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Photochemistry of copper(I) complexes

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CONTENTS

ABSTRACT

Copper(I) complexes with simple inorganic ligands having no acceptor orbitals of low energy (*e.g.* Cl^-, Br^-, I^-, and NH_3) are characterized by CTTS photochemistry. UV excitation of halocuprates(I) in aqueous solutions leads to the formation of a hydrated electron, which undergoes competitive recombination and scavenging reactions. The mechanism of the whole photoinduced redox process in these systems is rather medium-dependent and involves the formation and decay of hydride intermediates. Cyano (as pseudohalo) as well as mixed-ligand cyano-halo complexes of Cu(I) show similar photoredox features, demonstrating the dominance of CTTS reactivity. On the basis of their very remarkable luminescence properties, however, CTTS (or metal-centered $3d^94s^1$) excited states of these coordination compounds can

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decay via formation of emissive intermediates, which also eject an electron. This route is interpreted by an exciplex mechanism, which apparently plays an important role in the photoinduced charge-transfer properties of the homo- and heteroleptic halocuprates(I).

Cluster complexes of the type $Cu_4X_4L_4$ (X^- = halide, L = organic amine) show remarkably rich photophysics. Multiple emissions have been observed, but excited-state assignments are somewhat ambiguous. The photochemistry of these materials has yet to be extensively studied, although some bimolecular redox reactions have been reported.

Copper(I) complexes with polypyridine ligands are featured by MLCT reactivity. Formation of an exciplex (but non-emissive) via quenching of these excited states is also an essential reaction of these compounds. Differing from the CTTS character, however, they undergo photoinduced electron transfer only by means of direct redox quenching. Two-photon photochemistry is also shown by these complexes. MLCT excited states of other cationic copper(I) complexes have been involved in both intra- and intermolecular reactions via oxidative quenching. Photocatalytic applications of Cu(I) coordination compounds are also demonstrated.

1. INTRODUCTION

Although the coordination chemistry of copper was thoroughly studied several decades ago [1], before 1970 only scant attention was paid to light-induced reactions of Cu complexes [2]. The photochemical significance of these compounds has considerably grown in the past 10–15 years [3]. A detailed review by Ferraudi *et al.* [4] summarizes the results in the area before 1980, while most of the recent work surveys rather selected topics [5–10]. The goal of this article is to discuss the photochemical properties of copper(I) complexes, emphasizing current results. Photophysical characterizations of the representative compounds are also given, especially if they are germane to the photochemical behavior, but pure luminescence studies are not covered by this paper.

In Cu(I) complexes the completely filled *d* subshell of the metal center excludes stabilization via the ligand field; therefore the reactivities of charge-transfer excited states determine the photochemistry of these compounds. As a consequence of the large reducing tendency of copper(I), the inter- and intramolecular photoinduced redox reactions of its complexes are generally initiated by the population of MLCT and CTTS excited states, depending on the ligands and the medium.

2. ANIONIC COMPLEXES

2.1. *Homoleptic halo and pseudohalo complexes*

2.1.1. *Absorption and luminescence*

The negatively charged copper(I) complexes which have so far been photochemically studied contain exclusively halo (Cl^-, Br^-, I^-) and pseudohalo (CN^-) ligands. In de-aerated aqueous solutions of halide ions, copper(I) is distributed among kinetically labile complexes such as CuX_2^-, CuX_3^{2-} and CuX_4^{3-}, which are in equilibrium with each other. Since the stepwise formation constants for the

CuX_2^-–CuX_3^{2-} (X=Cl or Br) and CuX_3^{2-}–CuX_4^{3-} (X=I) equilibria are rather low (Table 1), a significantly high ligand concentration (0.1–5 M) is necessary to influence the relative mole fraction of these complexes. Although the halocuprate(I) complexes of various numbers of ligands display different absorption spectra, all of them are characterized by a relatively (especially in the case of trihalocuprates) strong band at 273–281 nm (Table 2).

Since halide ions have no acceptor orbitals of low energy, which are required for MLCT transitions, the photochemistry of these complexes is characterized by CTTS reactivity. According to Mulliken's charge-transfer theory, the energy of CTTS excited states is basically determined by the ionization potential of the metal center and the electron affinity of the solvent acceptor orbital. Thus, in aqueous solutions the absorption bands due to the lowest energy CTTS (or $d^{10}s^0 \rightarrow d^9s^1$) transition of the halocuprate(I) complexes can be found in a very narrow range of wavelengths (see Table 2). From the position of these bands, an ionization energy of about 290 kJ mol^{-1} can be estimated for the metal center [4]. The molar absorbances and therefore the oscillator strengths of these bands increase remarkably in the order $Cl^- < Br^- < I^-$, indicating a significant change in the probability of the transition, depending on the ligand. This strong effect may be attributed to the different polarizabilities of the halide ions.

Cyanocuprates(I) display some similar features, although their absorption bands were assigned mostly as MLCT transitions owing to the strong π-acceptor character of CN^- ligands [20]. The bands listed in Table 2 are those suggested as

TABLE 1

Overall (β_j) and stepwise (K) stability constants of halo- and cyanocuprate(I) complexes in aqueous solutions at 25°C

Complex	log β_j	K (M^{-1})	μ (M)	Ref.
$CuCl_2^-$	6.06		5	11
$CuCl_3^{2-}$	5.94	0.74±0.08	5	11, 12
		1.05±0.15	3	13–15
		0.65±0.08	1, 5	15
$CuBr_2^-$	6.28		5	11
$CuBr_3^{2-}$	7.48	14.8±2.0	5	11
	7.36	10.8±2.0	5	16
		5.3±1.0	1	16
CuI_2^-	≈8.7		5	11
CuI_3^{2-}	10.43		5	11
CuI_4^{3-}	9.40	0.093±0.015	5	11
$Cu(CN)_2^-$	23.9		≈0	17
$Cu(CN)_3^{2-}$	29.2	$2.00 \pm 0.05 \times 10^5$	≈0	17
$Cu(CN)_4^{3-}$	30.7	32±15	≈0	17

TABLE 2

Spectroscopic properties of halo- and cyanocuprate(I) complexes in aqueous solutions[a]

Complex	λ_{max} (nm)	ε_{max} ($M^{-1}\,cm^{-1}$)	f	τ^b (ns)	μ (M)	Ref.
$CuCl_2^-$	233	943			1	15
	232	1060			3	13
		855			3	18
	231	1030			5	15
	274	186	0.00164	670	1	15
		140			3	13
		16			3	18
		513	0.00595	180	5	15
$CuCl_3^{2-}$	230	1640			1	15
	231	1550			3	13
		1490			3	18
	230	1670			5	15
	276	3720	0.0439	26	1	15
	274	3980			3	13
		3340			3	18
		4920	0.0586	19	5	15
$CuBr_2^-$	271	1070			1	16
	275	1760			5	16
$CuBr_3^{2-}$	281	9260			1	16
	277	8640	0.14	8.2	5	16
CuI_3^{2-}	274	17000	0.26	4.3	5	3, 19
$Cu(CN)_2^-$	244	5250	0.051	18	≈0	20
	263	1670	0.025	42	≈0	20
$Cu(CN)_3^{2-}$	222	4940	0.066	12	≈0	20
	250	1970	0.018	52	≈0	20

[a] In the cases of chloro- and bromocuprates all solutions contained 1 M H^+.

