Synthesis, Photophysical and Electrochemical Properties of Luminescent Dinuclear Copper(I) Diimines

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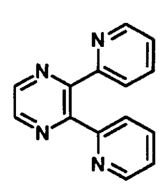
Reaction of $[Cu(PPh_3)_2(MeCN)_2]BF_4$ with bridging diimine ligands (L) in CH_2Cl_2 gave dinuclear copper(I) complexes $[\{Cu(PPh_3)_2\}_2L]^{2+}$ [L = 2,3-bis(2-pyridyl)pyrazine, 6,7-dimethyl-2,3-bis(2-pyridyl)quinoxaline, 2,3-bis(2-pyridyl)quinoxaline, 6,7-dichloro-2,3-bis(2-pyridyl)quinoxaline or 2,3-bis(2-pyridyl)benzo[*g*]quinoxaline], which exhibit rich photophysical and electrochemical properties.

Copper(I) diimine complexes have been shown to be effective redox photocatalysts[1] and recently their interactions with biopolymers have also been widely investigated.[2] However, these complexes are generally limited to mononuclear species while the photochemistry of copper(I) supramolecules[3] is relatively not as extensively explored as that of the ruthenium(II) diimine systems.[4] In this communication we report a series of dinuclear copper(I) complexes bridged by 2,3-bis(2-pyridyl)pyrazine and its analogues. Polyazines of this type have been employed previously to co-ordinate with metal centres such as Ru^{II},[5a] Os^{II}[5b] and Re^{I}.[5c] We believe that their co-ordination to copper(I) would also show interesting spectroscopic and electrochemical tunabilities through the systematic variation of the diimine ligands.

All the complexes **1**–**5** were prepared by addition of 0.5 equivalent of the corresponding azine[6] to the precursor complex $[Cu(PPh_3)_2(MeCN)_2]BF_4$ in CH_2Cl_2 under an inert atmosphere of nitrogen. Crystals were obtained, in high yields, by vapour diffusion of diethyl ether into concentrated dichloromethane solutions of the complexes. All the compounds gave satisfactory elemental analyses and have been characterized by ^1H NMR and FAB mass spectroscopy.[†,‡]

The electronic absorption, luminescence, and cyclic voltammetric data of the complexes are collected in Table 1. All show intense absorption bands typical of metal-to-ligand charge transfer (m.l.c.t.) $[d(Cu) \longrightarrow \pi^*(L)]$ in the 400–600 nm region in CH_2Cl_2 (Fig. 1). The transition energies of these absorptions follow the order $[\{Cu(PPh_3)_2\}_2(dppyz)]^{2+}$ **1** > $[\{Cu(PPh_3)_2\}_2(dmdpq)]^{2+}$ **2** > $[\{Cu(PPh_3)_2\}_2(dpq)]^{2+}$ **3** > $[\{Cu(PPh_3)_2\}_2(dcdpq)]^{2+}$ **4** > $[\{Cu(PPh_3)_2\}_2(dpbq)]^{2+}$ **5**, in accordance with the expected decrease in the π^* orbital energies of the bridging ligands. Similar trends have been observed in other solvents although the absorption coefficients in EtOH and MeOH are slightly lower compared with those in CH_2Cl_2 and $CHCl_3$. In acetonitrile solutions, the m.l.c.t. bands are blue-shifted relative to those found in the less-polar solvents and their intensities decrease significantly. This might arise as a result of displacement of the diimine bridging ligands by the co-ordinating acetonitrile, which has a high affinity towards copper(I) metal centres. However, in general, the m.l.c.t. bands occur at lower energies in low-polarity solvents such as dichloromethane and chloroform and at higher energies in high-polarity solvents such as ethanol and methanol. Solvatochromism of this type has been attributed to a larger outer-sphere reorganization energy in polar solvents assuming the dielectric continuum model,[7a] and has also been observed in other m.l.c.t. systems.[7b]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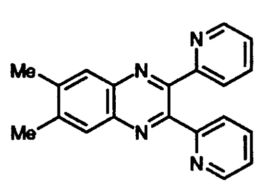
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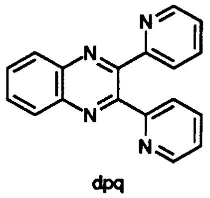
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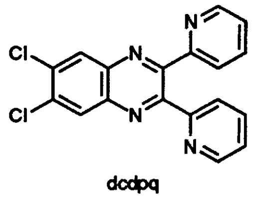
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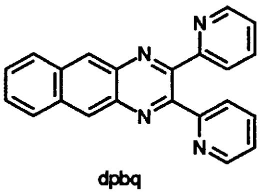
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The electronic absorption spectroscopy of the complexes in CH_2Cl_2 has been studied in detail. Unlike $[Cu(PPh_3)_2(dmphen)]^+$ (dmphen = 2,9-dimethyl-1,10-phenanthroline),[8] dissolution of **1** in CH_2Cl_2 did not generate the ligand-scrambled product, $[Cu(dppyz)_2]^+$, which is expected to absorb at lower energies. Moreover, the m.l.c.t. band at *ca.* 418 nm obeys the Beer–Lambert law, suggestive of minimum triphenylphosphine dissociation. This indicates that the dinuclear complex remains intact in solution. However, addition of an excess of PPh_3 to a CH_2Cl_2 solution of **1** gave an electronic spectrum in which the m.l.c.t. band intensity was substantially reduced and a blue shift in energy to λ 372 nm was observed, typical of the mononuclear $[Cu(PPh_3)_2(dppyz)]^+$ species,

