ELSEVIER

Inorganica Chimica Acta 225 (1994) 251–254

Inorganica Chimica Acta

Photophysical properties of mono-, di- and tetranuclear copper(I)–polypyridine complexes

Alberto Juris[a,*], Raymond Ziessel[b,*]

[a]Dipartimento di Chimica 'G. Ciamician', Università di Bologna, via Selmi 2, I-40126 Bologna, Italy

[b]Laboratoire de Chimie, d'Electronique et de Photonique Moléculaires, Ecole Europénne des Hautes Etudes des Industries Chimiques de Strasbourg, IPCMS/GMI, 1 rue Blaise Pascal, F-67008 Strasbourg, France

Received 14 April 1994

Abstract

We report results concerning the absorption spectra, luminescence spectra, luminescence lifetimes and emission quantum yields for two dinuclear copper(I) complexes $[Cu(L_1)]_2(ClO_4)_2$, (C_1), and $[Cu(L_2)]_2(ClO_4)_2$ (C_2), (L_1 = 1,2-bis(9-methyl-1,10-phenanthrolin-2-yl)ethane and L_2 = 1,2-bis(6′-methyl-2,2′-bipyridin-6-yl)ethane). For both complexes the lowest energy absorption band is metal-to-ligand charge transfer (MLCT) in nature, involving the oligopyridine ligand. The luminescence observed both at 77 K and at room temperature is due to an emitting MLCT level. Related mono-, di- and tetranuclear copper(I) complexes $\mathbf{C_3}$ to $\mathbf{C_5}$ were not found to emit showing that the metal is weakly protected from the surrounding medium. $\mathbf{C_3}$ = $[Cu(L_3)]_2(ClO_4)_2$ (L_3 = 5,5′,3″,5‴-tetramethyl-2,2′:6′,2″:6″,2‴-quaterpyridine); $\mathbf{C_4}$ = $[Cu(L_4)]BF_4$) (L_4 = bpy·bpy macrocycle); $\mathbf{C_5}$ = $[Cu_4(L_5)_2](ClO_4)_4$ (L_5 = 8,21-bis[(9-methyl-1,10-phenanthrolin-2-yl)methyl]-8,21,27,28,29,30-hexaazapentacyclo[21.3.1.1^{2,6}.1^{10,14}.1^{15,19}]triaconta-1(27),2,4,6(30),10,12,14(29),15,17,19(28),23,25-dodecaene).

Keywords: Photophysics; Copper complexes; Polypyridine complexes; Polynuclear complexes; Helicates; Macrocates

1. Introduction

The photophysical properties of Cu(I)–polypyridine complexes are attracting much attention since the discovery of the emission properties of $[Cu(dmphen)_2]^+$ (dmphen = 2,9-dimethyl-1,10-phenanthroline) [1]. This field of research has been the object of several reviews [2–4]. The chemistry of Cu(I) is also particularly interesting as it gives rise to a variety of structures, such as helicates [5], catenates [6], molecular knots [7] and macrocates [8]. Of recent interest is also the spontaneous and selective formation of double-stranded copper helicates [5] or copper macrocates [8] by a self-assembly process. Here we report on the photophysical properties of five Cu(I)–polypyridine compounds. Three of them are dimetallic helicate complexes: $[Cu(L_1)]_2(ClO_4)_2$ ($\mathbf{C_1}$) (L_1 = 1,2-bis(9-methyl-1,10-phenanthrolin-2-yl)ethane); $[Cu(L_2)]_2(ClO_4)_2$ ($\mathbf{C_2}$) (L_2 = 1,2-bis(6′-methyl-2,2′-bipyridin-6-yl)ethane); $[Cu(L_3)]_2(ClO_4)_2$ ($\mathbf{C_3}$) (L_3 = 5,5′,3″,5‴-tetramethyl-2,2′:6′,2″:6″,2‴-quaterpyridine). The macrocate precursor is a mononuclear copper(I) complex, $[Cu(L_4)](BF_4)$ ($\mathbf{C_4}$) (L_4 = bpy·bpy macrocycle), and the macrocate itself is a tetranuclear copper(I) complex, $[Cu_4(L_5)_2](ClO_4)_4$ ($\mathbf{C_5}$) (L_5 = 8,21-bis[(9-methyl-1,10-phenanthrolin-2-yl)methyl]-8,21,27,28,29,30-hexaazapentacyclo[21.3.1.1^{2,6}.1^{10,14}.1^{15,19}]triaconta-1(27),2,4,6-(30),10,12,14(29),15,17,19(28),23,25-dodecaene). Fig. 1 illustrates the formulas of the ligands and complexes studied. The structure and some physicochemical properties of the helicate and macrocate complexes have already been published [9–11].

