A Luminescent Tetrameric Zinc(II) Complex containing the 7-Azaindolate Ligand. Photophysical Properties and Crystal Structure†

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Reaction of Zn^{II} with 7-azaindole in methanol and in the presence of triethylamine gave a tetrameric zinc(II) complex characterized by X-ray crystallography to be $[Zn_4O(C_7H_5N_2)_6]$. The measured intramolecular Zn ••• Zn separations and Zn–O distances are 3.147(2)–3.209(2) and 1.903(8)–1.975(8) Å respectively. At room temperature the cluster displays intense photoluminescence at 448 nm in the solid state and 425 nm in acetonitrile. The lifetime and quantum yield of the emission are 0.1 μs and 0.17 respectively.

Polynuclear d^{10} metal complexes are of current interest because of their intriguing structural and photoluminescent properties.[1–4] Despite numerous studies on gold-, copper- and silver(I) systems,[2–4] there is only one report on luminescent zinc(II) clusters. Vogler and Kunkely[4d] first reported the absorption and emission spectra of $[Zn_4O(O_2CMe)_6]$ which is regarded as a molecular model for ZnO.[4d,5] However, the electronic excited state of this complex has a lifetime of 10 ns, which is too short for bimolecular photochemical reactions. Herein is described a new tetrameric zinc(II) cluster with 7-azaindolate as bridging ligand. This complex is of interest because it possesses a long-lived and high-energy electronic excited state in fluid solution at room temperature.

Experimental

Materials.—The chemicals for synthesis were of analytical grade. Organic solvents for photoluminescent studies were distilled twice prior to use.

Preparation of $[Zn_4O(C_7H_5N_2)_6]$.—A solution of 7-azaindole (1*H*-pyrrolo[2,3-*b*]pyridine) (1.5 mmol) in methanol (20 cm^3) was heated to boiling, mixed with a solution of zinc acetate dihydrate (1 mmol in 30 cm^3 methanol) and triethylamine (1 cm^3) was added. The colourless complex $[Zn_4O(C_7H_5N_2)_6]\cdot$MeOH (40% yield) was obtained after filtration. UV/VIS (CH_2Cl_2 solution): 296 ($\varepsilon = 3.17 \times 10^4$) and 325nm (sh) ($\varepsilon = 1.13 \times 10^4$ dm^3 mol^{-1} cm^{-1}). IR (KBr): 3082w, 1579s, 1558m, 1464s, 1423vs, 1337s, 1280vs, 1263m, 1160vs, 1118w, 1067w, 1053w, 939w, 913m, 797m, 789m, 767m, 732m, 638w, 611w, 577w, 520w and 468w cm^{-1} (Found: C, 49.85; H, 2.80; N, 16.10. Calc. for $C_{42}H_{30}N_{12}OZn_4\cdot CH_4O$: C, 50.95; H, 3.35; N, 16.60%).

Structure Determination.—The crystals of $[Zn_4O(C_7H_5N_2)_6]\cdot CH_2Cl_2\cdot H_2O$ used were obtained by slow diffusion of diethyl ether into a methylene chloride solution of $[Zn_4O(C_7H_5N_2)_6]$. To prevent loss of solvent the crystals were sealed in a layer of epoxy resin. The data were collected on an Enraf-Nonius CAD4 four-circle diffractometer. Unit-cell constants were obtained by a least-squares fit to the setting angles of 25 strong reflections. Intensity data were collected using graphite-monochromated Mo-Kα radiation (λ = 0.7093 Å). A ψ-scan absorption correction was applied. The structure was solved by the Patterson method. Final refinement was carried out with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were included at idealized positions with a fixed isotropic thermal parameter $U_H = U_C + 0.01$ Å^2. Crystallographic programs used were those of NRCCSDP[6] installed on a Micro Vax III computer. A summary of the crystal data is given in Table 1. Table 2 lists the atomic coordinates of non-hydrogen atoms and selected bond distances and angles are given in Table 3.

