Photoredox Properties of Luminescent Trinuclear Copper(I) Complexes with a Bridging Phosphine Ligand and Crystal Structure of $[Cu_3(dpmp)_2(MeCN)_2(\mu\text{-}Cl)_2]ClO_4$ [dpmp = Bis(diphenylphosphinomethyl)phenylphosphine]†

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The complexes $[Cu_3(dpmp)_2(MeCN)_2(\mu\text{-}X)_2]ClO_4$ were prepared by the reaction of CuX (X = Cl or I) with bis(diphenylphosphinomethyl)phenylphosphine (dpmp) in methanol followed by recrystallisation from acetonitrile. The complex cation $[Cu_3(dpmp)_2(MeCN)_2(\mu\text{-}Cl)_2]^+$ [triclinic, space group $P\bar{1}$ (no. 2), $a = 12.839(1)$, $b = 13.582(3)$, $c = 21.510(3)$ Å, $\alpha = 84.06(1)$, $\beta = 72.71(1)$, $\gamma = 78.00(1)^\circ$, $Z = 2$, $R = 0.083$ for 11 520 unique Mo-Kα data] consists of three copper(I) ions bridged by two chloride ions on the same side and by two dpmp ligands. The intramolecular Cu $\cdots$ Cu separations are 3.26 and 3.30 Å indicating no metal–metal interaction. Both $[Cu_3(dpmp)_2(MeCN)_2(\mu\text{-}Cl)_2]ClO_4$ and $[Cu_3(dpmp)_2(MeCN)_2(\mu\text{-}I)_2]ClO_4$ display room-temperature photoluminescence at 530 and 560 nm respectively. The photoredox properties of $[Cu_3(dpmp)_2(MeCN)_2(\mu\text{-}Cl)_2]^+$ have been investigated by flash photolysis and Stern–Volmer quenching experiments.

The photophysics and photochemistry of polynuclear d^{10} metal complexes continue to attract much attention.[1–6] Recently we have reported the photoluminescence and excited-state chemistry of polynuclear gold(I) complexes of bridging phosphines.[1a–c,e] Knowing the versatility of the tridentate ligands dpmp and dmmp [dpmp = bis(diphenylphosphinomethyl)phenylphosphine, dmmp = bis(dimethylphosphinomethyl)methylphosphine] in constructing trinuclear metal complexes,[1,7,8] the complexes $[Au_3(dmmp)_2][ClO_4]_3$[1a] and $[Ag_3(dpmp)_2(MeCN)_2][ClO_4]$[1c] were synthesised and found to display intriguing spectroscopic properties and photoluminescence in fluid solution at room temperature. Herein we describe the structure and photoredox properties of trimeric halide-bridged copper(I) complexes $[Cu_3(dpmp)_2(MeCN)_2(\mu\text{-}X)_2]ClO_4$ (X = Cl **1** or I **2**). Being built in a simple fashion, these two complexes may serve as models for understanding the photophysical behaviour of and metal–metal interaction in polynuclear halide-bridged copper(I) clusters.

Experimental

N-Ethylpyridinium hexafluorophosphate[1b] and the ligand dpmp were prepared by published methods. Acetonitrile (Ajax AR) was distilled over $KMnO_4$ and CaH_2 under nitrogen. Solvents used for synthesis were of analytical quality used without further purification. All solutions for photochemical experiments were degassed with no less than four freeze-pump-thaw cycles.

$[Cu_3(dpmp)_2(MeCN)_2(\mu\text{-}X)_2]ClO_4$.—A two-thirds equimolar quantity of dpmp ligand was added to a suspension of CuCl or CuI in methanol. The solution was heated at 60 °C until clear. It was filtered and addition of excess of $LiClO_4$ gave a white precipitate which was converted into crystals of **1** or **2** by vapour diffusion of diethyl ether into acetonitrile solution. The elemental analyses are in agreement with the formulation $[Cu_3(dpmp)_2(MeCN)_2(\mu\text{-}X)_2]ClO_4$ (Found: C, 55.95; H, 4.45; N, 2.05. Calc. for $C_{68}H_{64}Cl_3Cu_3N_2O_4P_6$: C, 56.10; H, 4.45; N, 1.90. Found: C, 49.95; H, 4.00; N, 1.60. Calc. for $C_{68}H_{64}ClCu_3I_2N_2O_4P_6$: C, 49.85; H, 3.95; N, 1.70%).

