 μM (spectra 12−16, the displayed absorbances are divided by 2).

Results

Equilibrium Measurements. The copper(I) complexing properties of four α,α′-disubstituted phenanthroline ligands (Figure 1) have been investigated by spectrophotometric titrations in the visible range by taking advantage of the strong metal-to-ligand charge-transfer bands (MLCT) occurring in this region. The experiments were carried out in two different solvents, pure acetonitrile for comparison purposes with the literature data and a ternary homogeneous mixture ($CH_3CN/CH_2Cl_2/H_2O$ 80/15/5 v/v) previously used in studies of copper(I) threaded complexes and molecular knots.[23,42] A typical set of absorption spectra recorded in the presence of variable amounts of 2,9-dianisyl-1,10-phenanthroline is presented in Figure 2. Below 380 nm (data not shown), the spectra of the free ligands are dominated by intense $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. In the presence of copper(I), these bands are slightly red shifted, broader and undergo hypochromic effects. However, the main feature is the appearance of broad absorption bands in the visible region due to MLCT charge transfer. At high metal-to-ligand concentration ratio, the main absorption band is centered at 360 nm for dmp. For the aromatic-substituted ligands (map, Memap, and dap), the corresponding transition is blue-shifted and thus overlaps with the ligand-centered transitions. As the concentration of ligand increases, an intense band develops at lower energy; its position and intensity are strongly dependent on the nature of the α,α′-substituents: $\lambda_{max} = 455$ (dmp), 435 (map and Memap), and 430 nm (dap).

Factor analysis of the spectrophotometric data recorded between 350 and 650 nm for the four ligands examined indicated the presence of three absorbing species in solution, one of them being readily assigned to the free ligand. In each case, the best refinement with the nonlinear least-squares programs Letagrop-Spefo[47−51] and SPECFIT[52] was achieved with the model including a mono- and a bischelate mononuclear complex. Identical results were obtained with both minimization methods. The adjustment led to a statistical distribution of the residues and their root-mean-square deviation was lower than the error in absorbance measurements ($\Delta A = 0.002$). The refined stability constants are defined by eqs 1 and 2.

$$Cu^+ + L \rightleftarrows CuL^+, \qquad K_1 = \frac{[CuL^+]}{[Cu^+][L]} \qquad (1)$$

$$CuL^+ + L \rightleftarrows CuL_2^+, \qquad K_2 = \frac{[CuL_2^+]}{[CuL^+][L]} \qquad (2)$$

$$Cu^+ + lL \rightleftarrows CuL_l^+, \qquad \beta_{1l} = \frac{[CuL_l^+]}{[Cu^+][L]^l} \qquad (3)$$

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Table 1. Stability Constants of Copper(I) Complexes

ligand	log K_1	log K_2	log β_2	log $K_2 - \log K_1$	ref
bipy			13.18		36[a]
	3.2(5)	2.7(1)	5.9	−0.5	37[b]
	3.69(8)	2.80(5)	6.49	−0.89	62[b]
	3.90(7)	2.94(2)	6.84	−0.96	62[c]
dmbipy	5.36(20)	4.81(20)	10.17	−0.55	66[d]
biq			16.5		36[a]
	4.00(3)	4.14(5)	8.14	0.14	62[b]
	4.4(1)	4.4(1)	8.80	0	40[d]
		6.4(3)			56[e]
		~9			56[f]
phen			15.82		36[a]
	5.2(1)	4.5(1)	9.7	−0.7	62[b]
	5.7(1)	4.9(1)	10.6	−0.8	62[c]
dmp	6.6(2)	5.7(4)	12.3	−0.9	this work[g]
	6.3(2)	5.4(4)	11.7	−0.9	this work[h]
	5.3(2)	4.6(1)	9.9	−0.7	62[b]
	5.93(7)	5.02(6)	10.95	−0.91	62[c]
	6.0(1)	4.9(2)	10.9	−1.1	38[i]
	6.0(1)	5.5(2)	11.5	−0.5	63[j]
	7.2(3)	7.0(3)	14.2	−0.2	40[d]
			19.1		36[a]
	8.8	10.2	19.0	1.4	57[k]
map	5.3(2)	6.0(5)	11.3	0.7	this work[g]
	5.5(3)	5.7(6)	11.2	0.2	this work[h]
Memap	5.0(1)	5.7(3)	10.7	0.7	this work[g]
	4.9(1)	5.5(2)	10.4	0.6	this work[h]
dap	4.7(2)	6.0(4)	10.7	1.3	this work[g]
	4.8(1)	6.4(3)	11.2	1.6	this work[h]
	5.0(2)	6.0(4)	11.0	1.0	68[l]
			~15		67[m]

[a] H_2O; $I = 0.1$ K_2SO_4; $T = 25$ °C; potentiometry. [b] CH_3CN; $I = 0.1$ $(C_2H_5)_4NClO_4$; $T = 25$ °C; potentiometry. [c] CH_3CN; $I = 0.1$ $(C_2H_5)_4NClO_4$; $T = 20$ °C; spectrophotometry. [d] CH_3CN; $I = 0.1$ $(C_2H_5)_4NClO_4$; $T = 25$ °C; spectrophotometry. [e] CH_3COCH_3; $T = 25$ °C; spectrophotometry. [f] CH_3OH; $T = 25$ °C; spectrophotometry. [g] CH_3CN; $I = 0.1$ $(n\text{-}C_4H_9)_4NCF_3SO_3$; $T = 25.0(2)$ °C; spectrophotometry. [h] $CH_3CN/CH_2Cl_2/H_2O$ 80/15/5 (v/v); $I = 0.1$ $(n\text{-}C_4H_9)_4NCF_3SO_3$; $T = 25.0(2)$ °C; spectrophotometry. [i] CH_3CN; spectrophotometry. [j] CH_3CN; $T = 25$ °C; spectrophotometry. [k] H_2O; pH = 5.2; $T = 22(1)$ °C; calculated from redox potential measurements. [l] $CH_3CN/CH_2Cl_2/H_2O$ 80/10/10 (v/v); $I = 0.1$ $(n\text{-}C_4H_9)_4NClO_4$; $T = 25$ °C; spectrophotometry. [m] $CH_3CN/CH_2Cl_2/H_2O$ 80/10/10 (v/v); $I = 0.01$ $(C_2H_5)_4NClO_4$; $T = 25$ °C; spectrophotometry.

