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Supramolecular Photochemistry and Photophysics. A [3]-Catenand and Its Mononuclear and Homo- and Heterodinuclear [3]-Catenates

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Abstract: The absorption, emission, and excitation spectra and the luminescence quantum yields and lifetimes of the emitting excited states of a [3]-catenand and some of its metal complexes ([3]-catenates) have been investigated. The [3]-catenand (**1**) is made of a central 44-membered ring, carrying two 1,10-phenanthroline units, interlocked with two 30-membered rings each of which carries a 1,10-phenanthroline unit. In CH_2Cl_2 solution at 298 K, **1** exhibits a strong fluorescence band (λ_{max} = 404 nm, τ = 2.4 ns, Φ = 0.33) which at 77 K is accompanied by a phosphorescence band (λ_{max} = 519 nm, τ = 0.8 s). In the dicopper(I) catenate, $Cu_2\cdot\mathbf{1}^{2+}$, the ligand centered (LC) fluorescence and phosphorescence bands are completely quenched and emission takes place from a metal-to-ligand charge-transfer (MLCT) excited state (298 K: λ_{max} = 735 nm, τ = 168 ns, $\Phi = 5.9 \times 10^{-4}$; 77 K: λ_{max} = 750 nm, τ = 1.4 μs). In the monocopper(I) species $Cu\cdot\mathbf{1}^{+}$, which contains a catenand-type and a catenate-type moieties, the LC fluorescence of the former moiety is strongly quenched (τ = 40 ps) by the presence of the latter. In the $Ag_2\cdot\mathbf{1}^{2+}$ catenate, the LC fluorescence cannot be observed, but a strong LC phosphorescence is present at 77 K (λ_{max} = 502 nm, τ = 17 ms). Investigations have also been made on three heterodinuclear [3]-catenates, whose synthesis is fully described. In the heterodimetallic $CuAg\cdot\mathbf{1}^{2+}$ catenate only the MLCT emission of the Cu^+-based moiety is present (298 K: λ_{max} = 735 nm, τ = 162 ns, $\Phi = 6.1 \times 10^{-4}$; 77 K: λ_{max} = 735 nm, τ = 1.8 μs). The $CuZn\cdot\mathbf{1}^{3+}$ catenate exhibits a weak and short-lived (90 ps) LC fluorescence from the Zn^{2+}-based moiety accompanied by the MLCT emission of the Cu^+-based one. For the $CuCo\cdot\mathbf{1}^{3+}$ catenate, no luminescence is observed, indicating that the potentially luminescent MLCT excited state of the Cu^+-based moiety is quenched by the Co^{2+}-based one. The quenching of the MLCT excited state of $Cu\cdot\mathbf{1}^{+}$, $Cu_2\cdot\mathbf{1}^{2+}$, $CuAg\cdot\mathbf{1}^{2+}$, and $CuZn\cdot\mathbf{1}^{3+}$ by oxygen and acetone has been investigated and photosensitization of singlet oxygen luminescence has been observed. The results obtained are discussed and compared with those previously reported for analogous [2]-catenates and knots.

Introduction

Interlocked macrocyclic species (*catenanes*)[2-4] are very interesting from a photochemical and photophysical viewpoint because of the properties which originate from the electronic interactions of the various subunits.[3-10] Catenanes that exhibit coordination ability (*catenands*)[3,11] can give rise to metal complexes (*catenates*) where the photochemical and photophysical properties are profoundly affected by the nature of the coordinated metal.[9]

The [3]-catenand **1** (Figure 1),[12-14] which is made of a central 44-membered ring interlocked with two 30-membered rings, contains four 2,9-diphenyl-1,10-phenanthroline chelating units. Therefore it can provide two tetrahedral-type coordination sites to metal ions. Mononuclear and dinuclear (homo- and heterometallic) complexes can thus be obtained with metal ions which like the tetrahedral coordination geometry (Figure 1).

We report here the results of an investigation on the absorption, emission, and excitation spectra and the quantum yields and lifetimes of the luminescent excited states of the free catenand **1** and the following catenates: monocopper(I), $Cu\cdot\mathbf{1}^{+}$; dicopper(I), $Cu_2\cdot\mathbf{1}^{2+}$; copper(I)silver(I), $CuAg\cdot\mathbf{1}^{2+}$; copper(I)zinc(II), $CuZn\cdot\mathbf{1}^{3+}$; copper(I)cobalt(II), $CuCo\cdot\mathbf{1}^{3+}$; and disilver(I), $Ag_2\cdot\mathbf{1}^{2+}$.[15] For the long-lived Cu(I)-based luminescent excited states, quenching by dioxygen and acetone has also been investigated. The results obtained are discussed and compared with those previously reported for mononuclear [2]-catenates[9] and knots.[16] The synthesis and characterization of the heterodinuclear [3]-catenates are also reported.

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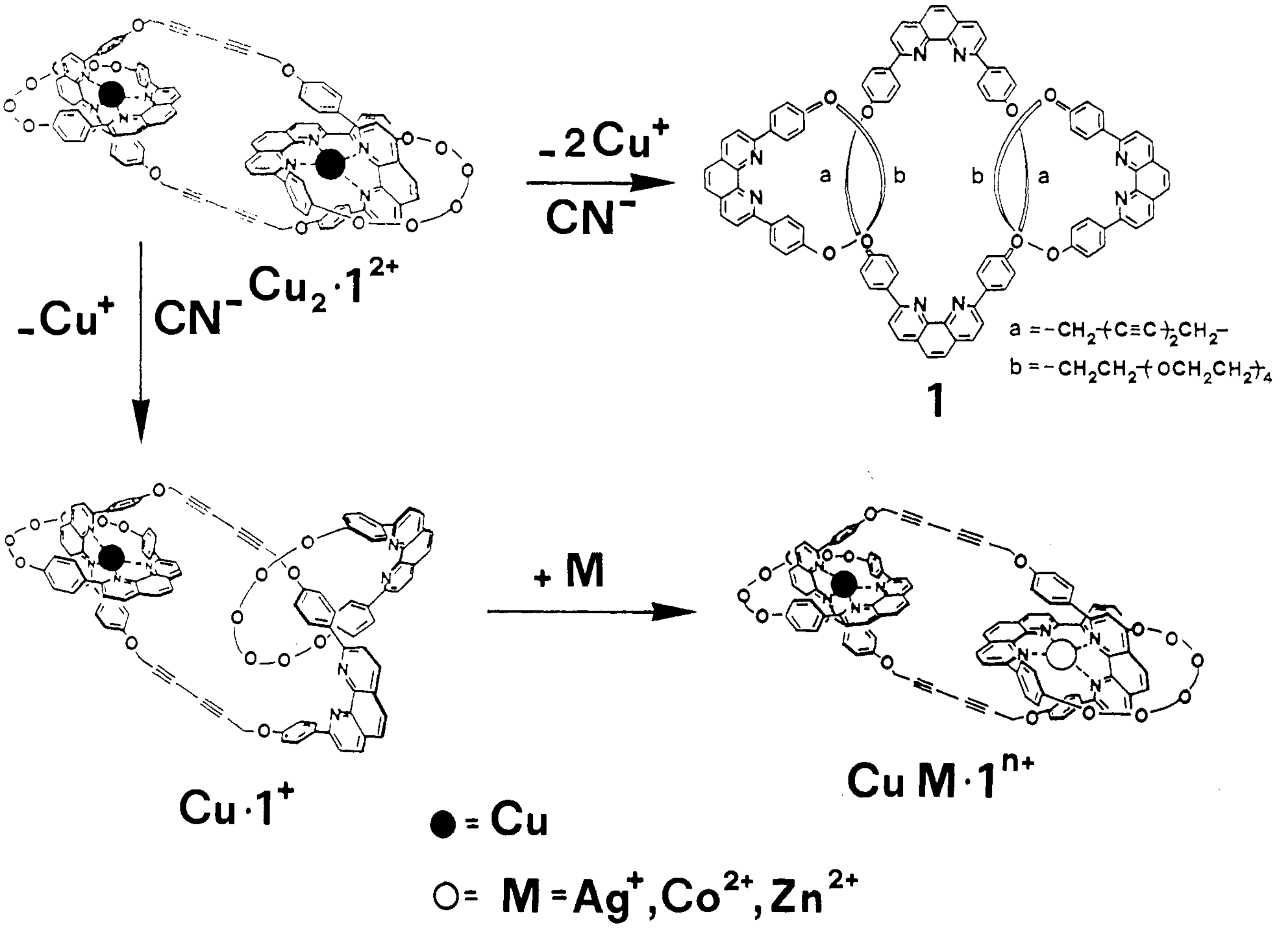