Physical Measurements and Instrumentation.—The UV/VIS spectra were recorded on a Milton Roy Spectronic 3000 diode-array spectrophotometer, and steady-state emission spectra on a SPEX Fluorolog-2-spectrofluorometer. The absolute luminescence quantum yield was measured by the method of Demas and Crosby[9] using quinine sulfate ($\approx 10^{-6}$ mol dm^{-3}) in 0.05 mol dm^{-3} sulfuric acid as standard. The emission lifetime and laser photolysis experiments were performed using standard instrumentation where the excitation source was the 355 nm output of a Quanta Ray DCR-3 Nd-YAG laser. Transient difference absorption changes of a photolysed solution were measured perpendicular to the laser excitation beam with a 100 W tungsten lamp as the monitoring light source. Stern–Volmer quenching experiments were carried out with a degassed acetonitrile solution of the metal complex in the presence of a quencher (Q). In each case a linear plot of τ_0/τ *versus* [Q] was obtained from which the bimolecular quenching rate constants k_q were deduced (τ_0 and τ refer to the emission lifetimes in the absence and presence of quencher).

Crystal-structure Determination of $[Cu_3(dpmp)_2(MeCN)_2(\mu\text{-}Cl)_2]ClO_4$ **1**.—*Crystal data.* $C_{68}H_{64}Cl_3Cu_3N_2O_4P_6\cdot H_2O$, $M_r = 1474.15$, triclinic, space group $P\bar{1}$ (no. 2), $a = 12.839(1)$ Å, $b = 13.582(3)$, $c = 21.510(3)$ Å, $\alpha = 84.06(1)^\circ$, $\beta = 72.71(1)$, $\gamma = 78.00(1)^\circ$, $U = 3450(1)$ Å^3, $Z = 2$, $D_c = 1.40$ g cm^{-3}, $\mu(\text{Mo-K}\alpha) = 12.03$ cm^{-1}, $F(000) = 1512$, number of parameters (p) 672, number of unique reflections measured 11 520, reflections (n) with $|F_o| > 6\sigma(|F_o|)$ 6833, $R_F = 0.083$, $R' = 0.103$. The weighting scheme used was $w^{-1} = \sigma^2(F_o) + 0.0003|F_o|^2$.

Intensities were measured at 20 °C on a Nicolet R3m/V diffractometer with graphite-monochromatised Mo-Kα radi-

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Table 1 Atomic coordinates (× 10^5 for Cu, × 10^4 for others) for complex **1**