Their average values calculated for at least three independent replicates are collected in Table 1 together with their corresponding standard deviation. Representative species distribution diagrams calculated for a given total copper(I) concentration (10^{-4} M) are shown in Figure 3 for 2,9-dimethyl- and 2,9-dianisyl-1,10-phenanthroline. In each case, the proportion of the monochelate complex reaches its maximum at equimolar ligand-to-metal ratio. Under the experimental conditions considered in the present work, $Cu(dmp)^+$ is formed up to 60% whereas $Cu(dap)^+$ corresponds at most to only 7% of the total metal concentration, thus reaching the limit of validity of the spectrophotometric method. Almost quantitative formation of the bischelate species occurs for 2.5 and 4 equiv of dap and dmp, respectively.

The calculated visible absorption spectra of the mono- and bischelate complexes formed with the four considered ligands are depicted in Figure 4 and the extinction coefficients corresponding to the absorption maxima are summarized in Table 2. The spectroscopic properties in pure acetonitrile or in the ternary solvent mixture were found to be identical within experimental error.

Kinetic Measurements. Cyanide anion is a strong nucleophile known to form stable copper(I) complexes (log β_{14} = 28),[58,59] and acts therefore as an efficient copper(I) scavenger. The demetalation kinetics of the bischelate $Cu(dmp)_2^+$, $Cu(Memap)_2^+$, and $Cu(dap)_2^+$ complexes has been studied by stopped-flow absorption spectrophotometry. The overall reaction is expressed by eq 4 where L represents the phenanthroline-based ligand.

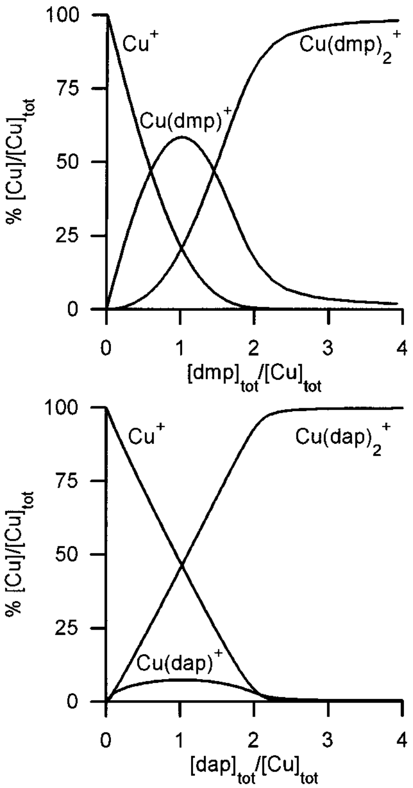

Figure 3. Species distribution diagrams of copper(I) complexes with dmp (top) and dap (bottom) in $CH_3CN/CH_2Cl_2/H_2O$ 80/15/5 (v/v). $I = 0.1$ $(n\text{-}C_4H_9)_4NCF_3SO_3$; $T = 25$ °C; $[Cu^+] = 10^{-4}$ M.

$$CuL_2^+ + 4CN^- \rightarrow 2L + Cu(CN)_4^{3-} \qquad (4)$$

Under pseudo-first-order conditions (excess CN^-), the reaction is quantitative as evidenced by the total disappearance of the characteristic color of the complexes. The monoexponential absorbance decay as a function of time, recorded at the maximum of the charge-transfer band, indicates a single rate-limiting decomplexation process. The variations of the pseudo-first-order rate constants k_{obs} with the analytical cyanide concentrations show a linear dependence (Figure 5; the raw data may be found in the Supporting Information). The corresponding rate law is expressed by eq 5 where k_D and k_{CN}, collected in Table 3, stand for the direct first-order and the cyanide-assisted bimolecular rate constants, respectively.

$$v = -\frac{d[CuL_2^+]_{tot}}{dt} = k_{obs}[CuL_2^+]_{tot} = \{k_D + k_{CN}[CN^-]_{tot}\}[CuL_2^+]_{tot} \qquad (5)$$