[b] The radiative lifetimes are estimated from the relation $\tau = 1.5/f\bar{v}^2$ [21].

corresponding to CTTS or d^9s^1 transitions. The lowest-energy bands occur at shorter wavelengths than those for halo complexes, indicating that in the case of cyanocuprates(I) the ligand also determines the energy of the transitions.

In neutral solutions, excitation of these lower-energy CTTS bands leads to luminescence in all halocuprate(I) systems under suitable conditions (Fig. 1, Table 3). The excitation bands correlate with the corresponding absorption bands in each case. The wavelengths of the emissions can be found in a relatively narrow range, indicating that the ligands play a negligible role in this process. The strongly deviating lifetimes show the order $Br^- > Cl^- > I^-$, which differs from that of the molar absorbances. In all cases this luminescence is quenched by a hydronium ion, following a Stern–Volmer relationship. The significant Stokes shifts and the calculation of the true luminescent lifetimes (see Table 2) suggested that the emitting state cannot be

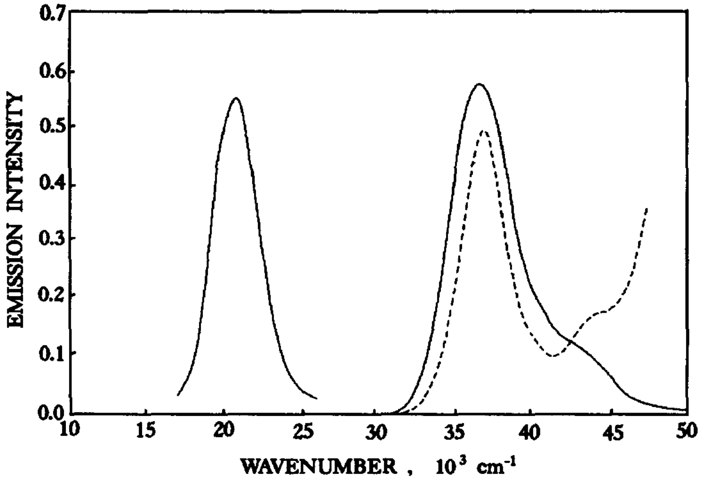

Fig. 1. Luminescence excitation spectrum monitored at 475 nm and emission spectrum excited at 274 nm of 1.3×10^{-4} M CuCl in 5 M NaCl at room temperature (_____) and molar absorption spectrum of $CuCl_3^{2-} \times 10^{-4}$ (- - -). (From ref. 15 with permission: © 1988 American Chemical Society.)

TABLE 3

Excitation (λ_{exc}) and emission (λ_{em}) maxima, luminescence lifetimes (τ), and rate constants for luminescence quenching by H^+ (k_H) for CuX_3^{2-} complexes at 5 M ionic strength

Ligand	λ_{exc} (nm)	λ_{em} (nm)	τ (ns)	k_H ($M^{-1} s^{-1}$)
Cl^- [a]	275	475	105	5.8 ± 10^8
Br^- [b]	279	465	710	6.2 ± 10^8
I^-	284	493	14.3	7.8 ± 10^9

[a] From ref. 15.
[b] From ref. 16.
Source: ref. 19 with permission. Copyright 1993 American Chemical Society.

the primarily excited CTTS (or d^9s^1) state [15]. Thus, this luminescence must originate from some relatively long-lived spin-forbidden state generated via intersystem crossing or, as discussed later (see Section 2.2), from an exciplex, the precursor of which is such a triplet state.

2.1.2. Photochemistry

Continuous irradiation of chloro- and bromocuprate(I) complexes ($\lambda_{ir} \geq 313$ nm) in deaerated acidic solution resulted in production of H_2 gas accompanied by oxidation of the metal center [22,23].

$$CuX_n^{(n-1)-} + H^+ \xrightarrow{h\nu} CuX_n^{(n-2)-} + \tfrac{1}{2}H_2 \qquad (1)$$

The primary photochemical step in this process is electron ejection from the excited complex [13,19,24].

$$^{*}\mathrm{CuX}_n^{(n-1)-} \rightarrow \mathrm{CuX}_n^{(n-2)-} + e_{aq}^{-} \qquad (2)$$

Knowing the fractions of light absorbed by the different species in these systems, the individual quantum yields regarding the photoactivity of the complexes with various coordination numbers can be determined. Such calculations require the corresponding equilibrium constants and the individual molar absorbances at the irradiation wavelength [25]. The quantum yields for the photo-oxidation of halo- and pseudohalocuprate(I) complexes are summarized in Table 4. In most cases, the efficiency is significantly higher for bis- than for triscoordinated complexes. This tendency in the quantum yields for hydrogen production can be interpreted by the effect of thermal reactions involving hydride intermediates (see later, eqns. (12)–(14)). For the primary

TABLE 4

Individual quantum yields for the photooxidation of halo- and cyanocuprate(I) complexes, determined by electron scavenging with H^+ (Φ_H), NO_3^- or N_2O (Φ_N), or by direct e_{aq}^- detection using flash photolysis (Φ_e)

Complex	λ_{exc} (nm)	Φ_H	Φ_N	Φ_e	μ (M)	Ref.
$CuCl_2^-$	254	0.60			3	18
	265	0.65			5	12
	266			≈0.7[a]	1	13
	274	0.81			5	12
		>0.51			5	15
	296	0.74			5	12
$CuCl_3^{2-}$	254	0.29			3	18
	265	0.09			5	12
	274	0.07			5	12
		0.12			5	15
	296	0.14			5	12
$CuBr_2^-$	266			0.67	1	24
$CuBr_3^{2-}$	266			0.34	1	24
CuI_3^{2-} [b]	308			0.28	1	19, 26
				0.23	5	26
$Cu(CN)_2^-$	254		0.31		≈0	27
			0.35		5	28, 29
	266		0.37		5	29
$Cu(CN)_3^{2-}$	254		0.03		≈0	27
$Cu(CN)_2Cl^{2-}$	254		0.18		5	28, 29
	266		0.21		5	29

[a] In 1 M NaCl solution containing both $CuCl_3^{2-}$ and $CuCl_2^-$. Recent unpublished results, however, indicate that Φ_e is independent of $[Cl^-]$ in the 0.5–3 M range.