Figure 1. Schematic representation of the synthetic procedure leading from the homodinuclear $Cu_2\cdot 1^{2+}$ catenate to the [3]-catenand **1** and its mononuclear $Cu\cdot 1^+$ and heterodinuclear $CuM\cdot 1^{n+}$ metal complexes ($M = Ag^+, Co^{2+}, Zn^{2+}$). In the formulas of the catenates, the $-CH_2CH_2-$ units that separate the oxygen atoms of the small rings are not shown for the sake of simplicity.

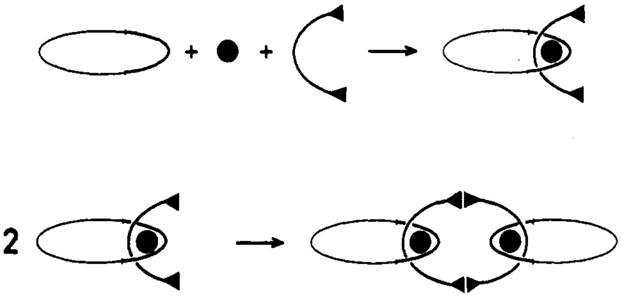

Figure 2. Scheme of the synthesis of a homodinuclear [3]-catenate by cyclodimerization of a difunctional precursor. The coordinating fragments are shown as thick lines. The circles represent the templating transition metals. The terminal functional groups to be coupled (terminal acetylenes in the present system) are indicated by black triangles.

Experimental Section

Materials. The free catenand **1** and the catenates $Cu_2\cdot 1^{2+}$ and $Ag_2\cdot 1^{2+}$ were synthesized according to literature method.[12-14] The synthetic principle to obtain $Cu_2\cdot 1^{2+}$ is illustrated by the scheme shown in Figure 2. $Ag_2\cdot 1^{2+}$ was prepared from the free ligand and $AgBF_4$. Figure 1 schematizes the way in which the other compounds have been obtained. All other chemicals were of the best commercially available grade and were used without further purification. ^1H NMR spectra were recorded with a Bruker WP 200 SY spectrometer. All compounds based on diphenylphenanthroline show a highly characteristic pattern: a singlet for H_5 and H_6, an AB pattern for H_3 or H_8 and H_4 or H_7 (coupling constant $J \approx 8.5$ Hz) and an AA'XX' system ($J \approx 8.7$ Hz) for H_o and H_m. H' designates the protons belonging to the central 44-membered macrocycle. H designates the protons belonging to the small 30-membered rings. Mass spectra were recorded on a ZAB-HF spectrometer (FAB). Melting points were measured with a Büchi SMP-20 apparatus.

Preparation of $Cu\cdot 1^+$, $CuAg\cdot 1^{2+}$, and $CuCo\cdot 1^{3+}$ was briefly described in a previous communication.[13b]

$Cu\cdot 1^+$. KCN (95 mg, 1.45 mmol) dissolved in 20 mL of H_2O was added at room temperature to a stirred solution of $Cu_2\cdot 1^{2+}$ (840 mg, 0.364 mmol) in 200 mL of CH_2Cl_2. The strictly controlled demetalation reaction was monitored by TLC (SiO_2, Kieselgel 60, 10% MeOH in CH_2Cl_2). After 3.5 h under stirring, no further evolution of the reaction was observed by TLC. After decantation, the aqueous layer was extracted twice with 40-mL portions of CH_2Cl_2. Combined organic layers, washed with three 100-mL portions of H_2O, were dried over $MgSO_4$, filtrated, and evaporated to dryness: crude $Cu\cdot 1^+$ was thus obtained quantitatively (785 mg) as a dark red solid. Column chromatography on silica gel (eluent CH_2Cl_2/hexane, 50:50) gave 370 mg of pure $Cu\cdot 1^+$ (47% yield, CH_2Cl_2 containing 1.2–2.5% MeOH).

$Cu\cdot 1^+$: dark red crystals (mp: 222–223 °C); ^1H NMR (CD_2Cl_2), the established nomenclature for the other compounds cannot be applied in the case of the monocopper complex. H^f designates the protons involved in the free moiety and H^c the protons involved in the copper complexes moiety: 8.56 to 7.56 (d and m, 24H, $H^c_{4,7}$, H^f_o, $H^f_{4,7}$, $H^f_{3,8}$, and $H^c_{3,8}$); 8.18 (s, 4H, $H^c_{5,6}$); 7.77 (s, 4H, $H^f_{5,6}$); 7.75 and 7,64 (d, 8H, H^c_o); 7.35 and 7.07 (d, 8H, H^f_m); 6.07 (d, 4H, H^c_m); 5.79 (d, 4H, H^c_m); 5.08 (s, 4H, $H^f_{CH-C\equiv C}$); 4.55 (s, 4H, $H^c_{CH-C\equiv C}$); 4.16 (t, 4H, H^f_α); 3.83–3.41 (m, 36H, $H^f_{\beta,\gamma,\delta,\epsilon}$ and $H^c_{\alpha,\beta,\gamma,\delta,\epsilon}$); MS calcd 2074.7, found 2074.6. Anal. Calcd for $C_{128}H_{104}N_8O_{16}CuBF_4CH_2Cl_2$: C, 69.46; H, 4.80; N, 4.98. Found: C, 69.50; H, 4.83; N, 5.00.