For $Cu(Memap)_2^+$, both the Student[60] and Hamilton[61] tests

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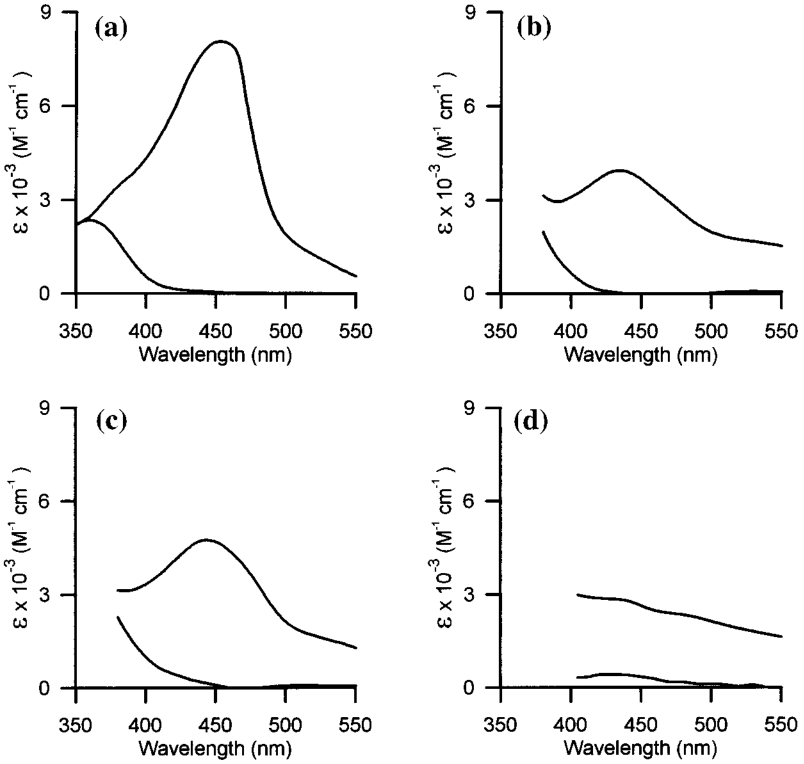

Figure 4. Calculated visible absorption spectra of the CuL^+ (less intense spectrum) and CuL_2^+ (most intense spectrum) species formed with (a) dmp, (b) map, (c) Memap, and (d) dap in $CH_3CN/CH_2Cl_2/H_2O$ 80/15/5 (v/v). $I = 0.1$ ($(n\text{-}C_4H_9)_4NCF_3SO_3$); $T = 25$ °C.

Table 2. Absorption Maxima (nm) and Extinction Coefficients (M^{-1} cm^{-1}) of the Mono- and Bischelate Copper(I) Complexes[a]

	λ_{max} (ϵ)		
complex	CH_3CN	$CH_3CN/CH_2Cl_2/H_2O$ 80/15/5 (v/v)	CH_2Cl_2[b]
$Cu(phen)_2^+$	435 (7000)[c]		
$Cu(dmp)^+$	360 (2300)	360 (2350)	
$Cu(dmp)_2^+$	455 (8000)	455 (8300)	454 (7950)
$Cu(map)_2^+$	435 (4000)	435 (4100)	
$Cu(Memap)_2^+$	435 (4700)	435 (4740)	
$Cu(dap)_2^+$	430 (2800)	430 (2800)	436 (2310)

[a] $I = 0.1$ ($(n\text{-}C_4H_9)_4NCF_3SO_3$); $T = 25$ °C. The errors are estimated to 1 nm for the wavelengths and to 5% for the extinction coefficients. [b] Reference 15. [c] Reference 7.

indicated that k_D was not statistically significant at the 95% probability level, and thus the experimental data were adjusted to a line passing through the origin by linear regression. In the case of $Cu(map)_2^+$, only a lower limit estimate of the bimolecular demetalation rate constant could be determined since the reaction proceeded to completion within the mixing-time (<4 ms) of the stopped-flow instrument even under stoichiometric conditions.

The experimental rate law supports the following mechanism which involves a dissociation path related to the intrinsic properties of the complex in absence of cyanide (k_D), and a cyanide first-order dependent pathway (k_{CN}). Since only one rate-limiting step is observed and the UV−vis spectra at the end of the reaction are identical to the spectra of the free ligands, the subsequent substitution steps at the copper(I) center by cyanide have to occur faster than its initial bimolecular attack (Scheme 1).

Discussion

Thermodynamic Properties. The complexation equilibria of 2,9-dimethyl-1,10-phenanthroline described in eqs 1 and 2 have been studied by several authors in pure acetonitrile. Owing to the apparent simplicity of the system, it might be expected that the reported values of the thermodynamic parameters are quite close to each other. However, examination of the data collected in Table 1 reveals high discrepancies (i.e., more than 2 orders of magnitude) which justified the reinvestigation of the copper(I)/dmp coordination equilibria. Leupin determined the formation constants of $Cu(dmp)^+$ and $Cu(dmp)_2^+$ in the presence of tetraethylammonium perchlorate as supporting electrolyte ($I = 0.1$) both by spectrophotometry and potentiometry using a copper wire as working electrode.[62] Despite the Nernstian behavior of the electrochemical $Cu/Cu(CH_3CN)_4^+$ half-cell, the potentiometric data afforded significantly lower K_1 and K_2 values. The stability constants obtained by spectrophotometry are in good agreement with those quoted by Atkins et al.[38] and Albrecht-Gary and Brenner[63] in absence of an inert electrolyte. In the latter studies, the ionic strength was defined by the total copper(I) concentration ($I \sim 10^{-4}$) since the titrations were carried out by increasing the concentration of dmp. The influence of the ionic strength on equilibria (1) and (2) is expected to be small and it was shown that the formation of $[Cu(dmp)_2]ClO_4$ ion-pairs in acetonitrile is negligible up to 4×10^{-3} M. The values of the formation constants determined in the present study (average of 4 replicates) using tetrabutylammonium trifluoromethanesulfonate to maintain the ionic strength at 0.1 are, within experimental error, in good agreement with the published data. Due to the high coordination tendency of dmp, the values of K_1 and K_2 are expected to be less accurate than their ratio $K_3 = K_2/K_1$ which corresponds to the equilibrium constant for eq 6:

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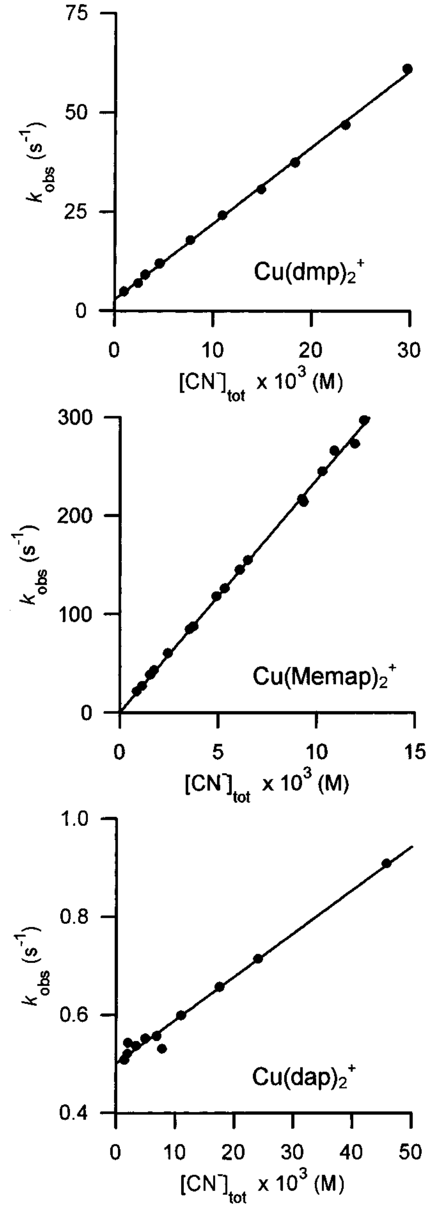

Figure 5. Plot of the pseudo-first-order rate constant k_{obs} as a function of cyanide concentration for Cu(dmp)$_2^+$ (top), Cu(Memap)$_2^+$ (middle), and Cu(dap)$_2^+$ (bottom) in $CH_3CN/CH_2Cl_2/H_2O$ 80/15/5 (v/v). $I = 0.1$ $(n\text{-}C_4H_9)_4NCF_3SO_3$; $T = 25$ °C.

$$2\mathrm{Cu(dmp)}^+ \overset{K_3}{\rightleftharpoons} \mathrm{Cu(dmp)_2}^+ + \mathrm{Cu}^+ \qquad (6)$$

The experimentally determined value of log $K_3 = -0.9$ is very close to that found by Leupin[62] and Atkins et al.[38] and suggests that the previously quoted stability constants are likely affected by systematic errors. These can originate from the presence of impurities which form complexes with copper(I), such as acetate ions or ammonia produced by the hydrolysis of acetonitrile.[64] Chloride anions contained in the copper(I) or in the tetraethylammonium perchlorate salt coordinate strongly to Cu$^+$ in acetonitrile (log $\beta_{11} = 4$, log $\beta_{12} = 9.55$, $I = 0.1$ $(C_2H_5)_4NClO_4$, $T = 25$ °C)[65] and thus interfere with the ligand. Furthermore, strict control of the temperature is required, since this factor affects not only the equilibria according to the van't Hoff equation, but also the extinction coefficients of the mono- and the bischelate complexes which increase linearly with $1/T$.[66] The significantly higher formation constants determined by Frei and Geier for Cu(dmp)$^+$ and Cu(dmp)$_2^+$ by a competition method using the less stable Cu(biq)$_2^+$ complex (biq = 2,2′-biquinoline) and dmp as competitor in 0.1 molar tetraethylammonium perchlorate solutions,[40] result from a high K_3 value (log $K_3 = -0.18(5)$) and suffer from the lower accuracy of the experimental design and from the uncertainty in the stepwise formation constants for Cu(biq)$^+$ (log $K_1 = 4.4(1)$) and Cu(biq)$_2^+$ (log $K_2 = 4.4(1)$).[40] In a previous report, Arnaud-Neu et al. have estimated the equilibrium constant of Cu(dap)$_2^+$ in $CH_3CN/CH_2Cl_2/H_2O$ 80/10/10 (v/v) from competitive measurements in the presence of dmp.[67] The reported stability (log $\beta_{12} \sim 15$) is overestimated by a factor of 10^4 compared to the values measured by direct titrations in three different solvents (Table 1).[68]

Table 3. Kinetic Parameters Relative to the Dissociation of Bischelate Copper(I) Complexes by Cyanide[a]

complex	$k_D(\sigma)$ (s^{-1})	$k_{CN}(\sigma)$ (M^{-1} s^{-1})
Cu(dmp)$_2^+$	2.9(3)	1.92(2) × 10^3
	4.8(6)[b]	0.82(4) × 10^3 [b]
Cu(map)$_2^+$	*c*	>10^7
Cu(Memap)$_2^+$	*c*	2.37(2) × 10^4
Cu(dap)$_2^+$	0.50(1)	8.8(4)
	0.48(1)[b]	6.5(7)[b]

[a] $CH_3CN/CH_2Cl_2/H_2O$ 80/15/5 (v/v); $I = 0.1$ $(n\text{-}C_4H_9)_4NCF_3SO_3$; $T = 25$ °C. [b] CH_3CN/H_2O 90/10 (v/v); $I = 0.1$ $(n\text{-}C_4H_9)_4NClO_4$; $T = 25$ °C; ref 41. [c] The value of k_D was constrained to zero.

Since copper(I) chemistry is largely controlled by the solvation properties of the bulk medium (permittivity, donating power, etc.), the presence of appreciable amounts of noncoordinating solvents of low polarity like dichloromethane is expected to have a marked influence on the complexation equilibria. Considering the substantial difference between the disproportionation constants of copper(I) in acetonitrile and in water (10^{-21} and 10^6 M^{-1}, respectively)[65,69] which is unable to stabilize the +I oxidation state, an even more important effect is expected when water is added to acetonitrile. In pure water, the bischelate complexes are stabilized with respect to the monochelate species (Table 1) due to the lower heat of solvation of copper(I) in water (−607 kJ mol^{-1}) compared to acetonitrile (−679 kJ mol^{-1}).[70] However, the experimental results displayed in Table 1 reveal no significant difference between pure acetonitrile and ternary mixtures containing 10−15% dichloromethane and 5−10% water. This suggests similar structures of the monochelate complexes in pure and water-containing acetonitrile solutions, with one or probably two bound acetonitrile molecules completing the approximately tetrahedral coordination polyhedron of copper(I).