[b] Also valid for CuI_4^{3-} because no $[I^-]$-dependence was experienced in the 1–5 M range [26].

photoreaction (*i.e.* formation of a hydrated electron) this phenomenon may be rationalized by a higher probability of radiationless energy dissipation in the case of the triscoordinated species.

The electron formed in the primary photochemical step in acidic solution is scavenged by H^+, giving a hydrogen radical. Since a hydronium ion also reacts with the luminescent excited state, probably via redox quenching, a mechanism involving both singlet and triplet states can be suggested for the whole process leading to the formation of a hydrogen radical [15].

$CuCl_n^{1-n} \xrightarrow{h\nu} {}^*CuCl_n^{1-n}$ UV excitation to $d^9s^1 = \mathrm{CTTS} =$ singlet primary geminate pair($^1\mathrm{PGP} = \{CuCl_n^{2-n} - e^-\}$) (3)

$^1\mathrm{PGP} \rightarrow {}^1\mathrm{SGP}$ secondary geminate pair formation ($^1\mathrm{SGP} = \{CuCl_n^{2-n}, e^-\}$) (4)

$^1\mathrm{SGP} + H^+ \rightarrow CuCl_n^{2-n} + H^\cdot$ singlet secondary pair scavenging (5)

$^1\mathrm{SGP} \rightarrow CuCl_n^{1-n}$ singlet secondary pair recombination (6)

$^1\mathrm{SGP} \rightarrow CuCl_n^{2-n} + e_{aq}^-$ aquated electron formation (7)

$\left.\begin{array}{l}{}^1\mathrm{PGP}\\ {}^1\mathrm{SGP}\end{array}\right\rangle \longrightarrow {}^3CuCl_n^{1-n}$ intersystem crossing or spin unpairing (8)

$^3CuCl_n^{1-n} \rightarrow CuCl_n^{1-n} + h\nu'$ luminescence of spin-forbidden state (9)

$^3CuCl_n^{1-n} \rightarrow CuCl_n^{1-n} + \Delta$ non-radiative deactivation of spin-forbidden state (10)

$^3CuCl_n^{1-n} + H^+ \rightarrow CuCl_n^{2-n} + H^\cdot$ luminescence quenching by hydronium ion (11)

On the basis of the experimental data, with a strong external magnetic field, the lower limit of the PGP lifetime in cyanocuprate(I) system was estimated to be about 4×10^{-11} s [20]. For halocuprate(I) complexes similar values can be expected. The scavenging reaction (eqn. (5)) competes with the secondary geminate recombination of the {Cu(II), e^-} pair (eqn. (6)), according to the Noyes model [30,31]. In the range of 0.01–1 M H^+ the quantum yield for hydrogen formation was a linear function of $[H^+]^{1/2}$ and leveled off above about 1 M owing to the complete scavenging of electrons escaping primary recombination [13,16,18]. However, the relation $1/\Phi$ *vs.* $1/[H^+]$ also proved to be linear for this system, indicating that there is a rate-controlling reaction of H^+ with a steady-state intermediate to produce dihydrogen. Reasonable candidates are hydride or hydrogeno complexes such as $HCuX_2^-$ or $HCuX_3^{2-}$, which can be formed by the reaction between a hydrogen radical and the copper(I) species [16,32].

$H^\cdot + CuX_n^{(n-1)-} \rightarrow HCuX_n^{(n-1)-}$ (12)

Decomposition of these steady-state intermediates leads to H_2 formation in competition with other processes giving longer-lived Cu(0) species [16,33–35].

$$\begin{tikzcd} \mathrm{HCuX}_n^{(n-1)-} \arrow[r, "k_{\mathrm{H}}{[\mathrm{H}^+]}"] \arrow[dr, "k_{\mathrm{d}}"'] & \mathrm{H}_2+\mathrm{CuX}_n^{(n-2)-} \qquad (13) \\ & \mathrm{H}^+ + \mathrm{CuX}_n^{n-} \qquad (14) \end{tikzcd}$$

This mechanism is confirmed by earlier observations that the formation of the latter, longer-lived intermediate (CuX_n^{n-}) is hindered by increasing hydrogen ion concentration [35]. Enhancing the ionic strength in the bromocuprate(I) system significantly decreased the quantum yield for the formation of the steady-state hydride intermediate ($HCuX_n^{(n-1)-}$): $\Phi_{hyd}=0.72, 0.60$ and 0.28 at $\mu=1, 2$ and 3 M, respectively (with 0.5 M Br^-, $\lambda_{ir}=279$ nm) [16]. This explains the fact that a more concentrated ionic medium decreases the overall quantum yield for H_2 production of chloro- and bromocuprate(I) complexes in acidic solution. Since the probability for the formation of a $HCuX_n^{(n-1)-}$ intermediate via reaction (12) is higher at lower n, *i.e.* $n=2$, in the cases where the fraction of the triscoordinated complexes predominates (>70%), the overall efficiency of hydrogen generation is lower than the value expected on the basis of the individual quantum yields determined by direct measurements of hydrated electron. Therefore, the Φ values determined by Cu(II)- or H_2-monitoring for chlorocuprate(I) systems (see Table 4) involve significant effects from thermal reactions (12)–(14).

When no added scavenger exists in these systems, an increase in copper(I) concentration shortens the lifetime of the hydrated electron formed in the primary photoreaction. This is a consequence of bimolecular electron scavenging by the ground-state Cu(I) species.

$$e_{aq}^- + CuX_n^{(n-1)-} \xrightarrow{k_e} CuX_n^{n-} \qquad (15)$$

The rate constant of this reaction depends significantly on the ligand concentration and ionic strength. Owing to the stronger coulombic repulsion, complexes of higher ligand number e_{aq}^- (Table 5) scavenge less efficiently. It is worth mentioning, however, that the back-reaction between Cu(II) and e_{aq}^- photochemically formed in iodocuprate(I) system was not influenced by the ligand concentration; the lifetime of the hydrated electron was 1.0×10^{-6} s at any $[I^-]$ ($[Cu(I)]\rightarrow0$) [26]. At lower ionic strength (0–0.2M), k_e linearly increases as a function of $\mu^{1/2}/(1+\mu^{1/2})$; the slope is proportional to the charge of the complexes in accordance with the Brønsted–Bjerrum theory of ionic reactions [36], as was observed for $Cu(CN)_2^-$ and $Cu(CN)_3^{2-}$, where, owing to the high formation constants (see Table 1), any ionic strength close to zero can be adjusted [29]. In the range of higher μ (2–5 M) any charged acceptor tends to behave as a neutral particle [37] and the increasing

TABLE 5

Rate constants (k_e) for the scavenging of hydrated electron by halo- and cyanocuprate(I) complexes in aqueous solution

Complex	k_e ($M^{-1} s^{-1}$)	μ (M)	Ref.
$CuCl_2^-$	5.51×10^9	5	29
$CuCl_3^{2-}$	1.36×10^9	5	29
$CuBr_2^-/CuBr_3^{2-}$ [a]	7.5×10^9	3	24
CuI_3^{2-}	3.25×10^9	5	26
CuI_4^{3-}	7.5×10^8	5	26
$Cu(CN)_2^-$	5.65×10^9	5	29
$Cu(CN)_3^{2-}$	1.4×10^9		
$Cu(CN)_4^{3-}$	1.4×10^9		

[a] At 0.5 M Br^- concentration, where both species exist in comparable amounts.

viscosity results in a monotonic decrease in the diffusion coefficient of the hydrated electron, hence diminishing k_e [26,29].