$CuAg\cdot 1^{2+}$. By the double-ended needle transfer technique, 15 mg (0.076 mmol) of $AgBF_4$ in degassed toluene (15 mL) were added under argon at room temperature to a stirred degassed solution of $Cu\cdot 1^+$ (150 mg,

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0.069 mmol) in CH_2Cl_2 (60 mL). The reaction was monitored by TLC (SiO_2, Kieselgel 60, 10% MeOH in CH_2Cl_2). After the solution was stirred for 1 h under argon at room temperature, the solvents were evaporated to dryness. The dry residue was taken up in 50 mL of CH_2Cl_2 and 50 mL of H_2O. The aqueous layer was extracted twice with 50-mL portions of CH_2Cl_2; combined organic layers were dried over $MgSO_4$, filtered, and evaporated to dryness: crude $CuAg\cdot\mathbf{1}^{2+}$ was thus obtained (150 mg) as a dark red solid. Column chromatography on silica gel (eluent CH_2Cl_2/hexane, 50:50) gave 138 mg of pure $CuAg\cdot\mathbf{1}^{2+}$ (85% yield, CH_2Cl_2 containing 1.7–2% MeOH).

$CuAg\cdot\mathbf{1}^{2+}$: dark red crystals (mp 200 °C, dec); ^1H NMR (CD_2Cl_2) protons involved in the silver complexed moiety: 8.70 (d, 2H, $H'_{4,7}$); 8.51 (d, 2H, $H_{4,7}$); 8.12 (s, 2H, $H'_{5,6}$); 8.11 (s, 2H, $H_{5,6}$); 7.92 (d, 2H, $H'_{3,8}$); 7.82 (d, 2H, $H_{3,8}$); 7.42 (d, 4H, H'_o); 7.30 (d, 4H, H_o); 6.18 (d, 4H, H'_m); 6.04 (d, 4H, H_m); 4.51 (s, 4H, $H_{CH_2\text{-}C\equiv C}$); 3.74 (s, 4H, H_e); 3.81 to 3.02 (m, 16H, $H_{\alpha,\beta,\gamma,\delta}$); protons involved in the copper complexed moiety: 8.60 (d, 2H, $H'_{4,7}$); 8.57 (d, 2H, $H_{4,7}$); 8.19 (s, 2H, $H'_{5,6}$); 8.17 (s, 2H, $H_{5,6}$); 7.76 (d, 2H, $H'_{3,8}$); 7.68 (d, 2H, $H_{3,8}$); 7.16 (d, 4H, H'_o); 7.09 (d, 4H, H_o); 5.83 (d, 4H, H'_m); 5.76 (d, 4H, H_m); 4.57 (s, 4H, $H_{CH_2\text{-}C\equiv C}$); 3.79 (s, 4H, H_e); 3.81 to 3.02 (m, 16H, $H_{\alpha,\beta,\gamma,\delta}$). MS calcd 2268.5, found 2268.1. Anal. Calcd for $C_{128}H_{104}N_8O_{16}CuAgB_2F_8$: C, 65.27; H, 4.45; N, 4.76. Found C, 65.38: H, 4.53; N, 4.50.

$CuCo\cdot\mathbf{1}^{3+}$. It was prepared by a procedure similar to that described for $CuAg\cdot\mathbf{1}^{2+}$. $Co(BF_4)_2\cdot 6H_2O$ (11 mg, 0.032 mmol) in 10 mL of MeOH was added to 50 mg (0.023 mmol) of $Cu\cdot\mathbf{1}^+$ in 50 mL of CH_2Cl_2. After 12 h stirring under argon at room temperature, the solvents were evaporated to dryness: crude $CuCo\cdot\mathbf{1}^{3+}$ was thus obtained quantitatively (53 mg) as a brown red solid. The dry residue was taken up in 10 mL of CH_2Cl_2, and 50 mL of EtOH was then slowly added to this solution: a brown red solid began to precipitate. After standing 48 h in the dark, crude $CuCo\cdot\mathbf{1}^{3+}$ was filtered and dried in vacuum: yield 36 mg (65%).

$CuCo\cdot\mathbf{1}^{3+}$: brown red crystals (mp 226 °C, dec); MS calcd 2219.6, found 2219.7. Anal. Calcd for $C_{128}H_{104}N_8O_{16}CuCoB_3F_{12}$: C, 64.24; H, 4.38; N, 4.68. Found C, 64.45: H, 4.37; N, 4.62.

$CuZn\cdot\mathbf{1}^{3+}$. This compound was prepared in the same way as $CuCo\cdot\mathbf{1}^{3+}$ from 60 mg (0.0398 mmol) of $[Cu\cdot\mathbf{1}]BF_4$ and 11.3 mg of $Zn(ClO_4)_2\cdot 6H_2O$ (0.044 mmol) in 80 mL of CH_2Cl_2–CH_3OH (15:1 v/v).

After anion exchange using $NaBF_4$ and precipitation of the complex using CH_2Cl_2 and ethanol, a low yield of $CuZn\cdot\mathbf{1}^{3+}$ was obtained (red solid; mp = 179–181 °C dec).

Absorption and Luminescence Measurements. The solvent used was CH_2Cl_2 (Merck, pro analysi). Since the 2,9-dianisyl-1,10-phenanthroline units of **1** have a strong affinity for protons,[17] and acid impurities are sometimes present in CH_2Cl_2, small amounts of 1,5-diazabicyclo[4.3.0]-non-5-ene (DBN) base were added when necessary. Acetone was a Merck Uvasol product. Absorption spectra were recorded with a Perkin-Elmer λ6 spectrophotometer using cells with 1-cm path. Corrected emission and excitation spectra and phosphorescence lifetimes (second time scale) were obtained with a Perkin-Elmer LS 50 spectrofluorimeter. Luminescence quantum yields were measured with a Perkin-Elmer 650–40 spectrofluorimeter by using the method described by Demas and Crosby[18] (standards used: anthracene in cyclohexane, $\Phi = 0.34$;[19] quinine sulfate in H_2SO_4 0.1 N, $\Phi = 0.52$;[20] $[Ru(bpy)_3]Cl_2$ in water, $\Phi = 0.028$;[21] $Os(bpy)_3{}^{2+}$ in CH_3CN $\Phi = 0.005$[22]). An Edinburgh single photon counting apparatus was used to obtain luminescence lifetimes (nano- and microsecond time scale). Single-exponential decays were observed in all cases.

Picosecond fluorescence lifetimes were detected with an apparatus based on a mode-locked, cavity-dumped Nd:YAG laser (Continuum PY62-10) and a streak camera (Hamamatsu C1587) equipped with a fast single sweep unit (M1952). The third harmonic (λ = 355 nm), with an energy of 5 mJ/pulse and a pulse duration of 35 ps at 10 Hz, was used to excite the samples. The light emitted was collected and fed into the entrance of a spectrograph (HR 250 Jobin-Yvon) and then focussed on the slit of the streak camera. Acquisition and processing of the streak images were performed via cooled CCD camera (Hamamatsu C3140) and related software running on a PC. Typical images were the average of 20–50 events. Data of emission intensity *vs* time over 20 nm around the maximum were averaged. The analysis of such profiles was performed with standard iterative nonlinear procedures. Time resolution of the system is 30 ps.

Estimated errors are as follows: band maxima, ±2 nm; quantum yields, ±20%; lifetimes, ±20%.