*Corresponding authors.

2. Materials and methods

Preparations of the ligands (L_1 [12], L_2 [12], L_3 [9], L_4 [13] and L_5 [14]) and of the complexes ($\mathbf{C_1}$ [10], $\mathbf{C_2}$ [10], $\mathbf{C_3}$ [9], $\mathbf{C_4}$ [8] and $\mathbf{C_5}$ [8]) have previously been published. For the photophysical measurements spectroquality methylene chloride was used as received (Uvasol Merck).

Absorption spectra were obtained in CH_2Cl_2 or CH_3CN solution at room temperature by means of a Perkin-Elmer Lambda-6 spectrophotometer. Lumines-

SSDI 0020-1693(94)04054-Y

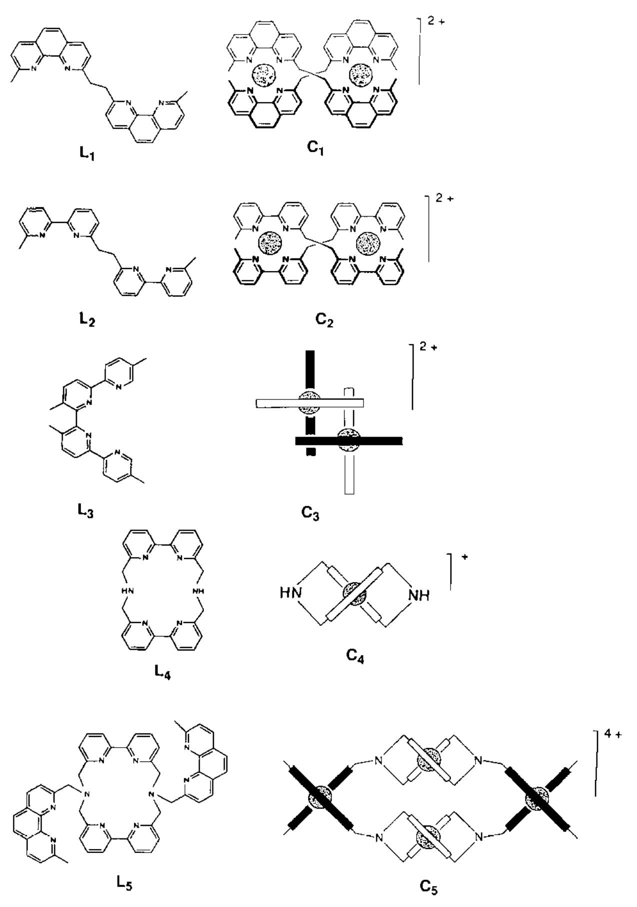

Fig. 1. Structural formulae for the ligands and schematic representation of their copper(I) complexes. ⊛ = Cu(I).

cence spectra were obtained with a Perkin-Elmer LS-50 spectrofluorimeter. Emission lifetimes were measured with an Edinburgh 199 single-photon counting equipment. Emission quantum yields were measured at room temperature (20 °C) with the optically dilute method [15] calibrating the spectrofluorimeter with a standard lamp. $[Ru(bpy)_3]^{2+}$ in aerated aqueous solution was used as a quantum yield standard, assuming a value of 0.028 [16]. When necessary, samples were deaerated by repeated freeze–pump–thaw cycles.

3. Results and discussion

Absorption spectra

The absorption spectrum of $\mathbf{C_1}$, $\mathbf{C_2}$ and $\mathbf{C_5}$ is practically unaffected during 2–3 days in CH_2Cl_2 solution. The absorption spectrum of $\mathbf{C_3}$ and $\mathbf{C_4}$, on the contrary, shows some modification. To avoid any problem, measurements were performed on freshly prepared solutions. Fig. 2 shows the absorption spectrum of compounds $\mathbf{C_1}$ and $\mathbf{C_2}$; Table 1 collects absorption data for all of the complexes, together with literature data

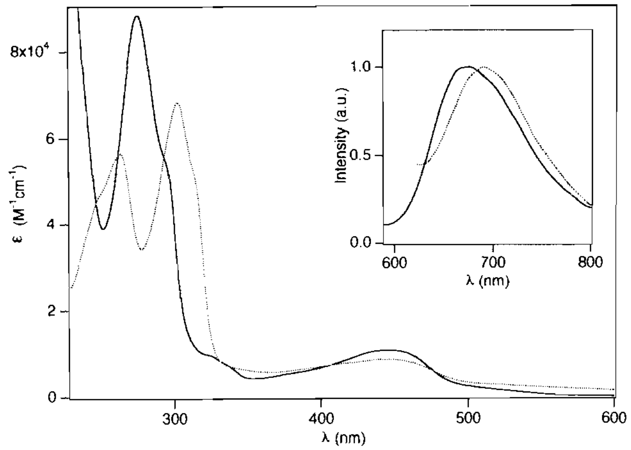

Fig. 2. Absorption spectra at room temperature and (inset) uncorrected emission spectra at 77 K of compounds $\mathbf{C_1}$ (full line) and $\mathbf{C_2}$ (dotted line) in dichloromethane solution.