While in the chloro and bromo systems the halide ions do not undergo apparent redox reaction in the photoinduced process, irradiation of iodo- and cyanocuprate(I) complexes leads to the oxidation of the ligands in reaction with the photochemically oxidized metal centers. In the case of the CuI_3^{2-} and CuI_4^{3-} complexes, formation of the longer-lived I_2^- intermediate ($\tau \approx 16\ \mu s$) was observed in neutral solution, due to reaction (16) [19].

$$CuI_n^{(n-2)-} + 2I^- \rightarrow CuI_n^{(n-1)-} + I_2^- \tag{16}$$

This species dismutates to the stable I_3^- and I^- ions or recombines with reduced products in the system (*e.g.* CuI_n^{n-}), giving the original ground-state reactants. According to the first reaction (*i.e.* dismutation), in earlier experiments continuous irradiation ($\lambda_{ir} = 254$ nm) of binuclear Cu_2I^{3-} in saturated KI solution led to I_3^- formation with a quantum yield of 0.02 [38].

In the photolysis of cyanocuprate(I) complexes, similarly to the iodo system, the copper(II) species generated in the primary step and excess cyanide reconvert copper back to the +1 oxidation state and produce cyano radicals

$$Cu(CN)_3^- + CN^- \rightarrow Cu(CN)_3^{2-} + {}^{\cdot}CN \tag{17}$$

which recombine to cyanogen,

$$2{}^{\cdot}CN \rightarrow (CN)_2 \tag{18}$$

Comparing with the hydrated electron production (see Table 4), the quantum yields for the cyanide conversion showed an opposite tendency, and apparently only tricyanocuprate(I) proved to be efficient in this respect ($\Phi_2 \approx 0$, $\Phi_3 = 0.36$, $\lambda_{ir} = 254$ nm, pH = 7.1) [39]. However, this result may be attributed to the fact that simply the higher [CN$^-$] necessary for $Cu(CN)_3^{2-}$ accelerates reaction (17).

2.1.3. Photocatalytic applications

Despite the fact that halo and pseudohalo complexes of copper(I) can only be excited in the UV region, there were some experiments to utilize their photoredox reactions for catalytic purposes. Photooxidation of chlorocuprate(I) complexes in aqueous solutions was applied for photocatalytic H_2 generation in both Cu(I)–Cu(II) and Cu(I)–Cu(II)/U(IV)–U(VI) systems [40,41]. Although this research is promising, further confirmation is needed with mechanistic details.

Photo-oxidation of bromocuprate(I) complexes for hydrogen production was also investigated in catalytic respects. For recovering CuBr, the thermal decomposition of $CuBr_2$ (at $T > 243°C$) was applied in this system [42]. This requires, however, the evaporation of the photolyzed solution, making the whole process energetically unfavorable.

2.2. Mixed-ligand complexes

The high formation constant for $Cu(CN)_2^-$ offers the possibility of producing mixed-ligand dicyanohalocuprate(I) complexes. The stepwise formation constants of these species are similar to those of the corresponding trihalocuprates(I) (Tables 1 and 6) [28,43]. The emission features of their excited states significantly differ from those of $^*Cu(CN)_2^-$ and resemble the luminescence characteristics of the homoleptic halocuprate(I) complexes [28]. The dependence of their luminescence lifetimes and quantum yields on the halide concentration revealed that these excited states can be considered as exciplexes because the constants for their formations from an excited $Cu(CN)_2^-$ complex and a halide ion ($^*K$) are at least one order of magnitude higher than those of the corresponding ground-state equilibria (K) (see Scheme 1 and Table 6).

TABLE 6

Equilibrium constants for excited-state ($^*Cu(CN)_2^- + X^- \rightleftharpoons {}^*Cu(CN)_2X^{2-}$, $^*K$) and ground-state ($Cu(CN)_2^- + X^- \rightleftharpoons Cu(CN)_2X^{2-}$, K) equilibria of mixed-ligand dicyanohalocuprate(I) complexes [28,43]

X^-	K (M^{-1})	$^*K$ (M^{-1})
Cl^-	0.70 ± 0.12	11 ± 3
Br^-	2.5 ± 0.6	27 ± 4
I^-	16 ± 4	430 ± 40

$$\begin{tikzcd}
{}^{*}\mathrm{Cu(CN)_2^-} + \mathrm{X^-} \arrow[r, shift left, "{}^{*}K"] \arrow[d, shift left, "k_{NR}"] & {}^{*}\mathrm{Cu(CN)_2X^{2-}} \arrow[l, shift left] \arrow[r, "+\mathrm{X^-}"] \arrow[d, shift left, "k_{NR} + k_{L}"] & \text{products} \\
\mathrm{Cu(CN)_2^-} + \mathrm{X^-} \arrow[r, shift left, "K"] \arrow[u, shift left, "h\nu"] & \mathrm{Cu(CN)_2X^{2-}} \arrow[l, shift left] \arrow[u, shift left, "h\nu"] &
\end{tikzcd}$$

Scheme 1. (NR = non-radiative decay, L = radiative decay)

No similar phenomenon was experienced with $\mathrm{Cu(CN)_3^{2-}}$, indicating that exciplex formation is favored when arising from a coordinatively more unsaturated excited state. A very recent study on the luminescence of homoleptic halocuprates(I) also suggests exciplex formation from dihalocuprate(I) complexes [44]. Ultraviolet excitation of both $\mathrm{Cu(CN)_2^-}$ and $\mathrm{Cu(CN)_2X^{2-}}$ leads to electron ejection (see Table 4) occurring on the picosecond or sub-picosecond time scale in competition with the creation of the precursor $^{*}\mathrm{Cu(CN)_2^-}$ and the luminescent species $^{*}\mathrm{Cu(CN)_2X^{2-}}$ of lower energy respectively, via internal conversion. This may be in accordance with eqns. (3)–(10), where a triplet state is directly assigned as luminescent [15], although in that case the emission may also originate from another species, the precursor of which is this triplet state.