Table 1 Crystallographic parameters

Formula	$C_{42}H_{30}N_{12}OZn_4\cdot CH_2Cl_2\cdot H_2$
M	1072.19
Colour	Colourless
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	10.263(1)
b/Å	10.447(1)
c/Å	20.817(3)
α/°	95.09(1)
β/°	94.22(1)
γ/°	96.26(1)
U/Å^3	2201.9(5)
Z	2
Crystal dimensions/mm	0.08 × 0.12 × 0.17
F(000)	1092
D_c/g cm^{-3}	1.617
Scan parameter	0.8 + 0.35tanθ
Scan speed/° min^{-1}	16.48/7 to 16.48/2
Maximum, minimum transmission	1.00, 0.87
2θ limit/°	45
hkl ranges	−11 to 10, 0–11, −22 to 22
Reflections collected	5727
Reflections observed [$I > 2\sigma(I)$]	2907
No. of variables	558
Maximum peak in difference map/ e Å^{-3}	0.640
Weighting scheme, *w*	$[\sigma^2(F) + 0.0001 F^2]^{-1}$
R	0.060
R′	0.054

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

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Table 2 Non-hydrogen atom coordinates for $[Zn_4O(C_7H_5N_2)_6]\cdot CH_2Cl_2\cdot H_2O$ with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Zn(1)	0.109 72(16)	0.611 86(15)	0.238 46(8)	N(1D)	−0.180 3(10)	0.899 9(10)	0.318 2(5)
Zn(2)	−0.125 90(15)	0.723 97(15)	0.307 07(8)	N(2D)	−0.039 8(10)	1.007 3(9)	0.248 2(5)
Zn(3)	−0.019 54(15)	0.851 28(15)	0.184 24(8)	C(1D)	−0.259 0(14)	0.942 2(13)	0.361 9(8)
Zn(4)	−0.175 46(17)	0.570 97(16)	0.167 66(9)	C(2D)	−0.253 1(15)	1.076 4(15)	0.371 8(8)
O(1)	−0.054 1(7)	0.690 4(7)	0.226 4(4)	C(3D)	−0.164 7(14)	1.117 5(12)	0.327 6(7)
N(1A)	0.124 7(10)	0.554 5(11)	0.325 6(5)	C(4D)	−0.112 6(16)	1.230 8(15)	0.310 0(8)
N(2A)	0.006 5(10)	0.709 5(11)	0.381 3(5)	C(5D)	−0.031 2(16)	1.237 9(13)	0.263 1(8)
C(1A)	0.208 0(14)	0.463 9(14)	0.347 9(8)	C(6D)	0.007 4(14)	1.126 4(13)	0.232 2(7)
C(2A)	0.222 5(16)	0.470 5(18)	0.414 7(8)	C(7D)	−0.123 4(12)	1.005 0(12)	0.293 7(6)
C(3A)	0.146 8(14)	0.573 5(16)	0.437 8(7)	N(1E)	−0.287 1(11)	0.452 8(10)	0.219 2(6)
C(4A)	0.123 5(18)	0.625 9(19)	0.493 9(8)	N(2E)	−0.271 2(10)	0.582 1(10)	0.322 4(6)
C(5A)	0.044 0(18)	0.725 7(19)	0.497 2(8)	C(1E)	−0.349 1(17)	0.335 0(15)	0.189 5(9)
C(6A)	−0.012 7(14)	0.762 3(16)	0.441 9(7)	C(2E)	−0.436 2(19)	0.268 5(18)	0.229 1(11)
C(7A)	0.089 6(12)	0.614 5(13)	0.379 4(6)	C(3E)	−0.413 6(15)	0.384 8(16)	0.303 1(9)
N(1B)	0.160 9(10)	0.869 8(9)	0.157 2(5)	C(4E)	−0.454(3)	0.392(3)	0.357 0(16)
N(2B)	0.266 6(10)	0.745 0(10)	0.230 1(6)	C(4E′)	−0.469(4)	0.278(4)	0.273(3)
C(1B)	0.210 4(13)	0.964 5(13)	0.120 7(6)	C(5E)	−0.412 0(17)	0.480 0(17)	0.391 8(11)
C(2B)	0.344 3(14)	0.991 5(14)	0.128 4(7)	C(6E)	−0.323 1(16)	0.582 3(17)	0.381 2(8)
C(3B)	0.387 1(13)	0.909 1(13)	0.175 0(6)	C(7E)	−0.318 7(12)	0.478 7(12)	0.278 7(7)
C(4B)	0.502 7(14)	0.882 8(15)	0.205 3(8)	N(1F)	−0.161 9(10)	0.862 8(10)	0.115 3(5)
C(5B)	0.502 3(14)	0.788 9(16)	0.245 4(8)	N(2F)	−0.302 2(10)	0.663 9(10)	0.118 0(5)
C(6B)	0.389 8(13)	0.719 9(14)	0.258 9(7)	C(1F)	−0.170 6(14)	0.973 5(13)	0.085 7(7)
C(7B)	0.268 8(12)	0.836 7(11)	0.190 5(6)	C(2F)	−0.292 0(18)	0.973 1(16)	0.046 1(7)
N(1C)	0.118 9(11)	0.479 1(11)	0.167 9(5)	C(3F)	−0.359 0(14)	0.843 9(16)	0.054 3(7)
N(2C)	−0.084 2(12)	0.470 3(11)	0.106 6(6)	C(4F)	−0.474 8(18)	0.769 8(22)	0.035 7(9)
C(1C)	0.231 4(16)	0.420 8(14)	0.160 2(7)	C(5F)	−0.507 3(19)	0.661 3(20)	0.055 6(10)
C(2C)	0.231 7(17)	0.334 9(16)	0.102 7(9)	C(6F)	−0.424 4(15)	0.606 4(15)	0.094 1(9)
C(3C)	0.093 6(17)	0.345 3(15)	0.073 3(7)	C(7F)	−0.272 7(12)	0.782 6(13)	0.096 6(6)
C(4C)	0.028 5(23)	0.300 4(19)	0.022 9(11)	C	0.793(4)	0.927(4)	0.583 2(20)
C(5C)	−0.092 0(19)	0.327 8(17)	0.009 7(9)	Cl(1)	0.615 9(18)	0.856 6(19)	0.538 0(9)
C(6C)	−0.143 0(17)	0.416 1(15)	0.050 4(9)	Cl(2)	0.718 1(22)	0.972 2(24)	0.641 4(11)
C(7C)	0.035 5(15)	0.434 7(11)	0.116 7(6)	O(2)	0.458 0(25)	0.779 0(25)	0.473 0(12)

