Synthesis, Crystal Structure, Photophysical Properties and Theoretical Studies of $[Cu_3(Ph_2PCH_2PPh_2)_3(WS_4)]ClO_4$†

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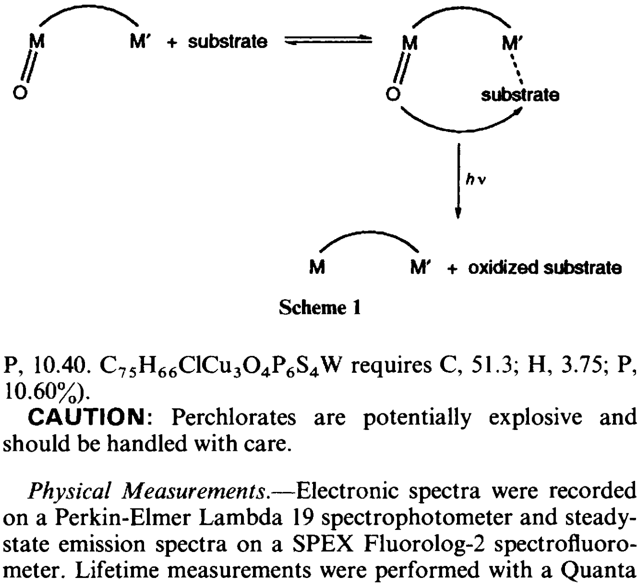
The reaction of $[Cu_2(dppm)_2(MeCN)_4]^{2+}$ [dppm = bis(diphenylphosphino)methane] with $[WS_4]^{2-}$ gives the cationic d^0–d^{10} complex $[Cu_3(dppm)_3(WS_4)]^+$, the crystal structure of which has been determined. The three copper atoms and the thiotungstate ligand form a distorted 'flywheel' array with W ··· Cu separations of 2.790(3), 2.803(3) and 2.834(3) Å. In the solid state the complex shows an intense emission with λ_{max} at 615 nm. Extended-Hückel molecular-orbital calculations reveal that the emitting state may arise from a $[\psi(Cu,P) \longrightarrow W^{VI}]$ charge-transfer transition.

The search for new luminescent metal complexes has been the subject of our photochemical studies.[1–3] Our interests in this area have recently been directed towards the exploration of the photo-physical and -chemical properties of heteronuclear metal complexes having a high-valent metal–oxo, metal–nitrido or metal–sulfido unit covalently linked to a low-valent metal–phosphine group.[4] The aim was to develop new photocatalysts whereby activation of organic substrates and photo-induced atom-transfer reactions could occur in close proximity (Scheme 1).

In this context, heteronuclear d^0–d^{10} metal complexes have received our attention.[4c] Those d^0 metal complexes with the metal ion multiply bonded to a heteroatom are potent atom-transfer reagents upon irradiation with UV/VIS light. In fact, interesting photo-physical and -chemical properties have been reported for the $[ReS_4]^-$ [5a] and $ReRO_3$ systems[5b] (R = alkyl or aryl). Low-valent d^{10} metal–phosphines are known to undergo binding reactions with unsaturated organic molecules.[6] It has been shown[7] that the reactions of thiometalates with Cu^I give Cu^I–W^{VI}=S complexes with diverse structural properties. Herein we describe a new cationic complex of this class, $[Cu_3(dppm)_3(\mu\text{-}WS_4)]^+$ [dppm = bis(diphenylphosphino)-methane], which is photoluminescent in the solid state at room temperature.



Scheme 1

Experimental

Synthesis.—All syntheses and manipulations were carried out under an inert atmosphere. The compound $[NH_4]_2[WS_4]$ was obtained from Aldrich and used as received. The complex $[Cu_2(dppm)_2(MeCN)_4][ClO_4]_2$ was prepared according to the literature.[8]

$[Cu_3(dppm)_3(WS_4)]ClO_4$. A mixture of $[Cu_2(dppm)_2(MeCN)_4][ClO_4]_2$ (200 mg, 0.16 mmol) and $[NH_4]_2[WS_4]$ (60 mg, 0.17 mmol) in acetonitrile (25 cm^3) was stirred at room temperature for 2 h. The volume of the solution was reduced to 5 cm^3 and upon addition of diethyl ether an orange precipitate was obtained. Vapour diffusion of diethyl ether into a dichloromethane solution gave $[Cu_3(dppm)_3(\mu\text{-}WS_4)]ClO_4$ isolated as an air-stable orange crystalline solid. Yield 25%. UV/VIS (CH_2Cl_2): λ_{max}/nm (10^{-4} ε_{max}/dm^3 mol^{-1} cm^{-1}): 260 (5.20), 320 (1.60), 370 (0.87), 465 (0.36) (Found: C, 50.8; H, 3.90; P, 10.40. $C_{75}H_{66}ClCu_3O_4P_6S_4W$ requires C, 51.3; H, 3.75; P, 10.60%).