3. NEUTRAL CLUSTERS

3.1. Spectroscopy

Neutral coordination compounds of copper(I) photochemically studied so far are basically tetranuclear mixed-ligand clusters. Since they contain both halide and some other type (mostly amine or phosphine) of ligand, they represent a natural transition between the anionic halocuprates(I) and the cationic Cu(I) complexes, the ligands of which are predominantly amine (or phosphine) derivatives. Thus, their photochemical properties lie between the two groups, but tend rather to resemble those of the cationic compounds. This is manifested mostly in their spectroscopic features.

The "cubane" Cu(I) clusters $\mathrm{Cu_4X_4L_4}$ ($\mathrm{X^-} = \mathrm{Cl^-}$, $\mathrm{Br^-}$, or $\mathrm{I^-}$; L = unsaturated amines) display double luminescence in solution (Table 7) [45–50]. The different emission lifetimes τ indicate a poor coupling between the two relevant excited states. An *ab initio* calculation clearly showed that excited-state assignments must account for major components of halide-to-metal charge transfer (XMCT) and halide-to-ligand charge transfer (XLCT) character for the low-energy (LE) and high-energy (HE) emissions, respectively [51]. The LE emission is of rather mixed d–s/XLCT character delocalized over the $\mathrm{Cu_4X_4}$ core, and thus referred to as cluster-centered (CC) [46,47].

TABLE 7

Wavelengths and lifetimes of high-energy (HE) and low-energy (LE) emissions of representative $Cu_4I_4L_4$ clusters in toluene solution ($\lambda_{exc}=337$ or 355 nm, $T=294$ K) [50]

L	HE		LE	
	λ_{em} (nm)	τ (μs)	λ_{em} (nm)	τ (μs)
Pyridine	480	0.45	690	10.6
4-*t*-butylpyridine	468	0.35	696	10.3
4-Benzylpyridine	473	0.56	692	11.0
4-Phenylpyridine	520	0.12	694	9.4
3-Chloropyridine	537	0.35	675	12.7
Piperidine			680	0.11
Morpholine			671	0.51
$P(n\text{-}Bu)_3$			654	2.23

In the case of $Cu_4I_4(py\text{-}x)_4$ complexes (py-x = susbtituted pyridine), the large Stokes shift for the LE emission band (see Table 7) is consistent with the mixed d–s/XMCT assignement for this excited state, in which, on the basis of *ab initio* calculations [51], the contributions from each component are roughly equal. The significant Stokes shifts also indicate a strong distortion in the excited state, owing to the enhanced Cu–Cu and less Cu–I bonding.

In contrast to the LE emissive state, much less distortion is expected for the XLCT states, on the basis of the smaller Stokes shifts for the HE emissions. The differences in the magnitude and direction of the respective distortion coordinates may explain the poor coupling between the two excited states, which are assigned as triplets on the basis of their lifetimes (Table 7).

Of course, $Cu_4I_4L_4$ clusters, where L is saturated amine, display only the more intense LE emission (see Table 7), indicating that this cannot be the result of a charge transfer involving an unsaturated π^* ligand orbital. When the unsaturated nitrogen heterocycle is the bulky diphenyl-2-methylpyridine (dpmp) ligand, the $Cu_4X_4(dpmp)_4$ clusters show only a single XLCT band in their luminescence spectra at 77 K, with the energy order I > Br > Cl [49]. At higher temperature, the iodo and bromo clusters display a long wavelength shoulder attributed to CC emission, but its lifetime is equal to that of the much stronger XLCT emission. Thus, deviating from $Cu_4I_4py_4$, for the dpmp clusters the d–s/XMCT and XLCT states are in thermal equilibrium [49].

3.2. *Luminescence quenching*

The HE emission can be quenched by pyridine and its derivatives via exciplex formation [46–48]. The mechanism of this reaction is supposed to be the same as has been suggested for $Cu(dmp)_2^+$ (see Section 4.2).

The long luminescence lifetime of $^*Cu_4I_4py_4$ also offered the possibility for energy or electron transfer via quenching with suitable reactants. This was demonstrated in CH_2Cl_2 solutions by using a series of uncharged tris(β-dionato)chromium(III) complexes with a wide range of reduction potentials ($E_{1/2}(Q/Q^-)$) [52]. While energy transfer occurs with all these complexes, competitive electron transfer can be operative with those of the least negative $E_{1/2}(Q/Q^-)$ ($\leqslant -1.4$ V *vs.* ferrocenium/ferrocene). Application of organic reactants such as dinitrobenzenes and 1,4-benzoquinone results in pure electron transfer quenching because they have $\pi\pi^*$ state energies too high for energy transfer to be viable [52]. The energy of the long-lived CC excited state of $Cu_4I_4py_4$ (I) was estimated to be 1.74 μm^{-1} [50], and its excited-state oxidation potential ($E_{1/2}(I/I^-)$) ~1.86 V [52].

The hexanuclear copper(I) complex $Cu_6(mtc)_6$ (mtc^- = di(n-propyl)-monothiocarbamate) is also luminescent under ambient conditions, *e.g.* $\lambda_{em}^{max} = 725$ nm, $\tau = 1$ μs in toluene at room temperature, with a Stokes shift of 0.97 μm^{-1} between the excitation and emission maxima [53]. The emission of this octahedral cluster, by analogy with the tetrahedral ones, was attributed to the presence of a low-energy triplet d–s/LMCT state.

4. CATIONIC COMPLEXES

While the anionic copper(I) complexes photochemically studied so far are exclusively halo- and pseudohalocuprates, in the corresponding, positively charged coordination compounds the am(m)ine and imine ligands dominate. In the case of am(m)ines, where no unsaturated orbitals of low energy are available, metal-centered or rather CTTS transitions determine the photochemical properties, indicating a similarity to those of halo complexes. The spectroscopy and photochemistry of Cu(I) complexes with unsaturated amines display predominantly MLCT properties.