Atom	*x*	*y*	*z*
Cu(1)	89 920(12)	14 671(1)	23 001(7)
Cu(2)	114 114(13)	80(11)	17 809(8)
Cu(3)	69 604(13)	33 526(12)	28 890(8)
P(1)	9 713(2)	2 613(2)	1 550(2)
P(2)	12 041(3)	1 290(2)	1 138(2)
P(3)	11 568(3)	−111(2)	2 800(2)
P(4)	9 269(3)	1 272(2)	3 293(2)
P(5)	7 458(3)	3 120(2)	3 815(2)
P(6)	7 796(3)	4 384(2)	2 101(2)
Cl(1)	9 608(3)	−150(2)	1 810(2)
Cl(2)	7 011(3)	1 811(3)	2 470(2)
C(1)	9 447(5)	2 629(5)	760(3)
C(2)	9 922	3 237	232
C(3)	9 706	3 219	−365
C(4)	9 015	2 594	−434
C(5)	8 540	1 987	94
C(6)	8 756	2 004	691
C(7)	12 153(5)	1 264(5)	276(3)
C(8)	11 531	657	110
C(9)	11 523	643	−536
C(10)	12 137	1 236	−1 017
C(11)	12 759	1 843	−851
C(12)	12 767	1 857	−205
C(13)	13 434(5)	1 413(5)	1 136(3)
C(14)	14 341	756	767
C(15)	15 405	747	811
C(16)	15 562	1 394	1 224
C(17)	14 656	2 050	1 594
C(18)	13 591	2 059	1 549
C(19)	12 962(5)	−86(5)	2 864(3)
C(20)	13 830	−793	2 510
C(21)	14 925	−762	2 477
C(22)	15 151	−25	2 798
C(23)	14 283	682	3 152
C(24)	13 188	651	3 185
C(25)	11 232(5)	−1 279(5)	3 289(3)
C(26)	10 927	−1 997	2 993
C(27)	10 652	−2 876	3 343
C(28)	10 683	−3 037	3 989
C(29)	10 989	−2 319	4 285
C(30)	11 263	−1 440	3 935
C(31)	8 621(5)	339(5)	3 888(3)
C(32)	8 667	262	4 531
C(33)	8 242	−499	4 956
C(34)	7 770	−1 184	4 737
C(35)	7 724	−1 107	4 094
C(36)	8 150	−345	3 669
C(37)	6 588(5)	2 440(4)	4 480(3)
C(38)	6 638	2 440	5 119
C(39)	6 001	1 881	5 612
C(40)	5 315	1 322	5 466
C(41)	5 265	1 321	4 827
C(42)	5 901	1 880	4 334
C(43)	7 407(7)	4 270(5)	4 202(3)
C(44)	8 322	4 527	4 325
C(45)	8 210	5 436	4 609
C(46)	7 184	6 087	4 769
C(47)	6 269	5 830	4 646
C(48)	6 381	4 291	4 363
C(49)	7 772(7)	5 656(5)	2 323(4)
C(50)	6 744	6 163	2 687
C(51)	6 649	7 123	2 899
C(52)	7 580	7 575	2 748
C(53)	8 607	7 068	2 385
C(54)	8 703	6 108	2 173
C(55)	7 252(6)	4 651(5)	1 393(3)
C(56)	7 655	5 308	876
C(57)	7 223	5 463	343
C(58)	6 388	4 962	326
C(59)	5 985	4 305	844
C(60)	6 416	4 149	1 377
C(61)	11 212(8)	2 529(7)	1 374(6)
C(62)	10 728(8)	943(8)	3 316(6)
C(63)	8 875(8)	2 420(8)	3 751(6)
C(64)	9 309(8)	3 944(8)	1 765(6)
C(65)	13 126(12)	−1 843(12)	1 027(8)
C(66)	14 027(14)	−2 654(13)	708(10)
C(67)	4 477(12)	4 578(13)	3 346(9)
C(68)	3 466(13)	5 406(14)	3 600(10)
N(1)	12 456(9)	−1 276(8)	1 290(6)
N(2)	5 262(9)	4 028(10)	3 178(6)
Cl(3)	1 587(5)	3 633(6)	3 301(5)
O(1)	2 744(13)	3 615(20)	2 895(11)
O(2)	1 131(12)	3 391(11)	2 828(7)
O(3)	1 291(18)	2 908(15)	3 900(11)
O(4)	1 135(16)	4 674(12)	3 477(11)
O(5)	2 234(17)	5 157(14)	1 719(11)

Table 2 Selected bond lengths (Å) and angles (°)