The steady-state infrared luminescence of singlet oxygen was measured with a constructed in-house apparatus consisting of an Ar ion laser, which excited the sample held in a 10 mm × 10 mm cuvette. A beam chopper (Standford Research Systems, Inc. Model SR540) was placed between the excitation source and the sample cuvette; luminescence was monitored at right angles to the excitation. After the light passed through cut-off and order-blocking filters, it crossed a monochromator (Edinburgh Instruments Ltd., computer controllable) with a grating of 1200 L/mm, 1-mμ blaze. The detector was a liquid-nitrogen-cooled germanium detector and preamplifier (Northcoast Scientific Corp. Model EO-817L). A Northcoast muon filter (Model 829B) was used as an electronic signal filter, after the signal was sent to a lock-in amplifier (Standford Research Systems, Inc. Model SR510). The system was interfaced to a data station consisting of an IBM compatible personal computer and a Hewlett-Packard plotter.

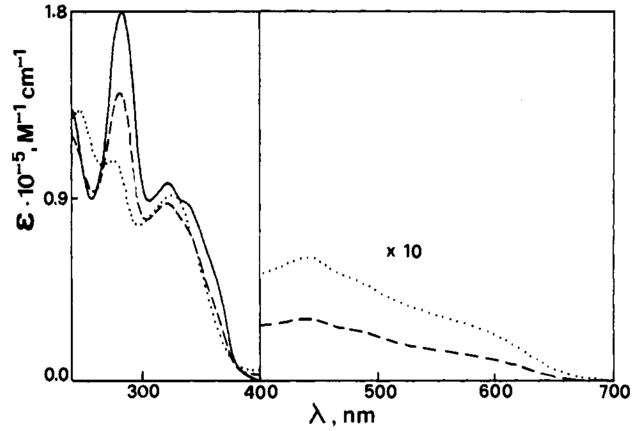

Figure 3. Absorption spectra in CH_2Cl_2 solution of **1** (—), $Cu\cdot\mathbf{1}^+$ (– –), and $Cu_2\cdot\mathbf{1}^{2+}$ (···).

Results and Discussion

Absorption Spectra. The absorption spectra of **1**, $Cu\cdot\mathbf{1}^+$, and $Cu_2\cdot\mathbf{1}^{2+}$ are shown in Figure. 3, and those of $CuZn\cdot\mathbf{1}^{3+}$ and $Ag_2\cdot\mathbf{1}^{2+}$ are displayed in Figure 4. The absorption spectrum of $CuCo\cdot\mathbf{1}^{3+}$ is very similar to that of $CuZn\cdot\mathbf{1}^{3+}$, and that of $CuAg\cdot\mathbf{1}^{2+}$ is very similar to that of $Cu_2\cdot\mathbf{1}^{2+}$, except for the intensity of the visible band which is 50% weaker.

In the UV region, **1** displays the characteristic $\pi \rightarrow \pi^*$ bands of 2,9-dianisyl-1,10-phenanthroline (dap).[17] Because **1** is highly insoluble in all solvents, its molar absorption coefficient was taken to be twice that of 2-cat,[17] whose molar absorption coefficient is twice that of dap.[9] Metal coordination causes noticeable and specific perturbations in the relative intensity of the ligand-centered (LC) bands, as already found for [2]-catenates[9] and knots.[16] In particular, metal coordination causes a strong decrease in intensity of the band with maximum at ~285 nm (Figure 3). For $Cu\cdot\mathbf{1}^+$ and $Cu_2\cdot\mathbf{1}^{2+}$, metal-to-ligand charge-transfer (MLCT) bands are present in the visible region, as is generally the case for Cu(I) complexes of phenanthroline-type ligands.[7,23–27] The visible spectrum of $Cu\cdot\mathbf{1}^+$ is almost identical to that of $Cu(2\text{-}cat)^+$,[9] and that of $Cu_2\cdot\mathbf{1}^{2+}$ is twice as intense as that of $Cu\cdot\mathbf{1}^+$, indicating that the two Cu(I)-based units of the dinuclear catenate do not appreciably affect each other.

The absorption spectra of $CuAg\cdot\mathbf{1}^{2+}$ and $Ag_2\cdot\mathbf{1}^{2+}$ show that the Ag(I)-based moieties do not absorb in the visible region, as is also

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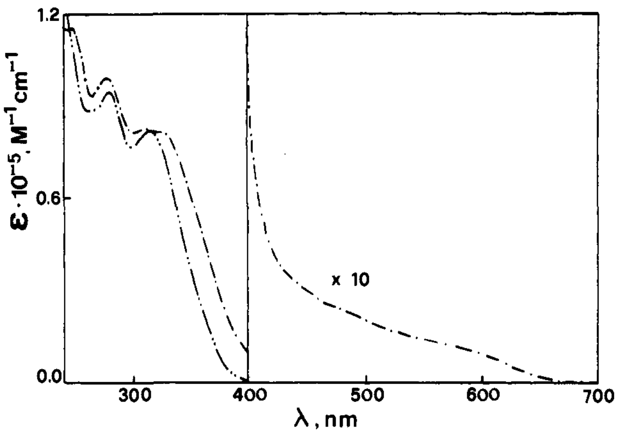

Figure 4. Absorption spectra in CH_2Cl_2 solution of $CuZn\cdot\mathbf{1}^{3+}$ (– • • –) and $Ag_2\cdot\mathbf{1}^{2+}$ (•• – ••).

Table 1. Luminescence Properties in Deaerated CH_2Cl_2 at Room Temperature

	^{1}LC[a]			MLCT[b]		
	λ_{max}[c] (nm)	τ (ns)	Φ_{em}[c]	λ_{max}[d] (nm)	τ[e] (ns)	Φ_{em}[d] × 10^4
1	404	2.4[e]	0.33			
$Cu\cdot\mathbf{1}^{+}$	399	0.040[f,g]	~0.01[h]	720	210	11.0
$Cu_2\cdot\mathbf{1}^{2+}$				735	168	5.9
$CuAg\cdot\mathbf{1}^{2+}$				735	162	6.1
$CuZn\cdot\mathbf{1}^{3+}$	457	0.090[f]	0.0068	725	163	[i]
$CuCo\cdot\mathbf{1}^{3+}$						
$Ag_2\cdot\mathbf{1}^{2+}$						

[a] Ligand centered fluorescence. [b] Luminescence from the lowest MLCT excited state. [c] Excitation at 320 nm. [d] Excitation at 500 nm. [e] Excitation at 337 nm. [f] Excitation at 355 nm. [g] A longer lived component (2.4 ns), attributed to some 3-cat impurities, is also observed. [h] Including some contribution from 3-cat impurities. [i] Impossible to evaluate because the MLCT emission overlaps with a higher energy luminescence band (see text).

the case for $Ag(2\text{-cat})^+$.[9] This result is related to the much higher oxidation potential of Ag(I) compared to Cu(I), and the consequent displacement of the MLCT transitions to higher energy. In the $CuZn\cdot\mathbf{1}^{3+}$ and $CuCo\cdot\mathbf{1}^{3+}$ catenates, the M(II) moiety contributes to the visible absorption with an intense tail of the LC band (Figure 4). For the Co(II)-based moiety, MLCT or LMCT bands might also contribute to the absorption around 450–500 nm, as it seems to be the case for $Co(2\text{-cat})^{2+}$.[9] Cu(I), Ag(I), and Zn(II) complexes, because of their d^{10} electronic configuration, do not exhibit low energy metal centered (MC) transition. This is not the case, however, for Co(II) complexes (d^7 electronic configuration), whose intraconfigurational d → d excited states may lie as low as ~8000 cm^{-1}.[28] The molar absorption coefficients of the corresponding bands, however, are too low to be observed under the dilution conditions used.