4.1. Ammine complexes

The coordination compounds of copper(I) with NH_3 are the simplest representatives of cationic Cu(I) complexes. In aqueous solution $Cu(NH_3)_2^+$ and $Cu(NH_3)_3^+$ are in equilibrium, the constant for which is 0.04–0.05 M^{-1} in the 0–1 M range of ionic strength [54,55]. While the diammine complex shows a rather featureless absorption spectrum in the UV range, triamminecopper(I) displays at least three bands of significantly different intensities (Fig. 2, Table 8) [54]. Excitations due to these transitions result in the formation of a hydrated electron, which can be efficiently scavenged by N_2O and, remarkably, NH_4^+ as well [54,56]. The latter reaction led to the generation of H_2.

$$Cu(NH_3)_3^+ + NH_4^+ \xrightarrow{h\nu} Cu(NH_3)_3^{2+} + \tfrac{1}{2}H_2 + NH_3 \qquad (19)$$

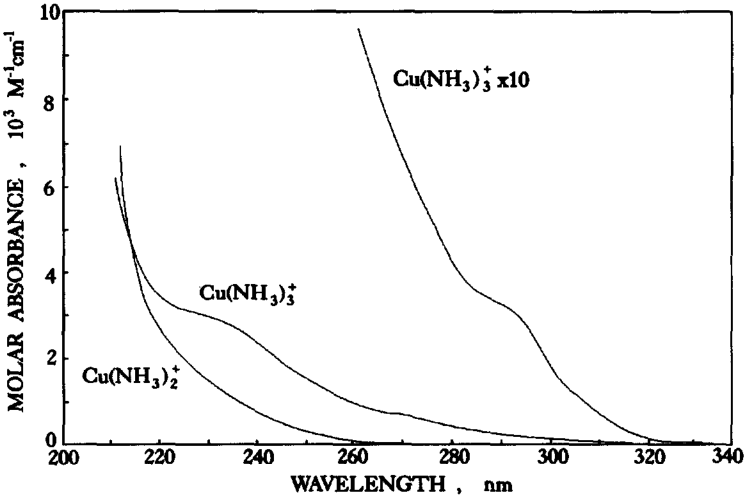

Fig. 2. Resolved UV spectra of $Cu(NH_3)_2{}^+$ and $Cu(NH_3)_3{}^+$ at 1 M ionic strength. (From ref. 54 with permission: © 1989 American Chemical Society.)

TABLE 8

Spectral features of $Cu(NH_3)_3^+$ in aqueous solution and quantum yields for its photo-oxidation at different excitation wavelengths in 1 M NH_4ClO_4 [54]

λ_{max} (nm)	ε_{max} (M^{-1} cm^{-1})	f	λ_{ir} (nm)	Φ_{H2}
			313	0.39
295	170	0.0018	297	0.56
270	330	0.0043	274	0.46
			266	0.49
229	2880	0.051	246	0.39

As in the case of halocuprates, the scavenging kinetics (by both N_2O and $NH_4{}^+$) can be described by the geminate recombination model suggested by Noyes [30,31]. In the 240–320 nm excitation range, only triamminecopper(I) proved to be photoactive, and the quantum yields for reaction (19) at different wavelengths (Table 8) confirm that its absorption bands in this region are of CTTS character. Notably, in opposition to other copper(I) complexes discussed here, $Cu(NH_3)_3{}^+$ and $Cu(NH_3)_2{}^+$ did not apparently show any luminescence.

4.2. Polypyridine complexes

Deviating from the complexes of copper(I) with simple inorganic ligands, its coordination compounds with aromatic diimines (NN) such as bipyridine (bpy), phenanthroline (phen), biquinoline (biq) and their substituted derivatives also display strong absorption bands in the visible range (Fig. 3). These bands have been attributed to MLCT transitions wherein an electron is promoted from a 3d orbital of copper to a low-lying π^* orbital of the ligands [58–65]. At low temperatures the absorption spectra of the $Cu(NN)_2{}^+$ complexes reveal three distinct band systems, but their detailed assignments are hampered by uncertainties about the ground-state symmetry [66]. From these MLCT states originates a rich variety of photophysical and photochemical properties, which have been thoroughly studied in the past decade. Since several publications discuss the light-induced features of Cu(I) polypyridine complexes in detail [9,67,68], only a rather brief summary of this topic is given in this section, with somewhat more emphasis on the charge-transfer reactions.

4.2.1. *Quenching via exciplex formation*

Under ambient conditions the $Cu(NN)_2{}^+$ complexes also exhibit characteristic emissions. For example, $Cu(dmp)_2{}^+$ (dmp = 2,9-dimethyl-1,10-phenanthroline) shows photoluminescence in CH_2Cl_2 at room temperature ($\lambda_{max} = 730$ nm, $\tau = 54$ ns, $\Phi = 2\times10^{-4}$, $C \sim 3\times10^{-5}$ M) [57]. This emission attributed to an MLCT excited state could be quenched by nitrobenzene derivatives via formation of encounter complexes, without electron transfer. The counter-ions in this system also showed a quenching effect, therefore dilution increased the luminescence lifetime [69]. Interpretation of this effect postulates the formation of an exciplex which is mediated by a ground-state ion pair. The quenching ability of the anions follows the order of their donor strength, *i.e.* $BPh_4{}^- \leqslant PF_6{}^- < BF_4{}^- < ClO_4{}^- < NO_3{}^-$. Several solvents, being also Lewis bases, operate in a similar way, ranging from the weak donor CH_3CN, to the

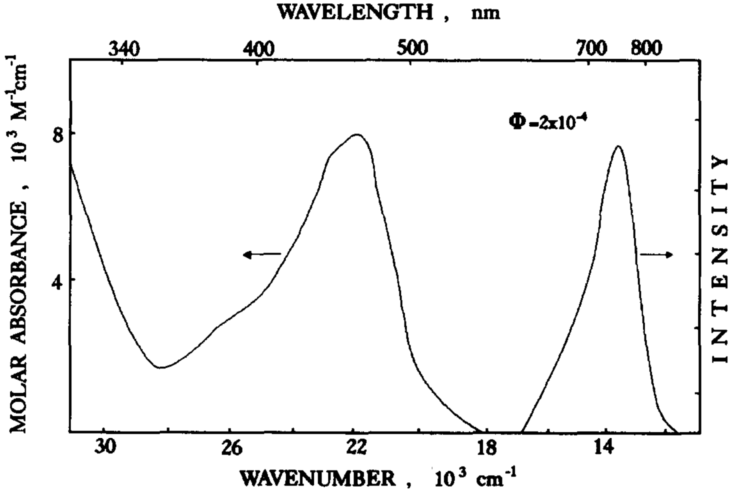

Fig. 3. Visible absorption and corrected emission spectra of $Cu(dmp)_2{}^+$ in CH_2Cl_2 at 25°C. (From ref. 57 with permission: © 1980 American Chemical Society.)

strong donor DMF [70,71]. Thus, of course, no or negligible emission was detected in acetonitrile, ethanol or water; the luminescence lifetime of $^*Cu(dmp)_2{}^+$ in CH_3CN was determined to be 2±0.3 ns [70]. In CH_2Cl_2 these quenching reactions were proposed to take place via formation of five-coordinate adducts with a coordinate covalent bond between the copper center and the Lewis base (Fig. 4) [57]. The rate constants shown in the figure are with respect to the simplified kinetic scheme,

$$^*Cu + Q \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} {}^*Cu \cdots Q \tag{20}$$

$$^*Cu \cdots Q \xrightarrow{k_Q} Cu + Q \tag{21}$$

where *Cu and Cu respectively denote the emissive CT excited state and the ground state of $Cu(dmp)_2{}^+$, Q represents the quencher, and *Cu···Q designates the exciplex. For Cu(I) complexes with bulkier ligands, such as dpp (2,9-diphenyl-1,10-phenanthroline) and bpc (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline), the emission quenching is much less favorable in this way, because the phenyl substituents are more effective in blocking access of various bases to copper coordination sites of the MLCT excited state. Studies of pressure effects on the luminescence quenching of $Cu(dmp)_2{}^+$ and $Cu(dpp)_2{}^+$ confirm this interpretation [72].