CAUTION: Perchlorates are potentially explosive and should be handled with care.

Physical Measurements.—Electronic spectra were recorded on a Perkin-Elmer Lambda 19 spectrophotometer and steady-state emission spectra on a SPEX Fluorolog-2 spectrofluorometer. Lifetime measurements were performed with a Quanta Ray DCR-3 Nd-YAG pulsed laser system. Sample solutions for photophysical experiments were degassed by at least four successive freeze–pump–thaw cycles.

Molecular Orbital Calculations.—Extended-Hückel molecular-orbital (EHMO) calculations were carried out by using the ICON program.[10] The geometric factors were obtained from the X-ray diffraction data. A total of 155 atoms and 442 orbitals were employed. The parameters of Cu and W were taken from the literature[9] whilst the others were acquired from the program.[10]

Crystal Structure Determination.—*Crystal data.* $C_{75}H_{66}ClCu_3O_4P_6S_4W_4$, $M = 1755.37$, monoclinic, space group $P2_1$ (no. 4), $a = 12.945(3)$, $b = 17.006(3)$, $c = 17.876(4)$ Å, $\beta = 92.64(3)°$, $U = 3931(1)$ Å^3, $Z = 2$, $D_c = 1.483$ g cm^{-3}, μ(Mo-Kα) = 25.7 cm^{-1}, $F(000) = 1760$, crystal dimensions 0.30 × 0.30 × 0.40 mm. Intensities were measured at 294 K on a Siemens P4/PC four-circle diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.710\,73$ Å) and were corrected for absorption using ψ-scan data.[11] 5027 Independent reflections were measured, 4089 of which with $|F_o| \geq 4\sigma|F_o|$ were used in the structural refinement. Patterson superposition yielded the positions of all non-hydrogen atoms. All phenyl rings of the cluster complex were treated as rigid groups (regular hexagons with edges of 1.395 Å), and the remaining non-

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Non-SI unit employed: eV ≈ 1.60 × 10^{-19} J.