In general, comparison with the absorption spectra of the corresponding [2]-catenates,[9] which can be considered as mononuclear model compounds, shows that the absorption spectra of the dinuclear [3]-catenates are practically given by the summation of the spectra of the two component moieties.

Luminescence Properties and Intercomponent Quenching Processes. The luminescence data are collected in Tables 1 and 2. The emission spectra in CH_2Cl_2 solution at 298 K of **1**, $Cu_2\cdot\mathbf{1}^{2+}$, $Cu\cdot\mathbf{1}^{+}$, and $CuZn\cdot\mathbf{1}^{3+}$ are displayed in Figure 5. The spectrum of $CuAg\cdot\mathbf{1}^{2+}$ is substantially similar to that of $Cu_2\cdot\mathbf{1}^{2+}$. $CuCo\cdot\mathbf{1}^{3+}$ and $Ag_2\cdot\mathbf{1}^{2+}$ do not emit under these experimental conditions. Figure 6 shows the luminescence bands observed in rigid matrix at 77 K for **1**, $Cu\cdot\mathbf{1}^{+}$, $Ag_2\cdot\mathbf{1}^{2+}$, and $Cu_2\cdot\mathbf{1}^{2+}$. The spectra of $CuZn\cdot\mathbf{1}^{3+}$ and $CuAg\cdot\mathbf{1}^{2+}$ are similar to that of $Cu_2\cdot\mathbf{1}^{2+}$, whereas $CuCo\cdot\mathbf{1}^{3+}$ does not show any emission.

Table 2. Luminescence Properties in CH_2Cl_2 at 77 K

	^{1}LC[a]		^{3}LC[b]		MLCT[c]	
	λ_{max}[d] (nm)	τ[e] (ns)	λ_{max}[d] (nm)	τ[d] (s)	λ_{max}[f] (nm)	τ[e] (μs)
1	382	2.6	519	0.8		
$Cu\cdot\mathbf{1}^{+}$	378	[g]	[h]		715	1.9
$Cu_2\cdot\mathbf{1}^{2+}$					750	1.4
$CuAg\cdot\mathbf{1}^{2+}$					735	1.8
$CuZn\cdot\mathbf{1}^{3+}$					730	1.7
$CuCo\cdot\mathbf{1}^{3+}$						
$Ag_2\cdot\mathbf{1}^{2+}$			502	0.017		

[a] Ligand centered fluorescence. [b] Ligand centered phosphorescence. [c] Luminescence from the lowest MLCT excited state. [d] Excitation at 320 nm. [e] Excitation at 337 nm. [f] Excitation at 500 nm. [g] No reliable data were obtained with the picosecond laser apparatus because of the light scattered by the nontransparent CH_2Cl_2 matrix. [h] Only a weak emission, due to impurities of **1**, was observed.

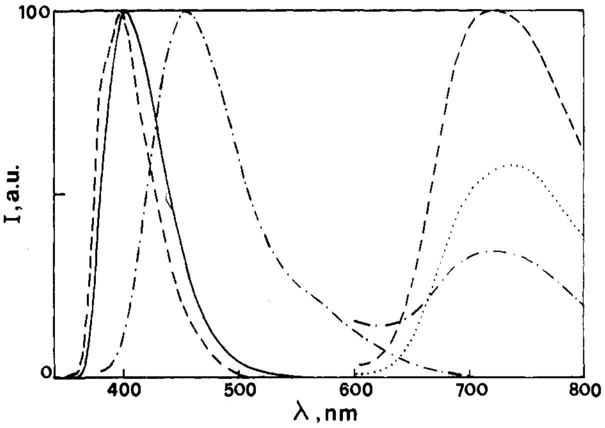

Figure 5. Emission spectra in CH_2Cl_2 solution at 298 K of **1** (—), $Cu\cdot\mathbf{1}^{+}$ (– –), $Cu_2\cdot\mathbf{1}^{2+}$ (•••), and $CuZn\cdot\mathbf{1}^{3+}$ (– • • –). The normalized ^{1}LC emission in the 350–500-nm spectral region has been obtained by exciting at 320 nm. The MLCT bands around 700 nm, obtained by exciting at 440 nm, are much weaker (see the quantum yields in Table 1).

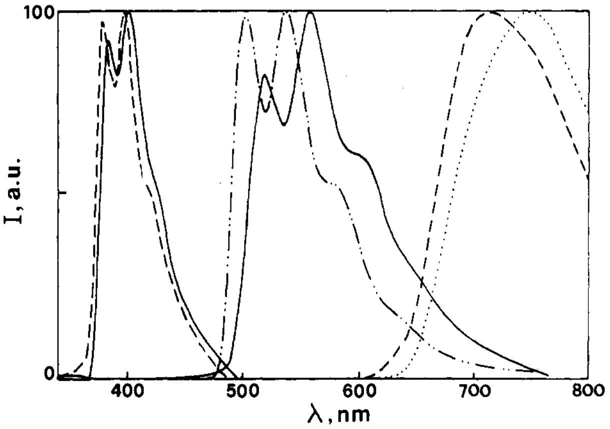

Figure 6. Normalized emission spectra in CH_2Cl_2 rigid matrix at 77 K of **1** (—), $Cu\cdot\mathbf{1}^{+}$ (– –), $Cu_2\cdot\mathbf{1}^{2+}$ (•••), and $Ag_2\cdot\mathbf{1}^{2+}$ (•• – ••).

The very intense band exhibited by **1** is the characteristic fluorescence of the dap unit (λ_{max} = 396 nm, τ = 2.2 ns, Φ = 0.29),[17] but it lacks a shoulder on the high-energy side, which could suggest some small interaction between the chromophoric units, in agreement with the results of NMR investigations carried out on a related [3]-catenand.[29] On passing to rigid matrix at 77 K (Figure 6) the fluorescence moves slightly toward higher energies (λ_{max} = 382 nm) because of its partial charge transfer character.[17] Under such experimental conditions, a phosphorescence band is also present in the visible region.

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(28) Jorgensen, C. K. Adv. *Chem. Phys.* **1963**, *5*, 33.

(29) Guilhem, J.; Pascard, C.; Sauvage, J.-P.; Weiss, J. *J. Am. Chem. Soc.* **1988**, *110*, 8711.