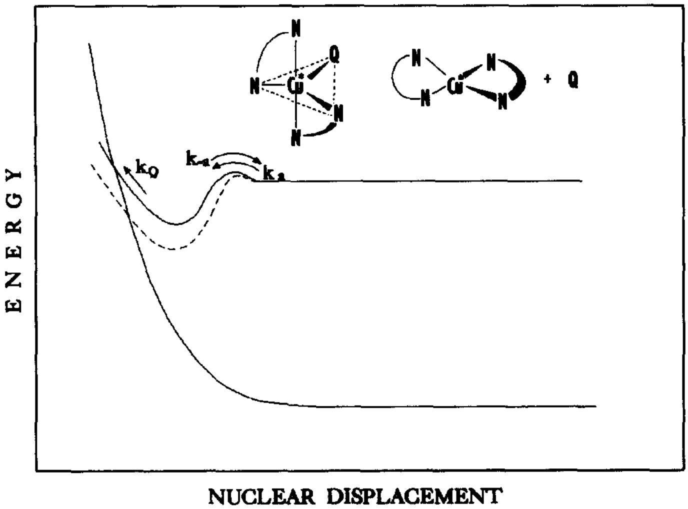

Fig. 4. Schematic enthalpy profile for the reaction of $^*Cu(dmp)_2{}^+$ with a Lewis base. The ground-state surface is assumed to be repulsive, but the excited state forms a five-coordinate adduct. The dashed curve corresponds to a stronger donor. See text for the definition of rate constants. (From ref. 71 with permission: © 1990 American Chemical Society.)

4.2.2. Quenching via energy and electron transfer

Similar to the case of tetranuclear copper(I) clusters (see Section 3), the emission of $Cu(dpp)_2{}^+$ in CH_2Cl_2 can be efficiently quenched by tris(β-dionato)chromium(III) complexes with a wide range of reduction potential [73]. Depending on the free-energy change for electron transfer (ΔG^0_{el}), three different quenching mechanisms dominate, as was also demonstrated by determination of the pressure effect, which can be conveniently represented by the volume of activation ($\Delta V^{\ddagger}{}_q$) for the quenching reaction [74].

1. With quenchers of unfavorable ΔG^0_{el} ($\gg 0$) relatively slow energy transfer is operative, and the absolute value $\Delta V^{\ddagger}{}_q$ is rather small, owing to the lack of solvation/desolvation effects from charge creation.
2. In the cases where ΔG^0_{el} is large and negative, the quenching rate constant approaches the diffusion limit (10^{10} M^{-1} s^{-1}), and $\Delta V^{\ddagger}{}_q$ is large (*e.g.* 8.0 cm^3 mol^{-1} for $Cr(hfac)_3$, $\Delta G^0_{el} = -0.62$ V), as a consequence of the increased viscosity and thus decreased diffusion rates.
3. When ΔG^0_{el} is positive but relatively close to zero, the electron transfer within the outer-sphere precursor complex dominates and is pressure-sensitive step in the mechanism. In such cases, the increased solvation and solvent rearrangement due to the charge creation result in large and negative $\Delta V^{\ddagger}{}_q$ values (*e.g.* -8.1 cm^3 mol^{-1} for $Cr(tfac)_3$, $\Delta G^0_{el} = 0.23$ V) [8,74]. This effect is more dramatic when nitrobenzenes are used as quencher; *e.g.* for *p*-chloronitrobenzene $\Delta V^{\ddagger}{}_q = -20.4$ cm^3 mol^{-1}, $\Delta G^0_{el} = 0.17$. Similar results were obtained in other solvents such as chloroform and tetrahydrofuran, indicating the generality of these pressure effects on bimolecular quenching of a metal-complex excited state by competitive energy and electron transfer [75].

Electron-transfer quenching of the MLCT state of $Cu(dmp)_2{}^+$ was also achieved by using Co(III) complexes in water/ethanol (70/30 vol.%) mixture [76]. The efficiency was rather low; the quantum yields for the loss of Cu(I) were of the order of 10^{-3} and proved to be sensitive to the nature of the Co(III) complex and to the polarity of the solvent.

4.2.3. Photocatalytic reactions

The quenching reactions via energy and electron transfer can be exploited for photocatalytic applications of $Cu(NN)_2{}^+$ complexes. The potential use of $Cu(dpp)_2{}^+$ as a photosensitizer for water splitting was studied in a system containing 9-carboxylate anthracene (AC^-) as relay for energy transfer, TEOA (2,2′,2″-triethanolamine) as sacrificial electron donor, MV^{2+} or *N*,*N*′-propylene 2,2′-bipyridinium (C_3-bpy) as electron acceptors, and colloidal Pt for H_2 generation from MV^+ or C_3-bpy^+ [77]. The main route to H_2 formation in this system proceeds via energy transfer between $^*Cu(dpp)_2{}^+$ and AC^- rather than through direct electron transfer quenching by MV^+. Thus, $Cu(dpp)_2{}^+$ is more advantageous in such systems than $Cu(dmp)_2^+$, having longer excited-state lifetime in polar solvents, owing to the more efficient shielding by the phenyl groups [77].

The photocatalytic reduction of Co(III) in 60/40 vol.% EtOH/H_2O mixture was realized by using mixed-ligand $Cu(NN)(PPh_3)_2{}^+$ complexes (NN = dmp or tmbpy = 4,4′,6,6′-tetramethyl-2,2′-bipyridine), upon excitation of the Cu(I) MLCT bands at about 360 nm [78]. The Cu(II) species formed were photochemically reduced by ethanol. A higher amount of water in the solvent system lengthened the lifetime of the excited Cu(I) complex, and thus improved its photocatalytic activity. This was also demonstrated by using MV^{2+} as electron acceptor [79]. When triphenylphosphine was replaced with larger phosphines such as cyclohexyldiphenylphosphine or tris(*p*-methoxyphenyl)phosphine, the excited state became longer-lived, and thus the quantum yield, Φ_{MV^+}, was enhanced [80].