Cu(1)–P(1)	2.253(3)	Cu(1)–P(4)	2.247(4)
Cu(1)–Cl(1)	2.413(3)	Cu(1)–Cl(2)	2.411(4)
Cu(2)–P(2)	2.240(3)	Cu(2)–P(3)	2.247(4)
Cu(2)–Cl(1)	2.352(4)	Cu(2)–N(1)	2.13(1)
Cu(3)–P(5)	2.240(4)	Cu(3)–P(6)	2.245(4)
Cu(3)–Cl(2)	2.345(4)	Cu(3)–N(2)	2.11(1)
P(1)–Cu(1)–P(4)	121.7(2)	P(1)–Cu(1)–Cl(1)	107.4(1)
P(4)–Cu(1)–Cl(1)	107.8(1)	P(1)–Cu(1)–Cl(2)	107.7(1)
P(4)–Cu(1)–Cl(2)	106.7(1)	Cl(1)–Cu(1)–Cl(2)	104.3(1)
P(2)–Cu(2)–P(3)	116.4(2)	P(2)–Cu(2)–Cl(1)	114.7(1)
P(3)–Cu(2)–Cl(1)	109.7(1)	P(2)–Cu(2)–N(1)	102.7(3)
P(3)–Cu(2)–N(1)	107.7(4)	Cl(1)–Cu(2)–N(1)	104.5(4)
P(5)–Cu(3)–P(6)	118.0(2)	P(5)–Cu(3)–Cl(2)	111.3(1)
P(6)–Cu(3)–Cl(2)	110.8(1)	P(5)–Cu(3)–N(2)	104.5(4)
P(6)–Cu(3)–N(2)	106.1(4)	Cl(2)–Cu(3)–N(2)	105.0(4)
Cu(1)–Cl(1)–Cu(2)	86.5(1)	Cu(1)–Cl(2)–Cu(3)	87.9(1)
Cu(2)–N(1)–C(65)	168(1)	Cu(3)–N(2)–C(67)	163(2)

ation (λ = 0.710 73 Å), ω scan mode ($2\theta_{max}$ = 50°, scan rate 3.00–15.60° min^{-1}) using a crystal of dimensions 0.40 × 0.41 × 0.50 mm. All data reduction and structure refinement were performed with the SHELXTL-PLUS package on a DEC Micro VAX-II system.[10] The residual extrema in the final difference map ranged from 0.79 to −0.54 e $Å^{-3}$. Table 1 lists the atomic coordinates of non-hydrogen atoms. Selected bond distances and angles are in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

The ligand dpmp has previously been employed to construct linear trinuclear metal complexes such as $[Ag_3(dpmp)_2(MeCN)_2][ClO_4]_3$[1c] and $[Rh_3(dpmp)_2(MeCN)_6][PF_6]_3$.[7] In this work, reactions of CuX with dpmp in methanol gave halide-bridged trinuclear copper(I) complexes in high yields. Attempts to prepare a trinuclear copper(I) complex of dpmp without bridging halide were unsuccessful. The reaction between $CuClO_4$ or $CuCF_3SO_3$ with dpmp in MeCN gave the dinuclear complex $[Cu_2(dpmp)(MeCN)_5]^{2+}$, which has been characterised by X-ray crystallography.*

Fig. 1 shows the crystal structure of the complex cation of **1**.

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* The structure of $[Cu_2(dpmp)(MeCN)_5][ClO_4]_2$ revealed[11] two copper atoms bridged by the dpmp ligand with intramolecular Cu ··· Cu separations of 4.193(3) and 4.679(4) Å.