Table 3 Selected bond distances (Å) and angles (°) of $[Zn_4O(C_7H_5N_2)_6]\cdot CH_2Cl_2H_2O$

Zn(1)···Zn(2)	3.176(2)	Zn(1)–N(2B)	2.04(1)	Zn(2)–N(1D)	1.98(1)	Zn(3)–N(2D)	2.05(1)
Zn(1)···Zn(3)	3.209(2)	Zn(2)···Zn(3)	3.193(2)	Zn(2)–N(2E)	2.05(1)	Zn(3)–N(1F)	1.99(1)
Zn(1)···Zn(4)	3.147(2)	Zn(2)···Zn(4)	3.165(2)	Zn(3)···Zn(4)	3.158(2)	Zn(4)–O(1)	1.941(7)
Zn(1)–O(1)	1.959(7)	Zn(2)–O(1)	1.903(8)	Zn(3)–O(1)	1.975(8)	Zn(4)–N(1E)	2.02(1)
Zn(1)–N(1A)	1.96(1)	Zn(2)–N(2A)	2.01(1)	Zn(3)–N(1B)	1.97(1)	Zn(4)–N(2F)	1.99(1)
Zn(2)–Zn(1)–Zn(3)	60.01(5)	Zn(1)–Zn(2)–N(2E)	112.6(3)	Zn(1)–Zn(3)–N(2D)	118.4(3)	Zn(1)–Zn(4)–O(1)	36.4(2)
Zn(2)–Zn(1)–Zn(4)	60.08(5)	Zn(3)–Zn(2)–Zn(4)	59.56(5)	Zn(1)–Zn(3)–N(1F)	132.8(3)	Zn(1)–Zn(4)–N(1E)	106.8(3)
Zn(2)–Zn(1)–O(1)	34.1(2)	Zn(3)–Zn(2)–O(1)	35.3(2)	Zn(2)–Zn(3)–Zn(4)	59.78(5)	Zn(1)–Zn(4)–N(2F)	141.3(3)
Zn(2)–Zn(1)–N(1A)	75.7(3)	Zn(3)–Zn(2)–N(2A)	117.2(3)	Zn(2)–Zn(3)–O(1)	33.8(2)	Zn(2)–Zn(4)–Zn(3)	60.66(5)
Zn(2)–Zn(1)–N(2B)	114.7(3)	Zn(3)–Zn(2)–N(1D)	77.5(3)	Zn(2)–Zn(3)–N(1B)	128.7(3)	Zn(2)–Zn(4)–O(1)	34.2(2)
Zn(3)–Zn(1)–Zn(4)	59.58(5)	Zn(3)–Zn(2)–N(2E)	136.0(3)	Zn(2)–Zn(3)–N(2D)	76.2(3)	Zn(2)–Zn(4)–N(1E)	79.2(3)
Zn(3)–Zn(1)–O(1)	35.5(2)	Zn(4)–Zn(2)–O(1)	35.0(2)	Zn(2)–Zn(3)–N(1F)	112.8(3)	Zn(2)–Zn(4)–N(2F)	105.9(3)
Zn(3)–Zn(1)–N(1A)	131.3(3)	Zn(4)–Zn(2)–N(2A)	131.1(3)	Zn(4)–Zn(3)–O(1)	35.9(2)	Zn(3)–Zn(4)–O(1)	36.6(2)
Zn(3)–Zn(1)–N(2B)	75.9(3)	Zn(4)–Zn(2)–N(1D)	117.9(3)	Zn(4)–Zn(3)–N(1B)	117.5(3)	Zn(3)–Zn(4)–N(1E)	139.1(3)