$Cu(NN)_2{}^+$ complexes with longer-lived MLCT states can also be used for photocatalysis of organic reactions. For example, for conversion of nitrobenzyl halides into their bibenzylic coupling products, $Cu(dap)_2{}^+$ was successfully utilized as a redox sensitizer in CH_2Cl_2 [81].

$$^*Cu(dap)_2^+ + ArCH_2Br \rightarrow Cu(dap)_2^{2+} + ArCH_2^{\cdot} + Br^- \qquad (22)$$

In the absence of oxygen, bibenzylic product was formed from the radical through several different routes, while in aerated solutions nitrobenzaldehyde was produced almost quantitatively. Triethylamine was applied as sacrificial electron donor to recover $Cu(dap)_2{}^+$.

In aerated CH_3CN solution, phen and bpy complexes of copper(I) proved to be effective in photocatalytic ($\lambda_{ir} > 315$ nm) oxidation of phenol to parabenzoquinone [82].

4.2.4. Two-photon photochemistry

Upon irradiation of $Cu(dmp)_2{}^+$ by high-energy laser light at 354.7 nm in CH_2Cl_2 at 20°C photo-oxidation was observed and interpreted as a two-photon process [63].

$$Cu(dmp)_2^+ + CH_2Cl_2 \xrightarrow{2h\nu} Cu(dmp)_2^{2+} + Cl^- + \text{products} \qquad (23)$$

No formation of solvated electrons was experienced, in accordance with earlier results obtained in aqueous solution [32], indicating that two-photon absorption populates a high-lying, reactive excited state of the complex, which then, in interaction with the solvent, undergoes an outer-sphere electron transfer [83].

$$Cu(dmp)_2^+|S \xrightarrow{h\nu} {}^*Cu(dmp)_2^+|S \qquad (24)$$

$$^*Cu(dmp)_2^+|S \rightarrow Cu(dmp)_2^+|S + \text{energy} \qquad (25)$$

$$^*Cu(dmp)_2^+|S \xrightarrow{h\nu} {}^{**}Cu(dmp)_2^+|S \qquad (26)$$

$$^{**}\mathrm{Cu(dmp)_2^+|S \rightarrow {}^*Cu(dmp)_2^+|S + energy'} \qquad (27)$$

$$^{**}\mathrm{Cu(dmp)_2^+|\mathit{S} \rightarrow Cu(dmp)_2^{2+} + products} \qquad (28)$$

$Cu(dmp)_2{}^+|S$ designates the ground-state complex with one of the solvent molecules in the second solvation shell. In neat CH_3CN the reaction (*i.e.* bleaching rate) was about ten times slower than in CH_2Cl_2, and in neat CH_3OH no bleaching could be detected. Irradiation by a Xe lamp of 1000 W power did not cause any net reaction in CH_2Cl_2 solution either, confirming that a two-photon process is operative. High laser intensity is necessary so that the excitation by a second photon (eqn. (26)) can compete efficiently with the deactivation of $^*Cu(dmp)_2{}^+|S$ (eqn. (25)) [83]. The solvent dependence observed can be interpreted by this competition and that between reactions (27) and (28). The results obtained with $Cu(phen)_2{}^+$ were similar, but the lifetime of its first excited state was estimated to be about ten times shorter than that of $^*Cu(dmp)_2{}^+$, because it did not give measurable luminescence in CH_2Cl_2 solution. Thus, a saturation of its first excited (CT) state is much more difficult to achieve.

4.3. Miscellany

The trinuclear complexes, $[Cu_3(dpmp)_2(CH_3CN)_2(\mu\text{-}Cl)_2]^+$ (**I**) and $[Cu_3(dpmp)_2(CH_3CN)_2(\mu\text{-}I)_2]^+$ (**II**) (dpmp = bis(diphenylphosphinomethyl)-phenylphosphine) display an intense band at about 250 nm in CH_3CN, besides a substantial absorption around 300 nm [84]. Upon excitation in the 300–400 nm range at room temperature, they show luminescence ($\lambda_{em} = 530$ nm, $\tau = 1.7$ μs, $\Phi = 0.023$ for **I**; $\lambda_{em} = 560$ nm, $\tau = 3.1$ μs, $\Phi = 0.035$ for **II**) attributed to the metal-centered $3d^9s^1 \rightarrow 3d^{10}s^0$ transition. The excited-state complexes proved to be powerful reductants; their emission could be quenched via electron transfer by *N*-ethylpyridinium ion and $[Os^{VI}LO_2]^{2+}$ (L = *N*,*N*,*N'*,*N'*-3,6-hexamethyl-3,6-diazaoctane-1,8-diamine) as well, obtaining linear Stern–Volmer plots [84].

The studies on photoredox properties of heteronuclear $(NH_3)_5Co^{III}L\text{–}Cu^I$ complexes (L = bridging ligand, *e.g.* $NH_2(CH_2)_nCH{=}CH_2$ or $NC_5H_4(CH_2)_n\text{-}CH{=}CH_2$) revealed that irradiation of these coordination compounds in aqueous solution at 306 nm, exciting only the Cu(I)–olefin MLCT transition, led to intramolecular electron transfer between the metal ions [85].

$$6\ \mathrm{H^+ + (NH_3)_5Co^{III}L\text{–}Cu^I \xrightarrow{h\nu} Co^{II} + Cu^{II} + HL + 5\ NH_4^+} \qquad (29)$$

The quantum yields were significantly higher for aminoalkene ligands (0.3–0.9) than for 4-alkylpyridines (<0.005–0.15) and dropped regularly as the number of methylene units in the bridging chain was increased.

Flash photolysis of the Cu(I) macrocyclic complex, $Cu^I(2,3,9,10\text{-}Me_4\text{-}[14]\text{-}1,3,8,10\text{-}tetraeneN_4)^+$, bound to poly(acrylic acid), resulted in the formation of metastable Cu^{II}(ligand radical)-poly(acrylate) in aqueous solution [86]. No photoreactivity of this complex was, however, experienced in methanol.

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APPENDIX: ABBREVIATIONS

bpy	2,2′-bipyridine
biq	2,2′-biquinoline
CTTS	charge transfer from complex to solvent
dap	2,9-bis(*p*-anisyl)-1,10-phenanthroline
dmp	2,9-dimethyl-1,10-phenanthroline
dpp	2,9-diphenyl-1,10-phenanthroline
f	oscillator strength
HE	high-energy
hfac	hexafluoroacetylacetonate
LE	low-energy
MV^{2+}	methylviologen
MLCT	charge transfer from the central atom to ligand
μ	ionic strength
PGP	primary geminate pair
phen	1,10-phenanthroline
py	pyridine
SGP	secondary geminate pair
tfac	1,1,1-trifluoro-2,4-pentanedionate
$\Delta V^{\ddagger}_{q}$	activation volume of quenching reaction