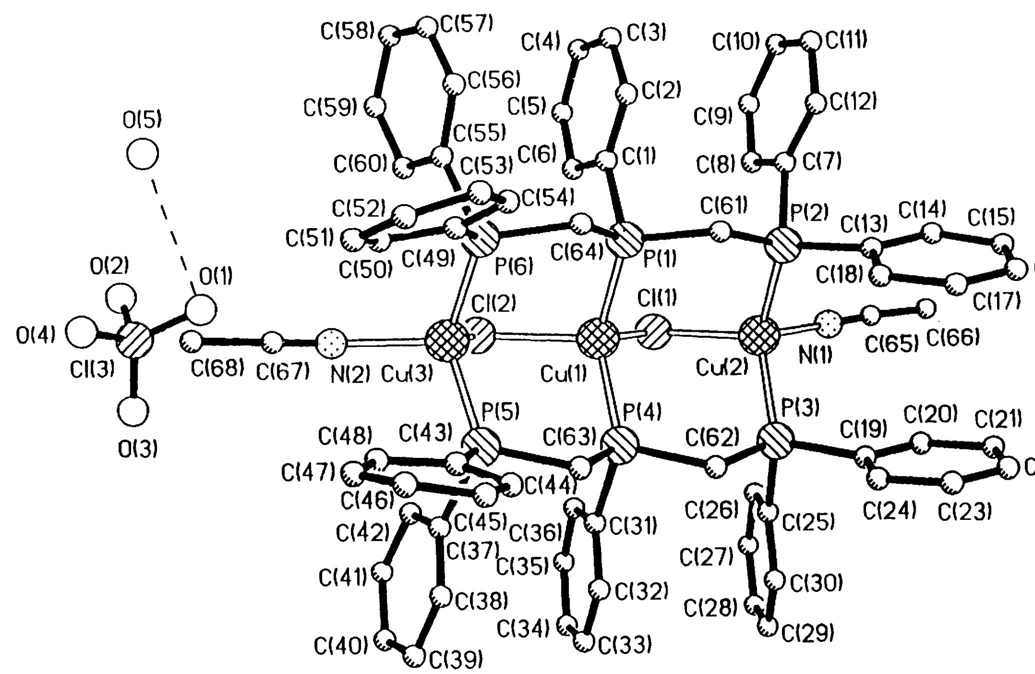


Fig. 1 An ORTEP plot of $[Cu_3(dpmp)_2(MeCN)_2(\mu\text{-}Cl)_2]ClO_4$ with the atom numbering scheme

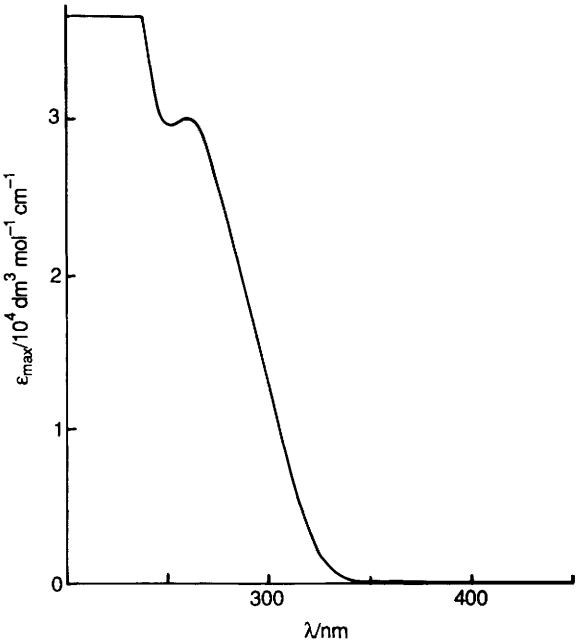


Fig. 2 The UV/VIS absorption spectrum of $[Cu_3(dpmp)_2(MeCN)_2(\mu\text{-}Cl)_2]ClO_4$ in acetonitrile at room temperature

The structure consists of three copper(I) ions in distorted-tetrahedral geometry bridged by two dpmp ligands with Cu–P distances ranging from 2.240 to 2.253 Å. These are slightly shorter than in $[Cu_2(dppm)_2(MeCN)_2]^{2+}$ **3** (dppm = $Ph_2PCH_2PPh_2$) [2.270(3) and 2.283(3) Å].[12] In contrast to the complexes $[Au_3(dmmp)_2][ClO_4]_3$[1a] and $[Ag_3(dpmp)_2(MeCN)_2][ClO_4]_3$[1c] where the P–M–P co-ordination is more or less linear, the P(1)–Cu(1)–P(4), P(2)–Cu(2)–P(3) and P(5)–Cu(3)–P(6) angles of **1** are 121.7(2), 116.4(2) and 118.0(2)°, respectively. This is rather similar to the case of **3** where the P–Cu–P angle is 119.9(1)°. Besides, the three copper(I) ions are bridged by two chloride ions on the same side with Cu(1)–Cl(1)–Cu(2) and Cu(1)–Cl(2)–Cu(3) angles of 86.5(1) and 87.9(1)° respectively. These values are greater than the Cu–Cl–Cu angle (83.4°) found in the binuclear complex $[\{Cu[P(C_6H_{11})_3](\mu\text{-}Cl)\}_2]$ **4**.[13] Each chloride ion is asymmetrically co-ordinated to the copper atoms with Cu(1)–Cl(1), Cu(2)–Cl(1), Cu(1)–Cl(2) and Cu(3)–Cl(2) distances equal to 2.413(3), 2.352(4), 2.411(4) and 2.345(4) Å, respectively. Both Cu(3) and Cu(2) have one acetonitrile ligand co-ordinated to them. It is noted that the two $Cu_2P_4C_2$ eight-membered rings are eclipsed, as in the case of **3**. The intramolecular Cu(1)···Cu(2) and Cu(1)···Cu(3) separations of 3.26 and 3.30 Å respectively are significantly shorter than that found in **3** [3.757(3) Å] but considerably longer than that of 2.497(2) Å in $[\{Cu(MeC_6H_4NNCHNC_6H_4Me)\}_2]$[14] and 3.0 Å in **4**.[13]