Table 1 Atomic coordinates (× 10^5 for W, × 10^4 for others) for $[Cu_3(dppm)_3(WS_4)]^+$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W	51 029(6)	50 000	76 820(4)	C(40)	7 645	8 569	6 372
Cu(1)	4 564(2)	6 323(2)	8 513(1)	C(41)	8 418	8 001	6 326
Cu(2)	4 576(2)	5 921(2)	6 430(1)	C(42)	8 159	7 205	6 314
Cu(3)	3 022(2)	4 476(2)	7 634(1)	C(43)	7 127	6 977	6 347
S(1)	5 995(4)	5 477(4)	8 661(3)	C(44)	6 354	7 544	6 393
S(2)	5 961(4)	5 052(5)	6 559(3)	C(45)	3 602(9)	8 121(7)	5 494(7)
S(3)	4 586(5)	3 793(3)	7 887(4)	C(46)	3 209	8 364	4 792
S(4)	3 649(4)	5 748(3)	7 500(3)	C(47)	3 693	8 130	4 148
P(1)	3 504(4)	5 993(4)	9 469(3)	C(48)	4 571	7 654	4 205
P(2)	2 384(4)	4 451(4)	8 807(3)	C(49)	4 964	7 411	4 907
C(1)	3 228(13)	4 913(12)	9 531(9)	C(50)	4 480	7 645	5 552
C(2)	4 964(8)	5 736(6)	10 633(6)	P(5)	3 481(4)	5 380(4)	5 526(3)
C(3)	5 499	5 912	11 307	P(6)	2 436(5)	4 030(4)	6 488(3)
C(4)	5 185	6 542	11 742	C(51)	3 201(14)	4 327(11)	5 684(9)
C(5)	4 337	6 997	11 501	C(52)	5 062(8)	4 969(6)	4 598(5)
C(6)	3 802	6 822	10 827	C(53)	5 588	4 935	3 935
C(7)	4 115	6 191	10 393	C(54)	5 143	5 257	3 279
C(8)	2 025(8)	7 040(7)	8 931(6)	C(55)	4 172	5 612	3 285
C(9)	1 116	7 476	8 966	C(56)	3 646	5 645	3 948
C(10)	463	7 361	9 556	C(57)	4 091	5 324	4 605
C(11)	720	6 809	10 111	C(58)	1 487(9)	5 544(7)	4 811(6)
C(12)	1 628	6 372	10 076	C(59)	554	5 939	4 668
C(13)	2 281	6 488	9 486	C(60)	352	6 635	5 047
C(14)	1 614(8)	2 940(7)	8 769(6)	C(61)	1 083	6 936	5 569
C(15)	1 610	2 135	8 922	C(62)	2 015	6 541	5 713
C(16)	2 333	1 819	9 442	C(63)	2 217	5 844	5 333
C(17)	3 060	2 307	9 808	C(64)	2 394(8)	2 526(8)	7 041(7)
C(18)	3 064	3 112	9 654	C(65)	2 306	1 709	7 013
C(19)	2 341	3 428	9 135	C(66)	2 302	1 320	6 326
C(20)	601(9)	4 496(7)	9 656(6)	C(67)	2 385	1 748	5 666
C(21)	−395	4 754	9 793	C(68)	2 473	2 566	5 693
C(22)	−893	5 288	9 305	C(69)	2 478	2 955	6 381
C(23)	−395	5 563	8 681	C(70)	640(10)	4 866(7)	6 640(6)
C(24)	601	5 304	8 544	C(71)	−385	5 085	6 481
C(25)	1 099	4 771	9 031	C(72)	−958	4 716	5 901
P(3)	4 875(4)	7 581(3)	8 134(3)	C(73)	−506	4 129	5 480
P(4)	4 997(4)	7 227(3)	6 410(3)	C(74)	520	3 910	5 639
C(26)	4 449(14)	7 808(11)	7 164(10)	C(75)	1 093	4 279	6 219
C(27)	6 295(9)	8 828(7)	8 304(5)	Cl(1)	−1 180(6)	4 108(5)	3 054(5)
C(28)	7 283	9 156	8 344	O(1)	−437(11)	4 251(11)	3 635(8)
C(29)	8 151	8 671	8 328	O(2)	−2 069(12)	4 575(12)	3 101(13)
C(30)	8 030	7 858	8 273	O(3)	−1 483(16)	3 306(7)	3 065(13)
C(31)	7 042	7 530	8 233	O(4)	−721(16)	4 246(15)	2 361(8)
C(32)	6 174	8 015	8 249	O(2′)	−838(18)	3 502(12)	2 584(13)
C(33)	4 342(8)	8 207(6)	9 471(6)	O(3′)	−1 357(18)	4 801(11)	2 626(14)
C(34)	3 805	8 693	9 947	O(4′)	−2 126(12)	3 885(16)	3 363(14)
C(35)	3 064	9 217	9 650	Cl(2)	1 231(12)	−2 674(10)	2 258(10)
C(36)	2 861	9 254	8 878	O(5)	1 056(18)	−3 211(14)	2 841(13)
C(37)	3 399	8 768	8 402	O(6)	1 402(18)	−1 902(11)	2 528(15)
C(38)	4 139	8 244	8 698	O(7)	349(15)	−2 668(17)	1 756(14)
C(39)	6 614(8)	8 340(7)	6 406(5)	O(8)	2 096(15)	−2 930(16)	1 865(14)

Occupancy factors 0.7 for Cl(1), O(1); 0.5 for O(2), O(3), O(4); 0.2 for O(2′), O(3′), O(4′); and 0.3 for Cl(2), O(5), O(6), O(7), O(8).

hydrogen atoms were subjected to anisotropic refinement. The last least-squares cycle was calculated with 4089 reflections and 365 parameters, leading to $R = 0.057$, $R' = 0.071$ and goodness of fit = 1.34. The weighting scheme used was $w = (\sigma^2|F_o| + 0.0010|F_o|^2)^{-1}$. The perchlorate anion was disordered and located in two cavities formed by the loose packing of the cluster complexes, and their site occupancies were assigned to be 0.7 and 0.3 after several cycles of occupancy refinement; in addition, the Cl–O bonds were restrained at 1.41(1) Å and the O–Cl–O angles at 109(2)°. All hydrogen atoms were generated geometrically (C–H bonds fixed at 0.96 Å) and allowed to ride on their respective parent C atoms; they were assigned the same isotropic thermal parameters ($U = 0.08$ Å^2) and included in the structure-factor calculations. Computations were performed using the SHELTXL-PC program package[12] on a PC-486 computer. Analytic expressions of atomic scattering factors were employed, and anomalous dispersion corrections were incorporated.[13] Table 1 lists the atomic coordinates of non-hydrogen atoms and selected bond distances and bond angles are given 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