The introduction of methyl groups α to the nitrogen donor atoms of 1,10-phenanthroline is known to stabilize the low oxidation state of copper in a pseudo-tetrahedral coordination geometry because the steric requirements of the substituents hinder the metal center from adopting a square planar or five-coordinate geometry favored by copper(II). Furthermore, the inductive effect of the methyl groups enhances the basicity of

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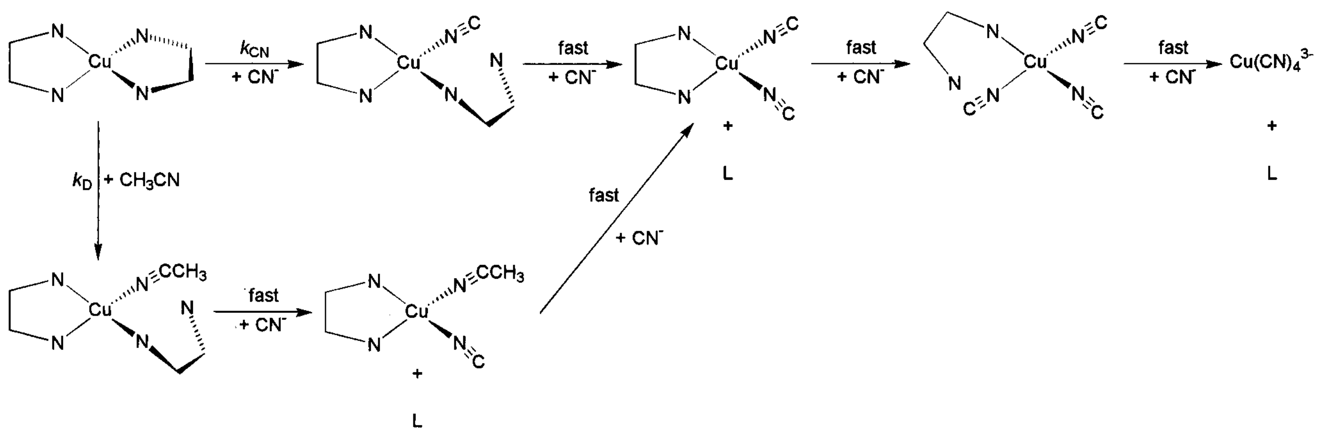
Scheme 1



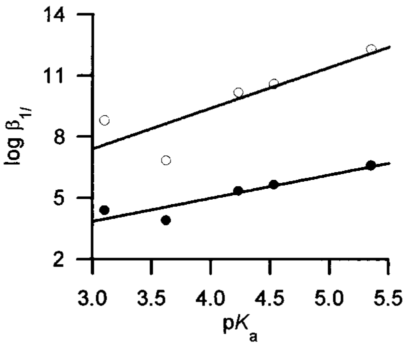


Figure 6. Linear free energy relationships between the overall stability constants (log β_{1l}) of CuL$^+$ (l = 1, closed circles) and CuL$_2^+$ (l = 2, open circles) complexes in acetonitrile, and the first protonation constants (pK_a) in water/dioxane 50/50 (v/v) of the corresponding ligands: biq (3.10), bipy (3.62), dmbipy (4.23), phen (4.53), and dmp (5.35). pK_a values are taken from refs 29 and 36.

Table 4. Stability Constants of Various dmp and dap Metal Complexes

cation		dmp	dap
Cu$^{+\,a}$	log K_1	6.3(2)	4.8(1)
	log K_2	5.4(4)	6.4(3)
	log K_2 − log K_1	−0.9	1.6
Ag$^{+\,b}$	log K_1	6.7(2)	5.8(2)
	log K_2	6.0(5)	5.4(4)
	log K_2 − log K_1	−0.7	−0.4
Zn$^{2+\,b}$	log K_1	5.9(1)	4.4(1)
	log K_2	4.8(2)	4.0(3)
	log K_2 − log K_1	−1.1	−0.4
Cd$^{2+\,b}$	log K_1	5.5(2)	3.4(1)
	log K_2	4.7(5)	4.1(3)
	log K_2 − log K_1	−0.8	0.7

[a] $CH_3CN/CH_2Cl_2/H_2O$ 80/15/5 (v/v); I = 0.1 (n-$C_4H_9)_4NCF_3SO_3$; T = 25(2) °C; this work. [b] $CH_3CN/CH_2Cl_2/H_2O$ 80/10/10 (v/v); I = 0.01 $(C_2H_5)_4NClO_4$; T = 25 °C; ref 67.

the α,α′-diimine nitrogen atoms as evidenced by the values of the first protonation constants reported for bipy (3.62) and dmbipy (4.23), phen (4.53) and dmp (5.35) in water/dioxane (50/50 v/v, I = 0.3 KNO_3) mixtures.[29,36] Figure 6 shows the linear free energy relationship between the protonation and the stability constants of CuL$^+$ ($\beta_{11} = K_1$) and CuL$_2^+$(β_{12}) for L = biq, bipy, dmbipy, phen, and dmp in acetonitrile. For this series of ligands, both linear correlations indicate that the σ-donation of the nitrogen atoms to $Cu(CH_3CN)_4^+$ and to $CuL(CH_3CN)_x^+$ (x = 1 or 2) is enhanced by an increase of the electron density (i.e., the basicity) at the imine sites.