for the complexes $[Cu(dmphen)_2]^+$ and $[Cu(tmbpy)_2]^+$ (tmbpy = 4,4′,6,6′-tetramethyl-2,2′-bipyridine), which can be considered as monometallic analogues of $\mathbf{C_1}$ and $\mathbf{C_2}$, respectively.

The absorption spectrum of all of the compounds $\mathbf{C_1}$–$\mathbf{C_5}$ in the range 250–400 nm features very intense bands, with a shape and position similar to the absorption spectra of the respective free ligands. Small perturbations are expected on passing from the free ligand to the complex [17], and thus these UV bands of the complexes can be safely classified as intra-ligand (IL).

All of the compounds $\mathbf{C_1}$–$\mathbf{C_5}$ also display less intense bands (or shoulders) in the visible region, as listed in Table 1. Such bands (not present in the free ligand absorption spectrum) are typically present in Cu(I)–polypyridine complexes [4], and can be assigned as metal-to-ligand charge transfer (MLCT) transitions.

Emission properties

Only compounds $\mathbf{C_1}$ and $\mathbf{C_2}$ luminesce, both in the glass (77 K) and in fluid solution (room temperature) in a non-coordinating solvent like CH_2Cl_2. No luminescence is, on the contrary, observed in Lewis base solvents like MeOH or acetonitrile, that are known to quench Cu(I) emission [1,4]. Compounds $\mathbf{C_3}$, $\mathbf{C_4}$ and $\mathbf{C_5}$ were found to be non-luminescent, irrespective of the temperature and of the solvents employed (MeOH, CH_2Cl_2). Uncorrected emission spectra at 77 K for compounds $\mathbf{C_1}$ and $\mathbf{C_2}$ are shown in Fig. 2. Corrected luminescence emission maxima, quantum yields and lifetime values have been gathered in Table 1. As far as the 77 K measurements are concerned, the CH_2Cl_2 solution becomes opaque on freezing, but the emission intensity is sufficiently high to allow a clean detection of the luminescence signal.

The 77 K data (position and shape of the emission band and lifetime values) indicate that the emitting

Table 1
Spectroscopic and photophysical data[a]

Compound	Absorption[b] 298 K	Luminescence[c]				
		298 K			77 K	
	λ_{max} (nm) (ϵ)	λ_{max} (nm)	τ (ns)	Φ_{em}	λ_{max} (nm)	τ (μs)
C1	445 (10900)	663	16	1.0×10^{-4}	672	1.89
C2	445 (8760)	670	13	0.4×10^{-4}	690	0.335
C3	454 (12700)[d]					
C4	460 sh[d]					
C5	456 (11800)[d]					
$[Cu(dmphen)_2]^{+}$[e]	454 (7950)	670	90	2.1×10^{-4}		1.90[f]
$[Cu(tmbpy)_2]^{+}$[e]	454 (7180)	680	18	0.5×10^{-4}		

[a]In CH_2Cl_2 solution, unless otherwise noted.
[b]Lowest energy spin-allowed band.
[c]Emission maxima are corrected; luminescence lifetimes and quantum yield values in deaerated solution.
[d]In CH_3CN solution.
[e]Ref. [18].
[f]In 4:1 vol./vol. ethanol–methanol.

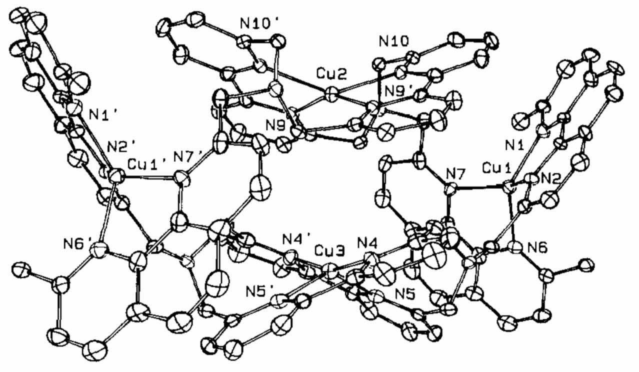

Fig. 3. X-ray crystal structure of the copper(I) macrocate complex C_5 [8]. The two copper ions (Cu2 and Cu3) lie on the C_2 axis of the molecule.

level is MLCT in nature, as typically observed in Cu(I)–polypyridine complexes [3,4]. Compound $\mathbf{C_2}$ features a shorter lifetime with respect to $\mathbf{C_1}$. In this regard, it should be noted that ligand L_2 is more flexible than L_1, and it is known that ligand flexibility enhances excited state deactivation via radiationless transitions.