It has previously been reported[7] that the formation of heterobimetallic Cu^I–W^{VI}=S complexes by treating $[WS_4]^{2-}$ with Cu^I yields complexes with Cu : W ratios ranging from 1–6 : 1 which have intriguing structural features. However, all of the reported heterobimetallic Cu^I–W^{VI}=S clusters are either anionic or neutral. In this work, the reaction between $[Cu_2(dppm)_2(MeCN)_4]^{2+}$ and $[WS_4]^{2-}$ in acetonitrile gave $[Cu_3(dppm)_3(\mu\text{-}WS_4)]^+$, which is the first cationic complex of this kind. The

Table 2 Bond lengths (Å) and bond angles (°) for $[Cu_3(dppm)_3(WS_4)]^+$

(*i*) Co-ordination geometry about W atoms			
W–Cu(1)	2.802(3)	W–Cu(2)	2.790(3)
W–Cu(3)	2.834(3)	W–S(1)	2.207(6)
W–S(2)	2.184(5)	W–S(3)	2.195(6)
W–S(4)	2.283(5)		
S(1)–W–S(2)	112.4(2)	S(1)–W–S(3)	111.4(2)
S(2)–W–S(3)	110.4(3)	S(1)–W–S(4)	107.8(2)
S(2)–W–S(4)	107.8(2)	S(3)–W–S(4)	106.8(2)
(*ii*) Co-ordination geometry about Cu atoms			
Cu(1)–S(1)	2.351(7)	Cu(1)–S(4)	2.333(6)
Cu(1)–P(1)	2.310(6)	Cu(1)–P(3)	2.286(6)
S(1)–Cu(1)–S(4)	101.6(2)	S(1)–Cu(1)–P(1)	105.1(2)
S(4)–Cu(1)–P(1)	100.1(2)	S(1)–Cu(1)–P(3)	117.2(2)
S(4)–Cu(1)–P(3)	104.6(2)	P(1)–Cu(1)–P(3)	124.4(2)
Cu(2)–S(2)	2.344(7)	Cu(2)–S(4)	2.323(6)
Cu(2)–P(4)	2.289(6)	Cu(2)–P(5)	2.291(6)
S(2)–Cu(2)–S(4)	101.3(2)	S(2)–Cu(2)–P(4)	115.7(3)
S(4)–Cu(2)–P(4)	105.5(2)	S(2)–Cu(2)–P(5)	108.3(2)
S(4)–Cu(2)–P(5)	101.7(2)	P(4)–Cu(2)–P(5)	121.2(2)
Cu(3)–S(3)	2.360(7)	Cu(3)–S(4)	2.326(6)
Cu(3)–P(2)	2.290(6)	Cu(3)–P(6)	2.282(6)
S(3)–Cu(3)–S(4)	100.2(2)	S(3)–Cu(3)–P(2)	99.1(2)
S(4)–Cu(3)–P(2)	104.7(2)	S(3)–Cu(3)–P(6)	104.8(2)
S(4)–Cu(3)–P(6)	108.7(2)	P(2)–Cu(3)–P(6)	134.2(3)
W–S(1)–Cu(1)	75.8(2)	W–S(2)–Cu(2)	76.0(2)
W–S(3)–Cu(3)	76.9(2)	W–S(4)–Cu(1)	74.7(2)
W–S(4)–Cu(2)	74.6(2)	Cu(1)–S(4)–Cu(2)	108.9(2)
W–S(4)–Cu(3)	75.9(2)	Cu(1)–S(4)–Cu(3)	118.5(2)
Cu(2)–S(4)–Cu(3)	113.5(2)		
(*iii*) Bis(diphenylphosphino)methane ligands			
P(1)–C(1)	1.88(2)	P(1)–C(7)	1.83(1)
P(1)–C(13)	1.80(1)	P(2)–C(1)	1.83(2)
P(2)–C(19)	1.84(1)	P(2)–C(25)	1.81(1)
Cu(1)–P(1)–C(1)	113.8(6)	Cu(1)–P(1)–C(7)	112.1(4)
C(1)–P(1)–C(7)	101.7(7)	Cu(1)–P(1)–C(13)	116.9(5)
C(1)–P(1)–C(13)	106.7(7)	C(7)–P(1)–C(13)	104.1(6)
Cu(3)–P(2)–C(1)	114.2(6)	Cu(3)–P(2)–C(19)	109.1(4)
C(1)–P(2)–C(19)	101.9(7)	Cu(3)–P(2)–C(25)	124.8(5)
C(1)–P(2)–C(25)	103.8(7)	C(19)–P(2)–C(25)	100.0(6)