Among the four ligands studied, dmp forms the most stable monochelate complex. The presence of one anisyl substituent adjacent to the nitrogen atoms in map and Memap lowers the K_1 value by about 1.5 logarithmic units. However, the introduction of a second anisyl group in position 9 induces only a slight destabilization of the Cu(dap)$^+$ species compared to Cu(map)$^+$ or Cu(Memap)$^+$. This effect appears not to be restricted to copper(I) alone, since silver(I), zinc(II), and cadmium(II) form monochelate complexes with dap that are 10 to 100 times less stable than the corresponding species involving dmp (Table 4).[67] Considering the electron donating properties of the anisyl ring, the basicity of the nitrogen sites is expected to increase with respect to phenanthroline. However, map, Memap, and dap form mononochelate copper(I) complexes which are less stable than Cu(phen)$^+$. The fact that the correlation displayed in Figure 6 does not apply to these ligands, outlines a major difference between the alkyl- and the aryl-substituted α,α′-diimine ligands. The lower coordination power of aryl-substituted phenanthroline ligands may be ascribed to steric, electronic, and solvation effects. The conjugation of the anisyl substituents with the phenanthroline core may favor a flattened structure of the free ligand which hinders metal binding. In absence of crystallographic data, it is difficult to discuss this point further but it is reasonable to assume a distortion of the coordination geometry induced by the bulky anisyl group in Cu(map)$^+$ and Cu(Memap)$^+$. Likely, such distortions are less severe with the symmetric ligand dap. The tilted orientation of both anisyl rings with respect to the phenanthroline plane also provides a more shielded environment around the metal center which slows down the solvent exchange reaction. The similar stabilities of Cu(map)$^+$, Cu(Memap)$^+$, and Cu(dap)$^+$ may also be due to the increased basicity of dap compared to map or Memap which cancels in part the destabilization introduced by a second anisyl substituent.

The overall stability of the bischelate complexes decreases as the steric hindrance and the lipophilicity of the phenanthroline derivatives increase (Table 1). It is interesting to note that the decrease of the β_{12} values reflects only the destabilization of the monochelate species, since the stepwise stability constants K_2 remain almost constant along the ligand series. Thus, the mono- and the bischelate complexes involving both monoanisyl ligands exhibit a similar stability, whereas Cu(dap)$_2^+$ is about 30 times more stable than Cu(dap)$^+$. Furthermore, the thermodynamic data collected in Table 4 clearly indicate that the cooperative formation of the bis(2,9-dianisyl-1,10-phenanthroline) species observed for copper(I) extends to silver(I), zinc(II), and cadmium(II), whereas the formation constants with 2,9-dimethyl-1,10-phenanthroline point out a relative destabilization of the bis- over the monochelate complexes. In the general case, the stepwise stability constants decrease steadily as the number of bound ligands increases due to (i) statistical, (ii) steric, and (iii) Coulombic effects. For a metal ion that binds a maximum of two ligands, the statistical factor is expressed by the relation: $K_2/K_1 = 1/4$ ($\log K_2 - \log K_1 = -0.60$).[71] Exceptions to this rule are rare, but a few positively cooperative systems (i.e., the experimental K_{i+1}/K_i ratio is greater than the statistical factor) are well-known. Classical examples include the mercury(II)/chloride system ($K_4 \sim K_3$)[64] and the silver amine complexes where the first ammonia displaces one water molecule from a tetrahedral silver(I) cation, while the second displaces the three remaining water molecules in $[\mathrm{Ag(NH_3)(H_2O)_3}]^+$ to give a linear $\mathrm{Ag(NH_3)_2}^+$ ion.[59,72] Despite the net increase in the number of molecules in the second complexation reaction, the associated entropy is negative and therefore the anomalous stability inversion is due to the change in hybridization which is an enthalpic effect. The iron(II)/phen equilibria afford another case of reversed order of the formation constants ($K_3 > K_2$).[64] The higher stability of $\mathrm{Fe(phen)_3}^{2+}$ relative to $\mathrm{Fe(phen)_2}^{2+}$ has been ascribed to the high- to low-spin crossover which occurs upon coordination of the third phen ligand. Albrecht-Gary et al. have reported the cooperative formation of neutral calcium and magnesium ionophore complexes which is driven by the higher lipophilicity of the neutral $\mathrm{ML_2}$ species in methanol compared to the charged ML^+ complex.[73] Positive cooperativity of entropic origin (solvation effects) has recently been quoted for a number of lanthanide complexes formed with tripodal tridentate aminophenol binders where the coordination number of the metal changes as the equilibrium shifts from the mono- to the bisligand species.[74] In the case of dap and to a lesser extent of map and Memap, the origin of the cooperative formation of the corresponding bischelate metal complexes is likely enthalpic and is assigned to interligand $\pi-\pi$ stacking effects. In the solid state, $\mathrm{Cu(dap)_2}^+$ shows an encaged structure due to strong charge-transfer interactions between the anisyl substituents and the overlapping phenanthroline core of the second chelating unit.[75] Proton NMR studies have demonstrated that the entwined topography is maintained in solution with tilted anisyl moieties (ca. 50° with respect to the phenanthroline plane) that provide an efficient shielding of the central metal cation.[76] In turn, the almost statistical formation of the dmp metal complexes (Table 4) is easily rationalized since this ligand cannot lead to electronic donor−acceptor interactions.