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[†] $[\{Cu(PPh_3)_2\}_2(dppyz)][PF_6]_2\cdot CH_2Cl_2$ **1** (Found: C, 58.6; H, 3.9; N, 3.1. Calc. C, 58.5; H, 4.1; N, 3.1%): ^1H NMR (270 MHz, CD_2Cl_2, 298 K) δ 8.5 (m, 4 H, dppyz), 7.9 (m, 2 H, dppyz) and 7.5–7.1 (m, 64 H, dppyz and PPh_3); positive FAB mass spectrum, ion clusters at *m*/*z* 884, $[\{Cu(PPh_3)\}_2(dppyz)]^+$; 587, $[Cu(PPh_3)_2]^+$; and 559, $[Cu(PPh_3)(dppyz)]^+$. $[\{Cu(PPh_3)_2\}_2(dmdpq)][BF_4]_2\cdot 2H_2O$ **2** (Found: C, 64.8; H, 4.5; N, 3.1. Calc. C, 65.1; H, 4.8; N, 3.3%): ^1H NMR δ 8.6 (m, 2 H, dmdpq), 7.9 (m, 2 H, dmdpq), 7.5–7.1 (m, 66 H, dmdpq and PPh_3) and 2.0 (s, 6 H, Me); positive FAB mass spectrum, ion clusters at *m*/*z* 962, $[\{Cu(PPh_3)\}_2(dmdpq)]^+$; 587, $[Cu(PPh_3)_2]^+$; and 637, $[Cu(PPh_3)(dmdpq)]^+$. $[\{Cu(PPh_3)_2\}_2(dpq)][BF_4]_2\cdot 0.5CH_2Cl_2$ **3** (Found: C, 64.7; H, 4.3; N, 3.1. Calc. C, 64.8; H, 4.4; N, 3.3%): ^1H NMR δ 8.6 (m, 2 H, dpq), 7.9 (m, 2 H, dpq) and 7.6–7.1 (m, 68 H, dpq and PPh_3); positive FAB mass spectrum, ion clusters at *m*/*z* 934, $[\{Cu(PPh_3)\}_2(dpq)]^+$; 587, $[Cu(PPh_3)_2]^+$ and 609, $[Cu(PPh_3)(dpq)]^+$. $[\{Cu(PPh_3)_2\}_2(dcdpq)][BF_4]_2$ **4** (Found: C, 63.4; H, 4.0; N, 3.2. Calc. C, 63.5; H, 4.1; N, 3.3%): ^1H NMR δ 8.6 (m, 2 H, dcdpq), 8.0–7.6 (m, 8 H, dcdpq) and 7.4–7.1 (m, 60 H, PPh_3); positive FAB mass spectrum, ion clusters at *m*/*z* 1002, $[\{Cu(PPh_3)\}_2(dcdpq)]^+$; 587, $[Cu(PPh_3)_2]^+$; and 677, $[Cu(PPh_3)(dcdpq)]^+$. $[\{Cu(PPh_3)_2\}_2(dpbq)][BF_4]_2\cdot H_2O$ **5** (Found: C, 66.4; H, 4.3; N, 3.2. Calc. C, 66.3; H, 4.5; N, 3.3%): ^1H NMR δ 8.7 (m, 2 H, dpbq), 8.3 (m, 2 H, dpbq), 8.0 (m, 2 H, dpbq) and 7.7–7.1 (m, 68 H, dpbq and PPh_3); positive FAB mass spectrum, ion clusters at *m*/*z* 984, $[\{Cu(PPh_3)\}_2(dpbq)]^+$; 587, $[Cu(PPh_3)_2]^+$; 659, $[Cu(PPh_3)(dpbq)]^+$.

[‡] The crystal structure of **1** has also been determined (to be published elsewhere).