Table 3 The energies (eV) and composition (%) of the near frontier orbitals

In $[Cu_3(dppm)_3(WS_4)]^+$

		Composition			
Orbitals	Energy	W	4S	3Cu	3dppm
ψ_4(W)	−9.0255	60.90	36.24	2.18	0.69
ψ_3(W)	−9.0621	60.63	35.813	2.41	1.14
σ_3*(W–S)	−9.2866	58.49	32.65	7.85	1.01
σ_2*(W–S)	−9.6126	56.88	35.42	4.84	2.86
σ_1*(W–S)	−9.6240	56.71	35.76	4.93	2.60
LUMO–HOMO energy gap, 2.2652 eV					
$\psi_2[Cu(d_{z^2}) + P(p_z)]$	−11.8892	5.05	15.97	28.83	50.15
ψ_1(Cu,P)	−11.9190	3.48	14.00	28.79	53.73
π_3(dppm)	−12.1276	0.43	14.25	15.36	69.97
π_2(dppm)	−12.3052	1.66	9.42	10.63	78.29
π_1(dppm)	−12.3318	0.77	4.21	7.66	87.36

In the $[Cu_3(dppm)_3]^{3+}$ core

		Composition	
Orbitals	Energy	Cu	dppm
φ_5(Cu)	−6.0261	96.36	3.64
φ_4(Cu)	−6.2665	85.01	14.99
φ_3(Cu)	−6.2686	84.94	15.06
φ_2(Cu)	−6.4103	83.25	16.75
φ_1(Cu, P)	−6.5269	48.15	51.85
LUMO–HOMO energy gap, 4.615 eV			
π_3(dppm)	−11.1419	10.86	89.14
π_2(dppm)	−11.7111	17.49	82.51
π_1(dppm)	−11.7229	17.68	82.32

In $[WS_4]^{2-}$

		Composition	
Orbitals	Energy	W	4S
θ_7(W)	−9.1332	62.53	37.47
θ_6(W)	−9.1834	63.20	36.80
θ_5(W)	−9.9434	60.30	39.70
LUMO–HOMO energy gap, 3.0655 eV			
θ_4(S)	−13.0089	0.00	100.00
θ_3(S)	−13.0469	0.02	99.98
θ_2(S)	−13.8624	2.59	97.41
θ_1(S)	−13.8882	2.82	97.18

complex has been shown by X-ray crystallography to have a μ_4-S moiety asymmetrically bonded to two kinds of metal ions.

An ORTEP[14] drawing of the complex cation is shown in Fig. 1. The tungsten atom has retained its initial tetrahedral co-ordination, with S–W–S angles in the range 106.8(2)–112.4(2)°. The three copper atoms and the thiotungstate ligand form a distorted 'flywheel' array. There are two different co-ordination modes of the bridging sulfurs. The atoms S(1), S(2) and S(3) are bonded to W and only one Cu atom but S(4) adopts a μ_4-bridging mode, being bonded to W and the three Cu atoms. Complexes with a μ_4-S moiety[15] asymmetrically bonded to two kinds of metal ions are not unprecedented in the literature. Examples include $[Zn_4S(S_2AsMe_2)_6]$[16] and $[MCu_4S_4Cl_5]^{3-}$ [7e] (M = Mo or W). The Cu–S–W angles [74.6(2)–76.9(2)°] are comparable with those of $[WCu_4S_4Cl_5]^{3-}$ [71.3(2)–72.7(1)°].