Photophysical and Photochemical Properties.—Fig. 2 shows the electronic absorption spectrum of complex **1** measured at room temperature. The absorption spectra of **1** and **2** are dominated by intense absorption around 250 nm (**1**, λ_{max} = 250, $\varepsilon_{max} = 3.03 \times 10^4$; **2**, λ_{max} = 252 nm, $\varepsilon_{max} = 4.21 \times 10^4$ $dm^3\ mol^{-1}\ cm^{-1}$). However, both have substantial absorption around 300 nm which is not observed in the spectrum of the free dpmp ligand. At room temperature and upon excitation at 300–400 nm **1** and **2** display emission band maxima at 530 and 560 nm, respectively. Similar emissions are also observed from the solid form of the metal complexes. Cooling the sample to 77 K only leads to an increase in emission intensity as illustrated in Fig. 3. No vibrational fine structure has been observed. The emission exhibits simple first-order decay kinetics from which the lifetime is deduced. The long emission lifetimes of **1** (1.7 ± 0.1) and **2** (3.1 ± 0.1 μs), which are relatively insensitive to the concentration of the metal complexes in acetonitrile, suggest the phosphorescence nature of the emissions. Luminescence quantum yields of the emission relative to quinine sulfate are $(2.3 \pm 0.2) \times 10^{-2}$ (**1**) and $(3.5 \pm 0.3) \times 10^{-2}$ (**2**), respectively.

It is interesting that the emission energies of complexes **1** and **2** are very similar, despite the difference in bridging halide ions. Hence the possibilities of the excited states arising from halide-to-metal charge transfer or halide-to-phosphine charge transfer can be ruled out, because of the very small red shift in emission energy observed upon changing the bridging halide from chloride to iodide. In accordance with the invariance of the emission energy, an intraligand phosphine excited state, a metal-centred excited state, a metal-to-ligand charge-transfer state or

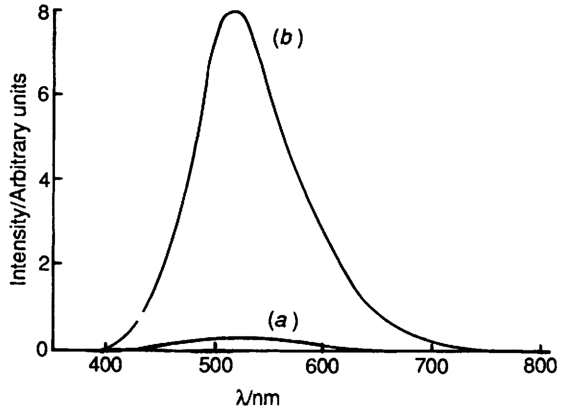


Fig. 3 Emission spectra of a solid sample of $[Cu_3(dpmp)_2(MeCN)_2(\mu\text{-}Cl)_2]ClO_4$ at room temperature and at 77 K. Excitation wavelength 330 nm

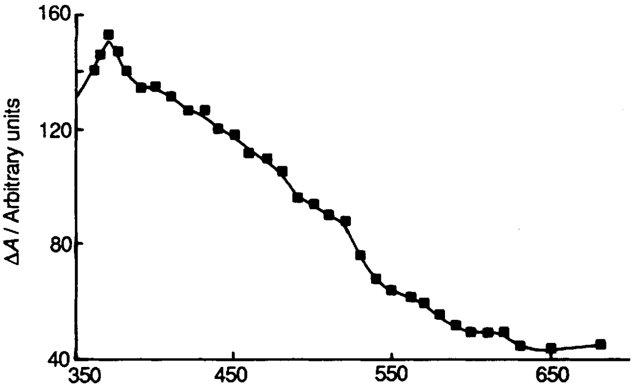


Fig. 4 Transient difference absorption spectrum recorded 10 μs after flashing a degassed acetonitrile solution of complex **1** (5×10^{-4} mol dm^{-3}) and *N*-ethylpyridinium ion (0.14 mol dm^{-3}) at room temperature