Table 1 Photophysical and electrochemical data for complexes **1–5**

	^{1}m.l.c.t. absorption (298 K), λ/nm (ε/dm^3 mol^{-1} cm^{-1})						^{3}m.l.c.t. emission,[a] λ/nm			Oxidation	Reduction
Complex	CH_2Cl_2	$CHCl_3$	Me_2CO	EtOH	MeOH	MeCN	CH_2Cl_2 (298 K)	Solid state	Alcohol glass[d]	E_{pa}/V *vs.* SCE[b]	$E_{\frac{1}{2}}$/V *vs.* SCE[c]
1	418 (5655)	417 (6990)	396 (4815)	387 (3995)	386 (3900)	363 (sh) (1490)	650	635 (298 K) 680 (77 K)	652	+1.25	−1.01
2	477 (4550)	471 (4595)	454 (sh) (4300)	420 (sh) (1665) 504 (sh) (3140)	419 (sh) (2980) 474 (sh) (3630)	415 (sh) (1640)	692	670 (298 K) 705 (77 K)	686	+1.51	−0.82
3	476 (3815)	478 (4455)	420 (sh) (4225)	416 (sh) (2715)	408 (sh) (2790)	410 (sh) (970)	708	675 (298 K) 708 (77 K)	710	+1.32	−0.67
4	482 (2900)	470 (2960)	437 (sh) (2780)	423 (sh) (2395)	420 (sh) (2245)	418 (sh) (495)	726	732 (298 K) 710 (77 K)	720	+1.63	−0.53 −1.43
5	496 (sh) (4415) 538 (sh) (4285)	482 (sh) (4520) 514 (sh) (4515)	475 (sh) (3860)	477 (sh) (3520) 563 (sh) (1480)	473 (sh) (3430) 558 (sh) (1585)	464 (sh) (1875)	770	828 (298 K) 827 (77 K)	740	+1.65	−0.52 −1.31

[a] All values were not corrected for instrumental response. [b] In CH_2Cl_2 (0.1 mol dm^{-3} $NBu^n{}_4PF_6$), glassy carbon electrode, scan rate 100 mV s^{-1}, 298 K; E_{pa} is the anodic peak potential. [c] For these quasi-reversible couples $E_{\frac{1}{2}}$ is the average of E_{pa} and E_{pc}. [d] EtOH–MeOH (4:1), at 77 K.

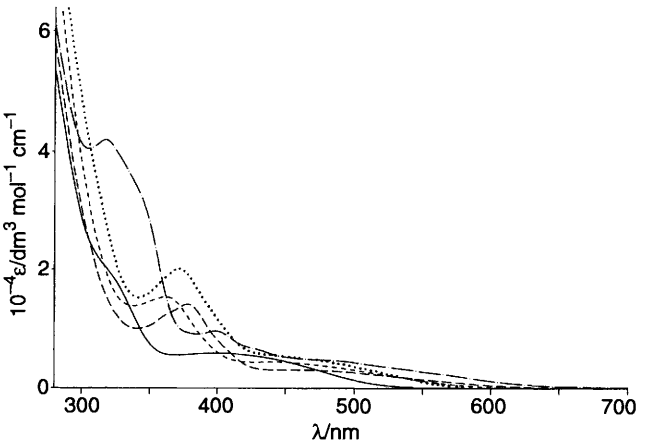

Fig. 1 Electronic absorption spectra of complexes **1** (——), **2** (· · · ·), **3** (- - - -), **4** (— — —) and **5** (— · —) in CH_2Cl_2 at 298 K

generated by mixing of $[Cu(PPh_3)_2(MeCN)_2]^+$ and dppyz in a 1:1 molar ratio in CH_2Cl_2. The m.l.c.t. absorption of **1** at lower energies than those of its mononuclear counterpart is in line with the greater electron deficiency of the bridged dppyz ligand.[9] Similar observations have been made for the other dinuclear complexes **2–5**. It is likely that the addition of free PPh_3 would actually degrade the complexes leading to the formation of mononuclear species [equation (1)].

$$[\{Cu(PPh_3)_2\}_2L]^{2+} + 2PPh_3 \longrightarrow [Cu(PPh_3)_2L]^+ + [Cu(PPh_3)_4]^+ \quad (1)$$

Excitation of the complexes in the solid state and in fluid solutions at λ > 350 nm resulted in a high-energy intraligand emission at *ca.* 400–500 nm and an orange-to-red low-energy emission at *ca.* 600–750 nm. Such dual luminescent behaviour has been observed in related copper(I) diimine systems.[8,10] The low-energy emission is likely to originate from the ^{3}m.l.c.t. state. The emission energies of the low-energy band follow the same order as those observed in the electronic absorption spectra.

Cyclic voltammetric studies of complexes **1–5** in CH_2Cl_2 solution revealed an irreversible oxidation wave and quasi-reversible reduction couples, the latter being attributed to ligand-based reductions. The ease of these diimine ligand-centred reductions follows the order dppyz < dmdpq < dpq < dcdpq < dpbq in accordance with the increasing stabilization of the π* orbitals. Assuming the irreversible oxidation wave to be metal-centred in nature and a zero–zero spectroscopic energy (E_{0-0}) of 2.25 eV (*ca.* 3.6 × 10^{-19} J), estimated from the m.l.c.t. absorption and emission data, an excited-state reduction potential, $E°(Cu^ICu^{II}–Cu^ICu^{I*})$ of < −1.0 V *vs.* saturated calomel electrode (SCE) can be determined for **1**. It is therefore envisaged that this series of dinuclear complexes would exhibit rich photoredox chemistry.

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