In the $\mathrm{Cu}_2\cdot\mathbf{1}^{2+}$ catenate, the four dap units are coordinated to the metal ions forming two Cu(I) complexes where the lowest excited state is a metal-to-ligand charge-transfer (MLCT) level.[24,26,30,31] As a consequence, fluorescence and phosphorescence of the dap ligands can no longer be observed, and a characteristic MLCT emission appears (Figures 5 and 6) which is similar to that found for $\mathrm{Cu(2\text{-}cat)}^+$ (298 K: $\lambda_{max} = 730$ nm, $\tau = 175$ ns, $\Phi = 1.1 \times 10^{-3}$).[9]

As schematically shown in Figure 1, in the mononuclear $\mathrm{Cu}\cdot\mathbf{1}^+$ species two dap units are engaged in metal coordination whereas the other two dap units are free. This compound can thus be considered as made of a catenand and catenate moieties. In the absence of intercomponent interaction, one would therefore expect to observe the LC fluorescence and phosphorescence of the two noncoordinated dap units, as it happens for **1**, as well as a MLCT luminescence like that observed for $\mathrm{Cu}_2\cdot\mathbf{1}^{2+}$. Excitation in the MLCT band at 500 nm gives rise to a MLCT luminescence similar, but not identical, to the MLCT emission of $\mathrm{Cu}_2\cdot\mathbf{1}^{2+}$ (Table 1). This suggests that the coordination geometry of the Cu^+ ion can be slightly different in the two species. Excitation in the LC band at 320 nm gives rise to a fluorescence band which is slightly blue-shifted compared to that of **1** (Tables 1 and 2). This indicates an interaction between the catenand and catenate moieties. Most important, the fluorescence lifetime decreases from 2.4 ns to 40 ps in passing from **1** to $\mathrm{Cu}\cdot\mathbf{1}^+$, and this decrease is accompanied by an almost parallel decrease in the fluorescence quantum yield (Table 1). These results show that the ^{1}LC level of the catenand moiety is quenched by the presence of the catenate moiety. The rate constant of the quenching process (2.5×10^{10} s^{-1}) can be obtained from eq 1, where τ and τ° are the fluorescence lifetimes of $\mathrm{Cu}\cdot\mathbf{1}^+$ and **1**, respectively:[32]

$$k_q = 1/\tau - 1/\tau^\circ \tag{1}$$

The quenching process can occur by either energy or electron transfer. In the excitation spectrum of the MLCT emission of $\mathrm{Cu}\cdot\mathbf{1}^+$ most of the contribution from the catenand moiety is lacking, indicating that energy transfer is not the predominant quenching mechanism. In fact, a quenching mechanism involving the transfer of an electron from the Cu^+ ion of the catenate moiety to the excited ligand centered level of the catenand moiety seems most likely in view of the high energy (>3 eV) of the ^{1}LC level, the reduction potential of dap (–2.1 V),[8] and the oxidation potential of the Cu-catenate moiety ($\mathrm{Cu}^{2+/+} = +0.57$ V).[13b]

The $\mathrm{Ag}_2\cdot\mathbf{1}^{2+}$ catenate does not show any emission at room temperature. The d^{10} Ag^+ ion does not possess any low-energy MC excited state and is not expected to give rise to low-energy MLCT levels. Being a heavy metal ion, however, Ag^+ is expected to promote intersystem crossing in the ligand centered manifold. In fact, the disappearance of the fluorescence band is accompanied by the appearance of a very intense, relatively short-lived phosphorescence at 77 K (Table 2). This behavior is exactly the same as that previously found for $\mathrm{Ag(2\text{-}cat)}^+$ ($\lambda_{max} = 498$ nm, $\tau = 0.012$ s).[9]

The mixed-metal $\mathrm{CuAg}\cdot\mathbf{1}^{2+}$ catenate shows only the MLCT emission of the Cu-based moiety both at room temperature and at 77 K, regardless of the excitation wavelength. This shows that the ^{1}LC and ^{3}LC levels of the Ag-based moiety populated upon 320-nm excitation are deactivated by the neighboring Cu-based moiety. In this case deactivation takes place by energy transfer since the excitation spectrum of the MLCT emission is practically coincident with the absorption spectrum throughout the entire spectral region. The rate constant of the process could not be measured lacking any reliable ^{1}LC or ^{3}LC luminescence from the Ag-based moiety.[33]

The $\mathrm{CuZn}\cdot\mathbf{1}^{3+}$ catenate contains again two different moieties. A good model for the Zn-based one is the $\mathrm{Zn(2\text{-}cat)}^{2+}$, which exhibits a strongly perturbed LC emission (298 K: $\lambda_{max} = 463$ nm, $\tau = 2.0$ ns, $\Phi = 0.082$; 77 K: $\lambda_{max} = 433$ nm; $\tau = 5.0$ ns; $\lambda_{max} = 495$ nm, $\tau = 0.78$ s)[9]. Upon 320-nm excitation at room temperature $\mathrm{CuZn}\cdot\mathbf{1}^{3+}$ exhibits a fluorescence band at 457 nm. Its lifetime and quantum yield, however, are 90 ps and 6.8×10^{-3}, respectively. This shows that the Zn^{2+}-based moiety is quenched by the Cu^+-based one with rate constant (eq 1) 1.1×10^{10} s^{-1} at room temperature. At 77 K the fluorescence of the Zn^{2+}-based moiety is completely quenched, within the experimental uncertainties caused by opaque $\mathrm{CH_2Cl_2}$ matrix. The MLCT emission of the Cu^+-based moiety can clearly be seen at 77 K, regardless of the excitation wavelength (320 or 500 nm). At room temperature, however, when excitation is performed below 500 nm, MLCT emission is hidden by a broad band with maximum at about 560 nm, whose tail extends up to the region of the expected MLCT emission. The origin of this broad band is not clear. An obvious explanation would be the presence of an impurity. However, such an emission is not present in any of the other compounds examined (including $\mathrm{Zn(2\text{-}cat)}^{2+}$) and cannot be observed at 77 K. Another possible explanation can be based on a CT interaction (in the ground and excited state) between the electron acceptor phen units coordinated to Zn^{2+}, strongly perturbed by the divalent ion,[9] and the electron donor anisyl groups belonging to the Cu^+-based moiety. The X-ray structure of $\mathrm{Cu}_2\cdot\mathbf{1}^{2+}$ shows, in fact, that the geometry of the dinuclear [3]-catenates is much more packed compared to that implied by the schematic representation shown in Figure 1.[34] Such a CT excited state could play a role in the quenching of the ^{1}LC fluorescence in $\mathrm{CuZn}\cdot\mathbf{1}^{3+}$.

The $\mathrm{CuCo}\cdot\mathbf{1}^{3+}$ catenate does not exhibit any luminescence under any condition. This means that the potentially luminescent MLCT level of the Cu^+-based moiety is quenched by the Co^{2+}-based one. A lower limit of 6.0×10^8 s^{-1} can be obtained from the equation

$$k_q = (1/\tau^0)\left(\frac{I^0}{I} - 1\right) \tag{2}$$

taking I^0 and τ^0 as the luminescence intensity and lifetime of $\mathrm{Cu}_2\cdot\mathbf{1}^{2+}$, and considering that the luminescence intensity I of $\mathrm{CuCo}\cdot\mathbf{1}$ is at least 100 times less than that of $\mathrm{Cu}_2\cdot\mathbf{1}^{2+}$. A possible quenching mechanism is energy transfer since the d^7 Co^{2+} metal ion has very low-energy levels (<10 000 cm^{-1}).[28] No emission can be expected for the Co^{2+}-based moiety, according to the behavior of the $\mathrm{Co(2\text{-}cat)}^{2+}$ model compound.[9] The quenching of the Cu^+-based moiety by the Co^{2+}-based one could also occur by electron transfer ($-\Delta G^\circ \sim 0.54$ eV).[35] Since no electron-transfer quenching takes place in $\mathrm{CuAg}\cdot\mathbf{1}^+$, where the process would involve practically the same free energy change,[36] an energy-transfer quenching mechanism in $\mathrm{CuCo}\cdot\mathbf{1}^{3+}$ seems more likely. We can also notice that electron-transfer quenching of the Cu^+-based excited state by the Zn^{2+}-based moiety is slightly exoergonic ($-\Delta G^\circ \sim 0.05$ eV),[37] but apparently it does not occur.