a mixture of these is possible. Free dpmp is found to exhibit very weak emission at 420 nm in acetonitrile at room temperature. The 530 or 560 nm emission could not come from an intraligand phosphine excited state because of the large red shift in energy from 420 nm. We therefore tentatively assign these emissions to a metal-centred $3d^94s^1 \longrightarrow 3d^{10}4s^0$ transition, where the lowest unoccupied (LUMO) and highest occupied molecular orbitals (HOMO) are likely to be modified by Cu···Cu interaction and/or mixing with the dpmp ligand.

Given the long excited-state lifetimes, it is not surprising to find that complexes **1** and **2** possess interesting photochemical properties. Our photochemical experiments established that the excited states of **1** and **2** are powerful reductants. *N*-Ethylpyridinium ion with a $E°$ of -1.36 V *vs.* saturated sodium chloride calomel electrode (ssce) is reduced by **1** or **2** upon photoexcitation [equation (1)]. The quenching rate constants of the emission by *N*-ethylpyridinium ion obtained from the Stern–Volmer plots are 9.9×10^7 and 4.6×10^7 dm^3 mol^{-1} s^{-1} for **1** and **2** respectively in acetonitrile at room temperature. Similarly, *N*,2,6-trimethylpyridinium ion having a $E°$ of -1.52 V *vs.* ssce quenches the emission of **1** and **2** with rate constants of 7.0×10^6 and 2.7×10^6 dm^3 mol^{-1} s^{-1} respectively.

A flash photolysis experiment provided spectroscopic evidence for equation (1). The transient difference absorption spectrum recorded 10 μs after flashing a degassed acetonitrile solution of complex **1** (5×10^{-4} mol dm^{-3}) and *N*-ethylpyridinium ion (0.14 mol dm^{-3}) is shown in Fig. 4. The spectrum reveals intense and broad absorptions ranging from 360 to 550 nm. The intense absorption from 350 to 400 nm, not present in Fig. 5 comes from the one-electron reduced form of *N*-ethylpyridinium ion, which absorbs strongly in this region and

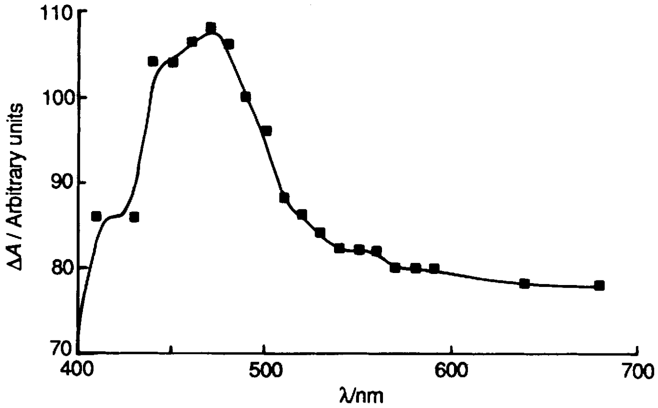
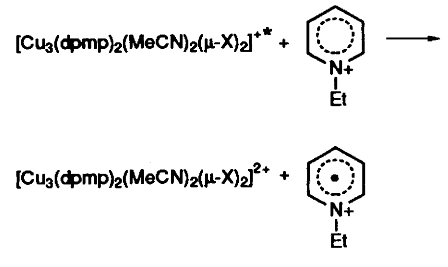


Fig. 5 Transient difference absorption spectrum recorded 10 μs after flashing a degassed acetonitrile solution of complex **1** (5×10^{-3} mol dm^{-3}) and *cis*-$[Os^{VI}LO_2]^{2+}$ (10^{-3} mol dm^{-3})