Each of the three copper atoms is in a distorted tetrahedron. The W ··· Cu separations of 2.790(3), 2.803(3) and 2.834(3) Å are longer than those in $[WCu_4S_4Cl_5]^{3-}$ [7e] [2.640(3)–2.693(2) Å], but comparable to those of $[MCu_3S_4(PPh_3)_3Cl]$ (M = Mo[17] or W[7b]) (2.700–2.717 Å). With such W ··· Cu separations one would expect weak intramolecular metal–metal interaction and the theoretical studies provide support for this claim.

Interestingly, the six-membered ring comprising Cu(2), S(4), Cu(3), P(6), C(51) and P(5) has a boat conformation, whereas the other two related rings have chair conformations. This is probably due to the rigidity of the $[WS_4]^{2-}$ group and the steric crowding of the phenyl groups of dppm.

Spectroscopic and Photophysical Properties.—The electronic spectrum of $[Cu_3(dppm)_3(WS_4)]^+$ is shown in Fig. 2. For the purposes of comparison, the UV/VIS spectrum of $[WS_4]^{2-}$ is also illustrated. The copper complex displays intense absorptions at 300–500 nm [λ_{max}/nm (10^{-4} ε_{max}/dm^3 mol^{-1} cm^{-1}): 320 (1.60), 370 (0.87), 465 (0.36)]. The low-energy band at 465 nm is red-shifted from the S $\longrightarrow$ W^{VI} charge-transfer band of $[WS_4]^{2-}$, which is located at 400 nm. The absorption band at 320 nm is due to the transition of the Cu^I–dppm moiety since a similar band is also found in $[Cu_2(dppm)_2(MeCN)_4]^{2+}$;[18] $[WS_4]^{2-}$ does not have any significant absorption at this energy range.

Extended-Hückel molecular-orbital calculations on $[Cu_3(dppm)_3(WS_4)]^+$, the $[Cu_3(dppm)_3]^{3+}$ core and $[WS_4]^{2-}$ were undertaken. The energies and composition of the near frontier orbitals are summarized in Table 3. For $[Cu_3(dppm)_3(WS_4)]^+$, the net charge on W, S(1)–S(3) and S(4) are +0.4263, −0.4 and