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(30) Parker, W. L.; Crosby, G. A. *J. Phys. Chem.* **1989**, *93*, 5692.

(31) Gordon, K. C.; McGarvey, J. J. *Inorg. Chem.* **1991**, *30*, 2986.

(32) When the picosecond equipment was not available, the ^{1}LC lifetime in $\mathrm{Cu}\cdot\mathbf{1}^+$ was reported to be 2.4 ns as in **1**.[15] Such a value is that corresponding to a small amount of **1** contained as an impurity in $\mathrm{Cu}\cdot\mathbf{1}^+$.

(33) Luminescence signals due to very small amounts of the strongly emitting free catenand **1** (Table 1) are present in all the samples used.

(34) Dietrich-Buchecker, C. O.; Guilhem, J.; Khemiss, A. K.; Kintzniger, J.-P.; Pascard, C.; Sauvage, J.-P. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 661.

(35) Evaluated from the approximate equation:

$$-\Delta G^\circ \approx \Delta E^{\circ\circ} - E'(\mathrm{Cu}^{2+/+}) + E'(\mathrm{Co}^{2+/+})$$

where $\Delta E^{\circ\circ} = 1.69$ eV (from the maximum of the 77 K emission) and $E'(\mathrm{Cu}^{2+/+})$ and $E'(\mathrm{Co}^{2+/+})$ are the energies for the one-electron reduction processes ($E_{1/2}(\mathrm{Cu}^{2+/+}) = +0.79$ V, $E_{1/2}(\mathrm{Co}^{2+/+}) = -0.36$V).

(36) See equation in footnote 35, with $E_{1/2}(\mathrm{Cu}^{2+/+}) = +0.67$ V and $E_{1/2}(\mathrm{Ag}^{+/o}) = -0.48$ V.[13b]

(37) See equation in footnote 35, with $E_{1/2}(\mathrm{Cu}^{2+/+}) = +0.67$ V (taken from the oxidation of $\mathrm{Cu}_2\cdot\mathbf{1}^+$)[13b] and $E_{1/2}(\mathrm{Zn}^{2+/+}) = -0.97$ V (taken from the reduction of $\mathrm{Zn}_2\cdot\mathbf{1}^{4+}$).[13c]

Table 3. Spectroscopic Energies, Oxidation Potentials, and Quenching Rate Constants of the MLCT Excited State of Cu(I) Compounds[a]

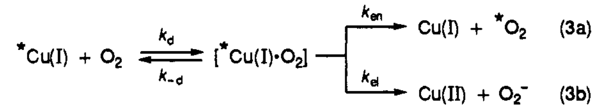
	*Cu(I)		dioxygen quenching	acetone quenching
	E^{oo} [b] (eV)	$E(^*Cu+/Cu^{2+})$ [c] (V)	$k_q[O_2]$ [d] $\times 10^{-6}$ (s^{-1})	k_q [e] $\times 10^{-5}$ (s^{-1} M^{-1})
$Cu(dmp)_2^+$	1.65	0.97	6.7	32.0
$Cu(dtp)_2^+$	1.72	1.03	3.0	13.0
$Cu(2\text{-cat})^+$	1.70	1.13	2.4	11.0
$Cu \cdot \mathbf{1}^+$	1.72	1.15	1.8	11.0
$Cu_2 \cdot \mathbf{1}^{2+}$	1.68	1.01	1.6	1.0
$CuAg \cdot \mathbf{1}^{2+}$	1.68	1.01	1.1	2.0
$CuZn \cdot \mathbf{1}^{3+}$	1.71	0.99	1.9	8.0
$Cu_2(m\text{-}43)_2^{2+}$	1.66	1.11	2.0[f]	2.0[f]
$Cu_2(knot\text{-}86)^{2+}$	1.65	1.04	2.1[f]	<0.3[f]

[a] Abbreviations used: dmp = 2,9-dimethyl-1,10-phenanthroline; dtp = 2,9-ditolyl-1,10-phenanthroline (see Vögtle, F.; Lüer, I.; Balzani, V.; Armaroli, N. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1133); $Cu_2(m\text{-}43)_2^{2+}$ is a face-to-face isomer of $Cu_2(knot\text{-}86)^{2+}$, whose structures are shown in ref 16. [b] From the maximum of the room temperature emission band. [c] From the energy of the Cu(I) excited state (previous column) and the oxidation potentials of the various compounds, obtained from the following references: McMillin, D. R.; Buckner, M. T.; Tae Ahn, B. *Inorg. Chem.* **1977**, *16*, 943. Alonso-Vante, N.; Ern, V.; Chartier, P.; Dietrich-Buchecker, C. O.; McMillin, D. R.; Marnot, P. A.; Sauvage, J.-P. *Nouv. J. Chim.* **1983**, *7*, 3. Dietrich-Buchecker, C. O.; Sauvage, J.-P.; Kern, J.-M. *J. Am. Chem. Soc.* **1989**, *111*, 7791; ref 13; ref 16. [d] Quenching by O_2, from excited-state lifetime measurements on air equilibrated and deaerated CH_2Cl_2 solutions. [e] Quenching by acetone, from luminescence intensity measurements on CH_2Cl_2 air equilibrated solutions containing various concentrations of acetone (up to 3 M). [f] From ref 16.

Finally, we would like to notice that none of the emissive Cu^+-based moieties of [3]-catenates shows strong broadening of the MLCT band in going from high to low temperature. Such a band-broadening, attributed to the presence of two emissive (triplet and singlet) MLCT levels separated by a 1000–2000 cm^{-1} energy gap, is very common in copper(I)–phenathroline type complexes,[27] including knots.[16] Presumably the energy gap between the two levels is too small in the [3]-catenates to affect the luminescence spectra.

Quenching by Dioxygen and Acetone. The luminescent MLCT excited state of the copper(I)–phenanthroline type complexes can be quenched by dioxygen and acetone.[38,39] In Table 3 we have collected the results obtained for our [3]-catenates as well as previously reported data concerning other Cu(I)-based species. The excited-state energy and the oxidation potential of the *Cu(I) species are also shown in Table 3.

Dioxygen possesses two low-energy excited states, $^1\Delta$ and $^1\Sigma$, which lie at 0.976 and 1.626 eV above the ground state, respectively.[40] Therefore, quenching by an energy-transfer mechanism (eq 3a, where Cu(I) stands for any one of the Cu-based chromophoric groups of our compounds) is thermodynamically allowed. Quenching by electron transfer (eq 3b) is another possibility, although the reduction potential of O_2 in CH_2Cl_2 is not known.