Electronic Absorption Properties. The spectrophotometric data of the various copper(I) complexes (Table 2) are consistent with the band energy and intensity assignments derived from molecular orbitals calculations. A general feature among the C_{2v}-symmetric α,α'-diimine ligands is the low energy gap (0.036 eV for phen) between the symmetric $b_1(\psi)$ LUMO and the antisymmetric $a_2(\chi)$ SLUMO orbitals which become accessible to MLCT transitions.[77,78] Extended Hückel computations revealed a higher coefficient of the nitrogen atom's pπ orbital (C_N) in the $b_1(\psi)$ than in the $a_2(\chi)$ molecular orbitals.[78,79] Within the general framework of Mulliken's theory of charge-transfer interactions,[80] the oscillator strength which is a measure for the absorption intensity is expressed by eq 7 where ν_{av} stands for the average transition energy of the absorption band, K is a scaling factor, and R represents the transition dipole length given by the separation between the charge centroids of the donor and acceptor orbitals.

$$\nu_{av}\int \epsilon(\nu)\mathrm{d}\nu = K(C^2_{N\psi}R^2_{\psi} + C^2_{N\chi}R^2_{\chi}) \qquad (7)$$

$\mathrm{Cu(dmp)_2}^+$ exhibits three overlapping MLCT transitions in agreement with a D_2-flattened geometry.[8,79,81,82] The most intense band ($\epsilon \sim 8000$ M^{-1} cm^{-1}), denoted as band II, appears at 455 nm and corresponds to the $b_2(xz) \rightarrow b_3(\psi)$ transition polarized along the z axis which joins the metal and ligand centers. The second symmetry-allowed transition showing z polarization is $b_3(yz) \rightarrow b_2(\psi)$ (band I) which gives rise to a shoulder at lower energy. This transition is sensitive to distortion since it arises from an inactive $^1A_2$ term associated with the $e(xz,yz) \rightarrow e(\psi)$ excitation in D_{2d} symmetry.[81,82] The high energy shoulder (band III) lies around 390 nm and is due to the $b_3(yz) \rightarrow a(\chi)$ and $b_3(yz) \rightarrow b_1(\chi)$ transitions polarized along the x and y axes, respectively. Band III is less intense than band II because the x and y components of the dipole moment operator provide less oscillator strength compared to the z component oriented toward the center of the ligand. Furthermore, the weak intensity of band III results also from a less efficient overlap of the metal-centered d and ligand-centered π^* orbitals as evidenced by the lower value of the $C_{N\chi}$ coefficient (0.2442) compared to that of $C_{N\psi}$ (0.4135).[79] In accord with the results of Dietrich-Buchecker et al.,[43] the blue-shift of the MLCT absorption maximum by 20−25 nm, the bandwidth broadening and the considerable intensity increase of band I relative to that of band II when anisyl substituents are introduced, clearly point out a splitting of the metal-centered d levels induced by a distortion of the coordination geometry.[79,82] Since the spectroscopic properties of $\mathrm{Cu(map)_2}^+$ and $\mathrm{Cu(Memap)_2}^+$ are intermediate between those of $\mathrm{Cu(dmp)_2}^+$ and of $\mathrm{Cu(dap)_2}^+$, it might be concluded that the former complexes exhibit a less flattened structure than $\mathrm{Cu(dap)_2}^+$.

The spectral intensity reflects mainly the sensitivity of the dipole length for the electronic properties of the substituents attached in positions 2 and 9 of the phenanthroline moiety (Table 2). Accordingly, Day and Sanders explained the hyperchromic effect observed for $\mathrm{Cu(dmp)_2}^+$ relative to $\mathrm{Cu(phen)_2}^+$ by a redistribution of the electronic density due to the electron donating properties of the methyl substituents.[83] Similarly, the 20% increase of the extinction coefficient of $\mathrm{Cu(Memap)_2}^+$ with respect to that of $\mathrm{Cu(map)_2}^+$ accounts for a lengthening of the transition dipole. In contrast, Phifer and McMillin have shown that the sharp decrease in the molar absorptivity in the presence of phenyl substituents correlates with a shortening of the transition dipole length as a consequence of the delocalization of the π-accepting LUMO and SLUMO orbitals over the aromatic substituents.[79] The strong hypochromic effect with respect to $\mathrm{Cu(phen)_2}^+$ ($\epsilon = 7000$ M^{-1} cm^{-1}) induced by anisyl substituents in the 2 and 9 positions ($\epsilon = 4000$ and 2800 M^{-1} cm^{-1} for $\mathrm{Cu(map)_2}^+$ and $\mathrm{Cu(dap)_2}^+$, respectively) supports this interpretation.

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Deconvolution by nonlinear least-squares refinement of the spectrophotometric data enabled the derivation of the absorption properties of the monochelate complexes (Figure 4). Although the theoretical treatment outlined above pertains primarily to monoligated metal complexes,[79] the monophenanthroline complexes have attracted much less attention due to the difficulty to stabilize and to isolate them. The spectrum of $Cu(dmp)^+$ has previously been reported by Atkins et al. and is in excellent agreement with that obtain in this study.[38] It shows a dramatic hypochromic blue shift of the absorption maxima of band II with respect to the spectrum of $Cu(dmp)_2^+$ and the concomitant disappearance of the second z-polarized transition, band I. These spectroscopic features are very similar to those exhibited by two mixed copper(I) complexes $[Cu(phen)(PPh_3)_2]^+$ ($\lambda_{max} = 366$ nm, $\epsilon = 2800$ M^{-1} cm^{-1}) and $[Cu(dmp)(PPh_3)_2]^+$ ($\lambda_{max} = 365$ nm, $\epsilon = 2700$ M^{-1} cm^{-1}), where PPh_3 designates triphenylphosphine.[14,84] In the ground state, the monochelate complexes adopt a distorted tetrahedral geometry of approximate C_{2v} symmetry. Under this assumption, two z-polarized transitions are allowed: $b_1(xz) \rightarrow b_1(\psi)$ and $a_2(xy) \rightarrow a_2(\chi)$. The absorption maximum occurring at 360 nm for $Cu(dmp)^+$ is assigned to the $b_1(xz) \rightarrow b_1(\psi)$ excitation on the basis of the more efficient overlap of the copper(I) d_{xz} orbital with the LUMO of dmp.[78] As expected, the influence of aryl substituents on the MLCT band's energy and intensity is qualitatively the same for the mono- as for the bischelate complexes,[79] and results in a weak ($\epsilon \sim 300$ M^{-1} cm^{-1}) and almost flat absorption spectrum for $Cu(dap)^+$ which might arise in part from the intrinsically weak $a_2(xy) \rightarrow a_2(\chi)$ absorption.