Zn(4)–Zn(1)–O(1)	36.0(2)	Zn(4)–Zn(2)–N(2E)	79.2(4)	Zn(4)–Zn(3)–N(2D)	129.7(3)	Zn(3)–Zn(4)–N(2F)	80.4(3)
Zn(4)–Zn(1)–N(1A)	115.5(3)	O(1)–Zn(2)–N(2A)	111.0(4)	Zn(4)–Zn(3)–N(1F)	76.6(3)	O(1)–Zn(4)–N(1E)	109.5(4)
Zn(4)–Zn(1)–N(2B)	131.1(3)	O(1)–Zn(2)–N(1D)	112.1(4)	O(1)–Zn(3)–N(1B)	110.5(4)	O(1)–Zn(4)–N(2F)	111.3(4)
O(1)–Zn(1)–N(1A)	109.0(4)	O(1)–Zn(2)–N(2E)	112.1(4)	O(1)–Zn(3)–N(2D)	109.5(4)	N(1E)–Zn(4)–N(2F)	105.3(5)
O(1)–Zn(1)–N(2B)	109.9(4)	N(2A)–Zn(2)–N(1D)	107.1(4)	O(1)–Zn(3)–N(1F)	110.4(4)	Zn(1)–O(1)–Zn(2)	110.6(4)
N(1A)–Zn(1)–N(2B)	108.5(4)	N(2A)–Zn(2)–N(2E)	100.8(4)	N(1B)–Zn(3)–N(2D)	108.4(4)	Zn(1)–O(1)–Zn(3)	109.3(4)
Zn(1)–Zn(2)–Zn(3)	60.50(5)	N(1D)–Zn(2)–N(2E)	113.1(4)	N(1B)–Zn(3)–N(1F)	115.7(4)	Zn(1)–O(1)–Zn(4)	107.6(3)
Zn(1)–Zn(2)–Zn(4)	59.50(5)	Zn(1)–Zn(3)–Zn(2)	59.49(5)	N(2D)–Zn(3)–N(1F)	101.7(4)	Zn(2)–O(1)–Zn(3)	110.9(3)
Zn(1)–Zn(2)–O(1)	35.3(2)	Zn(1)–Zn(3)–Zn(4)	59.23(5)	Zn(1)–Zn(4)–Zn(2)	60.42(5)	Zn(2)–O(1)–Zn(4)	110.9(4)
Zn(1)–Zn(2)–N(2A)	76.6(3)	Zn(1)–Zn(3)–O(1)	35.2(2)	Zn(1)–Zn(4)–Zn(3)	61.18(5)	Zn(3)–O(1)–Zn(4)	107.5(3)
Zn(1)–Zn(2)–N(1D)	132.4(3)	Zn(1)–Zn(3)–N(1B)	75.6(3)				

Physical Measurements.—Emission spectra were measured on a Spex-Fluorolog spectrofluorimeter. Lifetime measurements were conducted with a Quanta-Ray DCR-3 Nd-YAG pulsed laser system. The luminescence quantum yield was determined according to the method of Demas and Crosby.[7] Sample solutions for photochemical experiments were degassed by at least four successive freeze–pump–thaw cycles.