As one can see from Table 3, the experimental quenching constants are different for the various species but do not show any correlation with the small changes in the energetics of the energy or electron-transfer quenching processes. If the quenching mechanism involves energy transfer (eq 3a) one should obtain (either directly or via the upper $^1\Sigma$ level) the $^1\Delta$ excited state of O_2 which is known to exhibit luminescence in the near infrared spectral region (λ_{max} = 1269 nm).[40] For example, the oxygen quenching of the luminescent MLCT level of $Ru(bpy)_3^{2+}$ in acetonitrile leads to sensitized $^1\Delta$ emission.[41] In an attempt to elucidate the mechanism of the quenching reaction in our systems, we have performed a similar photosensitization experiment by exciting the Cu(I)-based chromophoric groups with the 488-nm line of the argon ion laser of our IR sensitive spectrofluorimeter. We have found that the quenching of the luminescent MLCT excited state of the Cu(I)-based chromophores is indeed accompanied by sensitization of the $^1\Delta$ emission of O_2. The efficiency of singlet oxygen formation is approximately the same for all the Cu(I) complexes.[42] As mentioned above, there is no correlation between the energy of the Cu(I) excited state and the quenching constant. The observed decrease in the latter quantity along the series shown in Table 3 can be attributed to an increasing steric hindrance toward orbital overlap between the $Cu(phen)_2^+$ chromophoric unit and O_2.

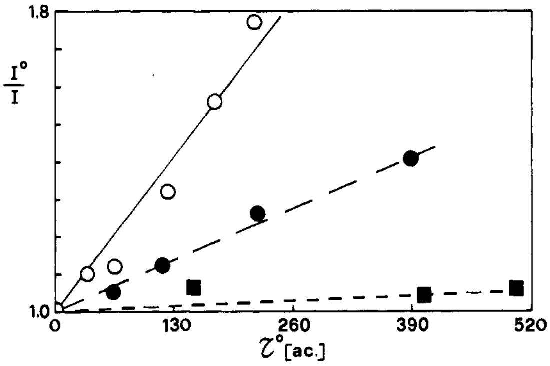


Figure 7. Stern–Volmer plots for the quenching of the luminescence intensity by acetone: (○) $[Cu(dmp)_2]^+$, (●) $[Cu(2\text{-cat})]^+$, and (■) $[Cu_2 \cdot \mathbf{1}]^{2+}$. For more details see text and Table 3.

In the case of acetone, quenching cannot take place by energy or electron transfer because this quencher does not possess low-energy excited states or redox levels. As previously shown by McMillin and co-workers,[38,39] quenching by acetone involves attack on the excited metal center to form a pentacoordinated exciplex species. This is the reason why, as shown in Table 3 and Figure 7, the quenching constant is very sensitive to the specific structure of the Cu(I) species. Expansion of the metal coordination number is clearly easier in the less sterically hindered species, like the mononuclear $Cu(dmp)_2^+$ compound, than in the more crowded catenates and knots. The data also show that the rigid structure of $Cu_2(knot\text{-}86)^{2+}$ offers a better shield toward coordination of acetone compared to the more flexible structure

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[38] McMillin, D. R.; Kirchhoff, J. R.; Goodwin, K. V. *Coord. Chem. Rev.* **1985**, *64*, 83.

[39] Palmer, C. E. A.; McMillin, D. R.; Kirmaier, C.; Holten, D. *Inorg. Chem.* **1987**, *26*, 3167.

[40] Turro, N. J. *Modern Molecular Photochemistry*, Benjamin/Cummings: Menlo Park, CA, 1978.

[41] For an extensive review on excited state quenching by oxygen, see: Wilkinson, F.; Helman, W. P.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1993**, *22*, 113.

[42] The intensity of the sensitized $^1\Delta$ emission in air equilibrated CH_2Cl_2 solutions of the Cu(I) compounds is about 30% that of an air equilibrated acetonitrile solution of $Ru(bpy)_3^{2+}$. The absolute value of the energy-transfer efficiency for the Cu(I) compounds cannot be established since no reference compounds have been examined in CH_2Cl_2 solution[41] and the use of a reference compound in a different solvent can lead to unpredictable errors.[43]

[43] Gorman, A. A.; Krasnowsky, A. A.; Rodgers, M. A. J. *J. Phys. Chem.* **1991**, *95*, 598.

of catenates. Among the [3]-cat compounds, it is interesting to note that the Cu(I) center is less protected in CuZn·**1**$^{3+}$ than in Cu$_2$·**1**$^{2+}$ and CuAg·**1**$^{2+}$, presumably because the electrostatic repulsion with the dipositive Zn^{2+}-based moiety leads to a less packed catenate structure.

Conclusions

We have reported the synthesis of a mononuclear and several heterodinuclear metal complexes of a [3]-catenand made of a 44-membered ring, which carries two 2,9-dianisyl-1,10-phenanthroline (dap) ligands, interlocked with two 30-membered rings, which carry a dap ligand. The [3]-catenand (**1**) and its metal complexes (catenates) are very interesting supramolecular species. In such compounds one can in fact identify two or more subunits, each of which possesses its own excited-state properties. Several of such subunits exhibit a characteristic luminescence in CH$_2$Cl$_2$ fluid solution at room temperature and/or in rigid matrix at 77 K. When different subunits are present in the same compound, electronic interaction leads to partial or complete luminescence quenching.

The ^{1}LC level of the free ligands of Cu·**1**$^+$ and the ^{1}LC level of the metal (Zn^{2+}) perturbed ligands of CuZn·**1**$^{3+}$ are quenched by the Cu-based moiety with rate constants of 2.5 × 10^{10} and 1.1 × 10^{10} s^{-1}, respectively. In its turn, the MLCT level of the Cu-based moiety of CuCo·**1**$^{3+}$ is quenched by the Co-based moiety with rate constant ≥6.0 × 10^8 s^{-1}. In the CuAg·**1**$^{2+}$ compound, the metal (Ag$^+$) perturbed ^{3}LC level is very efficiently quenched by the Cu-based moiety in rigid matrix at 77 K. The luminescent MLCT level of the Cu-based moieties of Cu·**1**$^+$, Cu$_2$·**1**$^{2+}$, CuAg·**1**$^{2+}$, and CuZn·**1**$^{3+}$ can also be quenched by dioxygen and acetone in CH$_2$Cl$_2$ solution at room temperature. The quenching by dioxygen takes place by energy transfer, as shown by the sensitized emission of the $^1\Delta$ O$_2$ level. The quenching by acetone is much less efficient and presumably occurs, as previously discussed by McMillin et al.,[38,39] by attack on the excited metal center to form a pentacoordinated exciplex species. Comparison with the results obtained for the quenching by dioxygen and acetone of the MLCT level of other Cu(I) complexes (including the simple Cu(dmp)$_2^+$ and the very complicated Cu$_2$(knot-86)$^{2+}$ species) shows that the value of the quenching constant decreases, as the crowding due to the ligands makes the Cu(I) core less accessible to the quencher molecules.

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