Moving to room temperature (Table 1) the lifetime becomes much shorter, the emission intensity weakens, and the emission quantum yields are very low. Luminescence behavior appears very similar to that featured by $[Cu(dmphen)_2]^+$ and $[Cu(tmbpy)_2]^+$, i.e., the monometallic analogues of $\mathbf{C_1}$ and $\mathbf{C_2}$ (Table 1). While the room-temperature emission of $\mathbf{C_2}$ is hardly detectable, the emission band of $\mathbf{C_1}$ can be neatly measured. This is in contrast with the results previously obtained by Yao et al. [11] who did not detect any luminescence from $\mathbf{C_1}$ at room temperature. Control experiments indicate that the emission we observe does indeed originate from $\mathbf{C_1}$. We performed also an excitation spectrum monitoring emission at the maximum of the luminescence band obtaining a good match with the absorption spectrum.

From the data reported in Table 1 it can be seen that on passing from room temperature to 77 K the emission band undergoes a red shift. For $\mathbf{C_1}$ this red shift is ~ 100 cm^{-1}. In the case of $\mathbf{C_2}$ the emission is much weaker, causing some uncertainty in the determination of the shift, that appears to be ~ 400 cm^{-1}. Also a greater red shift of the luminescence band on lowering the temperature has been observed in Cu(I)–polypyridine complexes. For example, Kirchhoff et al. [18] observed a red shift of about 700 cm^{-1} for $[Cu(dmphen)_2]^+$ in CH_2Cl_2 on passing from +24 to −35 °C; Parker and Crosby [19] observed a red shift of about 1000 cm^{-1} for $[Cu(bathocuproine)_2]^+$ in poly(methylmethacrylate) matrix (bathocuproine = 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline). This red shift has been attributed to the fact that emission originates from two closely spaced electronic states, and the higher energy one has a more favorable radiative rate constant [18–20]. Luminescence polarization experiments led to the conclusion [20] that these two emissive states originate from a singlet and a triplet CT level, associated with different electronic configurations.

It is worth noting that $\mathbf{C_2}$ is, to our knowledge, the second example of an emitting Cu(I) complex containing a 'bpy' ligand, the first one being $[Cu(tmbpy)_2]^+$ [18,20]. Differently from tmbpy, our ligand does not carry any methyl substituent in the 4,4′-positions. The presence of sterically protecting substituents in the 6,6′-positions in complex $\mathbf{C_2}$ is evidently sufficient to guarantee steric protection of the metal center [2,4,20–22], thus allowing luminescence emission.

As far as the lack of luminescence from compounds $\mathbf{C_3}$, $\mathbf{C_4}$ and $\mathbf{C_5}$ is concerned, the following considerations can be made. In compound $\mathbf{C_3}$ the ligand L_3 does not carry two substituents in the 'steric' positions (vide supra). For compound $\mathbf{C_4}$ the cyclic ligand imposes a considerably flattened structure to the complex, with dihedral angles between the two chelate subunits significantly different from 90°. This last consideration holds also for the tetramer $\mathbf{C_5}$, in which the dihedral angles for the two mean planes of the bpy units (N4/N5′ and N4′/N5 or N9/N10′ and N9′/N10) deviate from the ideal value of 90° by 35° and 34°, respectively, and for the phen (N1/N2 and N6/N7) by an angle of 22° (see Fig. 3). The distortion of the tetrahedral arrangement of the CuN_4 core is much less pronounced in complexes $\mathbf{C_1}$ and $\mathbf{C_2}$ (9° for the phen [11]; 3° and 8° for the two bpy complexation sites [10]). Thus, in all these three cases, $\mathbf{C_3}$–$\mathbf{C_5}$, the ligand does not efficiently protect the metal ion from the surrounding medium. As said before, this appears to be a requisite to observe luminescence from Cu(I)–polypyridine complexes; otherwise, deactivation via non-radiative processes dominates.

Acknowledgements

Financial support from the Ministero dell'Università e della Ricerca Scientifica e Tecnologica and the Centre National de la Recherche Scientifique is gratefully acknowledged. We also thank Dr M.-T. Youinou for helpful discussions.