Structural Effects on the Demetalation Kinetics. In the presence of cyanide, the four studied copper(I) bischelate complexes dissociate according to a single rate-limiting step mechanism which involves a bimolecular pathway first-order with respect to the nucleophile's concentration (k_{CN}) and a monomolecular, cyanide-independent path (k_D) as previously observed for related complexes.[23,41,42] The rate constants derived in the present study are compared in Table 3 with those obtained for $Cu(dmp)_2^+$ and $Cu(dap)_2^+$ under slightly different experimental conditions.[41] The solvent composition has a limited effect on the first-order rate constants k_D which is not unexpected considering that these values primarily reflect the thermodynamic stability of the complexes. However, for unsymmetrical complexes, the solvent-induced dissociation path is disfavored and becomes insignificant with respect to the cyanide-assisted path. In contrast, the data collected in the ternary solvent indicate a 2−3-fold enhanced reactivity of the cyanide anion toward the cationic complexes which is consistent with the lower permittivity of the reaction medium containing 15% dichloromethane compared to the acetonitrile/water mixture (90/10 v/v) and is qualitatively predicted by the theory of the activated complex.[85] Furthermore, the lower viscosity of dichloromethane favors the diffusion of the reactants.

The great sensitivity of the second-order rate constants to subtle variations in structural properties such as the compactness around the metal center,[23,41,42] is highlighted by the approximately 200-fold slower demetalation rate of $Cu(dap)_2^+$ relative to $Cu(dmp)_2^+$. This strong substituent effect has been attributed to an efficient shielding against cyanide provided by a tight packing of four bulky anisyl groups around an encapsulated copper(I) core.[41] The influence of a nonsymmetric ligand structure is evaluated by comparing the results obtained for $Cu(map)_2^+$, $Cu(Memap)_2^+$, and $Cu(dap)_2^+$. It may be expected that $Cu(dap)_2^+$ provides a more protective environment of the central copper(I) cation than $Cu(map)_2^+$ or $Cu(Memap)_2^+$ due to its compact structure. Replacement in $Cu(dap)_2^+$ of one anisyl substituent α to the nitrogen atoms by one methyl group increases the second-order cyanide-assisted demetalation rate constant by more than 3 orders of magnitude. As the steric hindrance of the nonaromatic substituent is further reduced, as in $Cu(map)_2^+$, the dissociation rates become too fast to be measured by stopped-flow technique, even under stoichiometric conditions. However, the fact that $Cu(Memap)_2^+$ dissociates 10 times more rapidly than the symmetrical and sterically less encumbered $Cu(dmp)_2^+$ complex is more surprising. This result clearly indicates that the metal center is more efficiently shielded by the ligands in $Cu(dmp)_2^+$ than in $Cu(map)_2^+$ and $Cu(Memap)_2^+$.

In agreement with the measurements carried out at equilibrium, the higher reactivity of the unsymmetrical compared to the symmetrical bischelate complexes toward the entering cyanide anions reflects the distortion of the coordination polyhedron induced by $\pi-\pi$ stacking interactions which create a steric anisotropy of the complex's topography. In absence of crystallographic data, the strong shielding of the anisyl proton resonances in the ^1H NMR spectra of $Cu(map)_2^+$ or $Cu(Memap)_2^+$ provides evidence for the overlap of the π-accepting phenanthroline core with the single π-donor anisyl substituent attached to the second phenanthroline core and vice versa. Similar effects assigned to $\pi-\pi$ interactions have previously been reported for $Cu(dap)_2^+$.[76] In addition, the deshielding of the methyl protons of $Cu(Memap)_2^+$ by ca. 0.2 ppm with respect to $Cu(dmp)_2^+$ further supports the idea of a distorted coordination polyhedron in $Cu(Memap)_2^+$ which deviates from the pseudo-tetrahedral geometry encountered in $Cu(dmp)_2^+$.

Thus, the molecular shape that emerges for $Cu(map)_2^+$ and $Cu(Memap)_2^+$ is an entwined structure where both ligands are tilted with respect to the pseudo C_2 axis, giving likely rise to two sets of unequal Cu−N distances.[86] The overlapping of the anisyl group of one ligand with the phenanthroline nucleus belonging to the second chelate obstructs a highly crowded pole which faces a widely open and thus accessible hemisphere oriented toward the hydrogen or the methyl substituents. This assumption is fully consistent with the X-ray structure of both coordination polyhedra described for a related dinuclear face-to-face complex.[86] Indeed, the similarities between the spectrophotometric and the kinetic properties of $Cu(Memap)_2^+$ and those corresponding to the dinuclear compound, suggest almost identical coordination geometries of the copper(I) cation in both complexes.[42]

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Supporting Information Available: Tables of the pseudo-first-order dissociation rate constants for $Cu(dmp)_2^+$, $Cu(Memap)_2^+$, and $Cu(dap)_2^+$. This material is available free of charge via the Internet at http://pubs.acs.org.

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