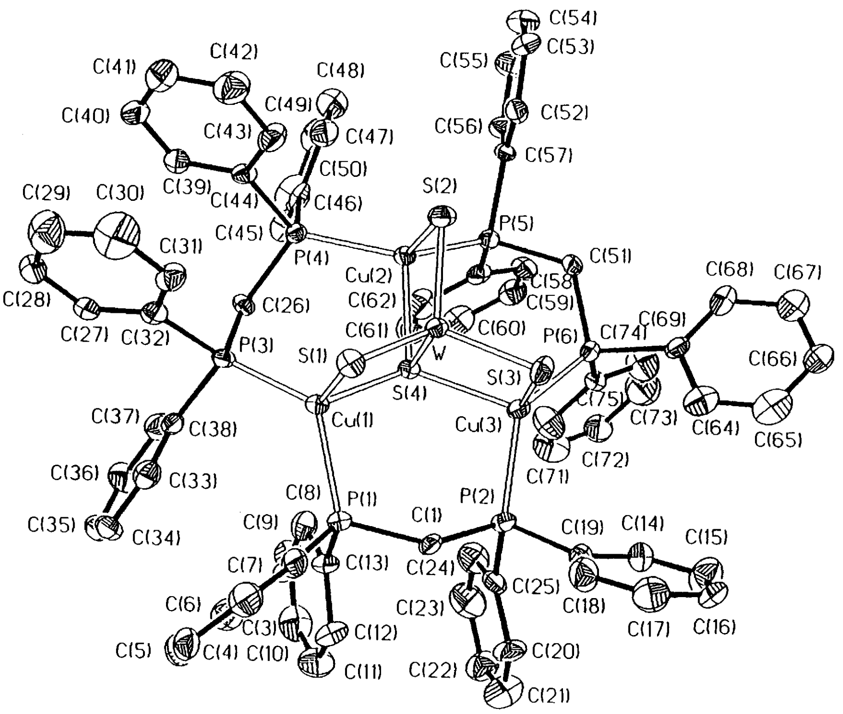

Fig. 1 An ORTEP drawing of $[Cu_3(dppm)_3(WS_4)]^+$ with atom numbering

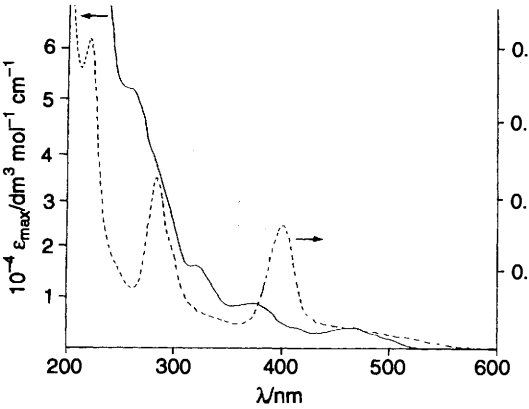

Fig. 2 The UV/VIS absorption spectrum of the $[Cu_3(dppm)_3(WS_4)]^+$ complex (——) and WS_4^{2-} (– – – –)

−0.03 e respectively. The electronic charge of the sulfur atoms is considerably lower than that of $[WS_4]^{2-}$, the sulfur atoms of which carry a charge of −0.638 e. Thus, on going from $[WS_4]^{2-}$ to $[Cu_3(dppm)_3(WS_4)]^+$, there is electron loss on the sulfur atoms. This in turn leads to an increase in electronic charge on the Cu atoms, which carry a charge of −0.385 to −0.395 e. The calculated overlap population between the three Cu and the W atoms is 0.0464–0.0628, and this mostly arises from the interaction of the 6p and 5d orbitals of W with the 4p orbitals of Cu.

The highest occupied molecular orbital (HOMO) at −11.8892 eV consists mainly of P(3p), Cu(d_{z^2}) and some S^{2-} character. On the other hand, the lowest unoccupied molecular orbitals (LUMO) are almost entirely σ*(W–S) in origin. Thus, the lowest energy allowed transition can be assigned to the [ψ(Cu,P) $\longrightarrow$ σ*(W–S)] transition with some mixing of $S^{2-} \longrightarrow W^{VI}$ charge-transfer character.

Photoluminescence of heterobimetallic d^0–d^{10} complexes has not been reported before. Fig. 3 shows the solid-state emission spectrum recorded at room temperature and at 77 K. At room temperature, two emissive bands, one at 440 nm and the other at 615 nm are observed. Upon cooling to 77 K the low energy emission band intensifies. The emission lifetime, monitored at 615 nm, is 2.8 ± 0.1 μs at room temperature, suggesting that this emission is phosphorescent in nature. No emission of the complex has been detected in CH_2Cl_2 or in acetonitrile. With reference to previous works on Cu^I–dppm complexes,[18] the high-energy emission is probably due to the intraligand emission of dppm. Based on the results of the EHMO calculations, we tentatively assign the 615 nm emission to the [ψ(Cu,P) $\longrightarrow$ σ*(W–S)] transition. Because the HOMO has only a small percentage contribution from the S atoms it is quite unlikely that the emitting state is ligand-to-metal charge transfer ($S^{2-} \longrightarrow W^{VI}$) transition in nature. In fact, $[NH_4]_2[WS_4]$ does not emit under similar reaction conditions.

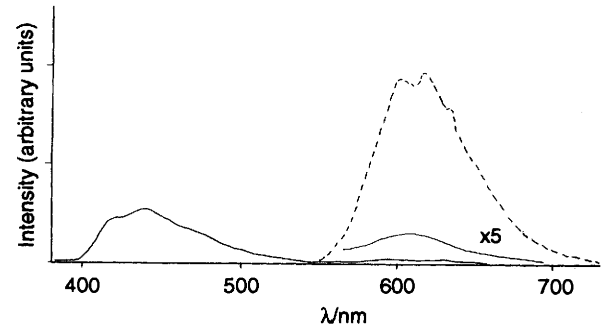

Fig. 3 Solid-state emission spectrum of $[Cu_3(dppm)_3(WS_4)]^+$ at room temperature (——) and at 77 K (– – – –)

Conclusion

Here we have illustrated, with one specific example, that heterobimetallic d^0–d^{10} complexes may possess intriguing photophysical properties. For the $[Cu_3(dppm)_3(WS_4)]^+$ complex studied the emitting state may be associated with the $Cu^I \longrightarrow W^{VI}$ transition. One would expect that for metal-centred transitions of this kind highly oxidizing and reducing metal centres in close proximity would be introduced after light excitation. By tuning the excited-state properties by appropriate choice of ancillary ligands, the photochemistry of heterobimetallic d^0–d^{10} complexes should be rich but yet is relatively unexplored.

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