References

[1] M.W. Blaskie and D.R. McMillin, *Inorg. Chem., 19* (1980) 3519.
[2] D.R. McMillin, J.R. Kirchhoff and K.V. Goodwin, *Coord. Chem. Rev., 64* (1985) 83.
[3] C. Kutal, *Coord. Chem. Rev., 99* (1990) 213.
[4] K. Kalyanasundaram, *Photochemistry of Polypyridine and Porphyrin Complexes,* Academic Press, London, 1991, Ch. 9.
[5] (a) J.-M. Lehn, A. Rigault, J. Siegel, J. Harrowfield, B. Chevrier and D. Moras, *Proc. Natl. Acad. Sci. U.S.A., 84* (1987) 2565; (b) J.-M. Lehn and A. Rigault, *Angew. Chem., Int. Ed. Engl., 27* (1988) 1095; (c) T.M. Garrett, U. Koert, J.-M. Lehn, A. Rigault, D. Meyer and J. Fischer, *J. Chem. Soc., Chem. Commun.,* (1990) 557.
[6] (a) C.O. Dietrich-Buchecker, J. Guilhem, A.K. Khemiss, J.-P. Kintzinger, C. Pascard and J.-P. Sauvage, *Angew. Chem., Int. Ed. Engl., 26* (1987) 661; (b) J.-P. Sauvage, *Acc. Chem. Res., 23* (1990) 319; (c) N. Armaroli, L. De Cola, V. Balzani, J.-P. Sauvage, C.O. Dietrich-Buchecker, J.-M. Kern and A. Bailal, *J. Chem. Soc., Dalton Trans.,* (1993) 3241.
[7] (a) C.O. Dietrich-Buchecker and J.-P. Sauvage, *Angew. Chem., Int. Ed. Engl., 28* (1989) 189; (b) C.O. Dietrich-Buchecker, J. Guilhem, C. Pascard and J.-P. Sauvage, *Angew. Chem., Int. Ed. Engl., 29* (1990) 1154; (c) C.O. Dietrich-Buchecker, J.-F. Nierengarten and J.-P. Sauvage, *Tetrahedron Lett., 33* (1992) 3625; (d) C.O. Dietrich-Buchecker, J.-F. Nierengarten, J.-P. Sauvage, N. Armaroli, V. Balzani and L. De Cola, *J. Am. Chem. Soc., 115* (1993) 11237.
[8] R. Ziessel and M.-T. Youinou, *Angew. Chem., Int. Ed. Engl., 32* (1993) 877.
[9] J.-M. Lehn, J.-P. Sauvage, J. Simon, R. Ziessel, C. Piccinni-Leopardi, G. Germain, J.-P. Declercq and M. Van Meerssche, *Nouv. J. Chim., 7* (1983) 4133.
[10] M.-T. Youinou, R. Ziessel and J.-M. Lehn, *Inorg. Chem., 30* (1991) 2144.
[11] Y. Yao, M.W. Perkovic, D.P. Rillema and C. Woods, *Inorg. Chem., 31* (1992) 3956.
[12] J.-M. Lehn and R. Ziessel, *Helv. Chim. Acta, 71* (1988) 1511.
[13] G.R. Newkome, R. Pappalardo, V.K. Gupta and F.R. Fronczek, *J. Org. Chem., 48* (1983) 4848.
[14] N. Sabbatini, M. Guardigli, I. Manet, F. Bolletta and R. Ziessel, *Inorg. Chem., 33* (1994) 955.
[15] J.N. Demas and G.A. Crosby, *J. Phys. Chem., 75* (1971) 991.
[16] K. Nakamaru, *Bull. Chem. Soc. Jpn., 55* (1982) 2697.
[17] G.A. Crosby, *Acc. Chem. Res., 8* (1975) 231.
[18] J.R. Kirchhoff, R.E. Gamache, Jr., M.W. Blaskie, A.A. Del Paggio, R.K. Lengel and D.R. McMillin, *Inorg. Chem., 22* (1983) 2380.
[19] W.L. Parker and G.A. Crosby, *J. Phys. Chem., 93* (1989) 5692.
[20] R.M. Everly and D.R. McMillin, *J. Phys. Chem., 95* (1991) 9071, and refs. therein.
[21] C.O. Dietrich-Buchecker, P.A. Marnot, J.-P. Sauvage, J.R. Kirchhoff and D.R. McMillin, *J. Chem. Soc., Chem. Commun.,* (1983) 513, and refs. therein.
[22] R.M. Everly, R. Ziessel, J. Suffert and D.R. McMillin, *Inorg. Chem., 30* (1991) 559.