(1)

probably masks the transitions of $[Cu_3(dpmp)_2(MeCN)_2(\mu\text{-}Cl)_2]^{2+}$. Reductive quenching has also been observed with *cis*-$[Os^{VI}LO_2]^{2+}$ (L = *N,N,N′,N′*-3,6-hexamethyl-3,6-diazaoctane-1,8-diamine) which has a reversible Os^{VI}–Os^{V} couple at 0.06 V *vs.* Ag–$AgNO_3$.[15] Fig. 5 shows the transient difference absorption spectrum recorded 10 μs after flashing a degassed acetonitrile solution of **1** (5×10^{-3} mol dm^{-3}) and *cis*-$[Os^{VI}LO_2]^{2+}$ (10^{-3} mol dm^{-3}).[15] Since both Os^{VI} and Os^{V} do not have significant absorption around 400–600 nm,[15] the broad absorption at 400–500 nm in Fig. 5 is likely due to $[Cu_3(dpmp)_2(MeCN)_2(\mu\text{-}Cl)_2]^{2+}$.

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References

1 (*a*) V. W. W. Yam, T. F. Lai and C. M. Che, *J. Chem. Soc., Dalton Trans.*, 1990, 3747; (*b*) C. M. Che, H. L. Kwong and V. W. W. Yam, *J. Chem. Soc., Dalton Trans.*, 1990, 3215; (*c*) C. M. Che, H. K. Yip, D. Li, S. M. Peng, G.-H. Lee, Y.-M. Wang and S.-T. Liu, *J. Chem. Soc., Chem. Commun.*, 1991, 1615; (*d*) C. M. Che, W. T. Wong, T. F. Lai and H. L. Kwong, *J. Chem. Soc., Chem. Commun.*, 1989, 243; (*e*) C. M. Che, H. K. Yip, V. W. W. Yam, P. Y. Cheung, T. F. Lai, S. J. Shieh and S. M. Peng, *J. Chem. Soc., Dalton Trans.*, 1992, 427.

2 P. D. Harvey, F. Adar and H. B. Gray, *J. Am. Chem. Soc.*, 1989, **111**, 1312; J. V. Caspar, *J. Am. Chem. Soc.*, 1985, **107**, 6718.

3 M. Henary and J. I. Zink, (*a*) *Inorg. Chem.*, 1991, **30**, 3111; *J. Am. Chem. Soc.*, 1989, **111**, 7407.

4 A. Vogler and H. Kunkely, (*a*) *Chem. Phys. Lett.*, 1989, **158**, 74; (*b*) *Chem. Phys. Lett.*, 1988, **150**, 135; (*c*) *J. Am. Chem. Soc.*, 1986, **108**, 7211.

5 K. R. Kyle, C. K. Ryu, J. A. DiBenedetto and P. C. Ford, *J. Am. Chem. Soc.*, 1991, **113**, 2954; C. K. Ryu, K. R. Kyle and P. C. Ford, *Inorg. Chem.*, 1991, **30**, 3982.

6 C. King, J. C. Wang, N. I. Md. Khan and J. P. Fackler, jun., *Inorg. Chem.*, 1989, **28**, 2145.

7 A. L. Balch, A. Fossett, J. K. Nagle and M. M. Olmstead, *J. Am. Chem. Soc.*, 1988, **110**, 6732.

8 R. R. Giumerans, M. M. Olmstead and A. L. Balch, *J. Am. Chem. Soc.*, 1983, **105**, 1677.

9 J. N. Demas and G. A. Grosby, *J. Phys. Chem.*, 1971, **75**, 991.

10 G. M. Sheldrick, *Computational Crystallography*, ed. D. Sayre, Oxford University Press, New York, 1982, p. 506.

11 C. M. Che and S. M. Peng, unpublished work.

12 J. Diez, M. P. Gamasa, J. Gimeno, A. Tiripicchio and M. T. Camellini, *J. Chem. Soc., Dalton Trans.*, 1987, 1275.

13 M. R. Churchill and F. J. Rotella, *Inorg. Chem.*, 1979, **18**, 166.

14 F. A. Cotton, X. Feng, M. Matusz and R. Poli, *J. Am. Chem. Soc.*, 1988, **110**, 7077.

15 C. M. Che and W. Y. Yu, unpublished work.

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