Results and Discussion

Tetrameric metal complexes having a M_4O (M = metal atom) core are not uncommon. It has been reported that the reactions of 7-azaindolate ($C_7H_5N_2^-$) with divalent metal ions such as Co^{II} and Cu^{II} would give complexes of the kind $[M_4O(C_7H_5N_2)_6]$.[8] In this work, the zinc(II) cluster was prepared by a similar method. It is an air-stable solid which is

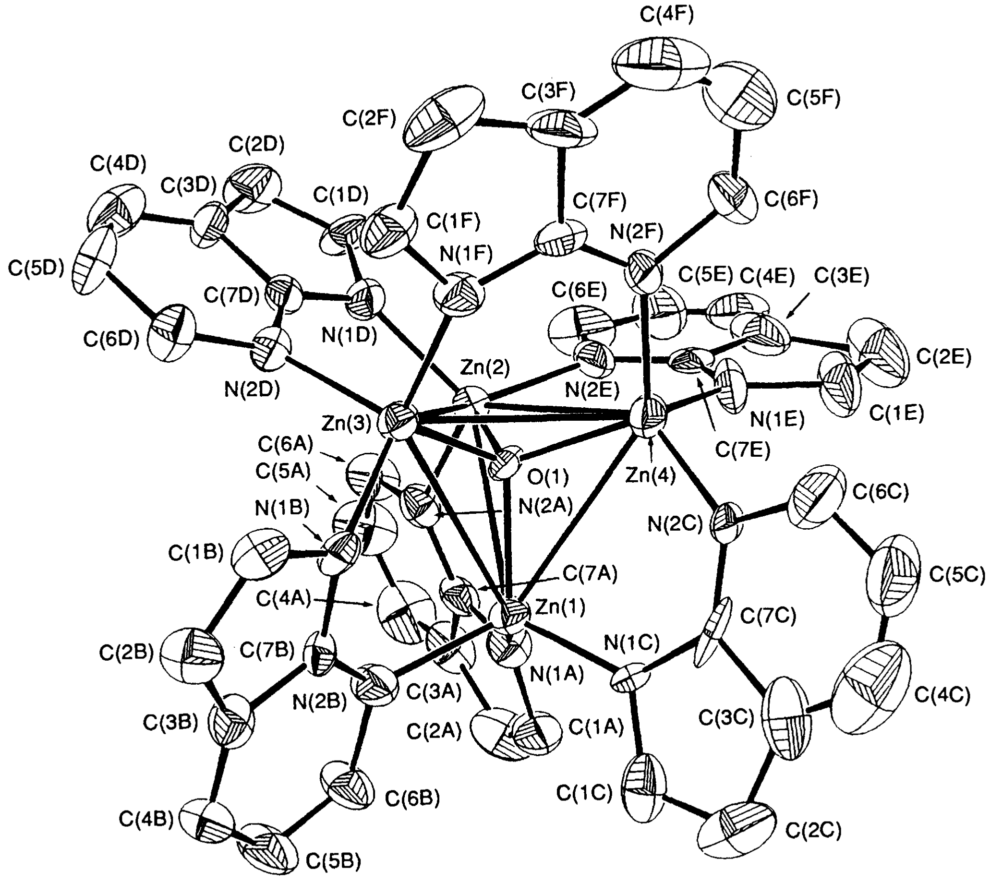

Fig. 1 A perspective view of $[Zn_4O(C_7H_5N_2)_6]$ showing the atom numbering

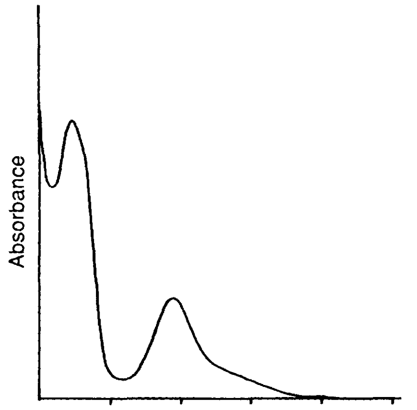

Fig. 2 The UV/VIS absorption spectrum of $[Zn_4O(C_7H_5N_2)_6]$ in acetonitrile

electrochemically inactive in acetonitrile. Although stable in acetonitrile, it undergoes degradation in dichloromethane or chloroform upon exposure to UV light. Fig. 1 shows a perspective view of the molecule with atom numbering. The complex is isostructural to $[Zn_4O(O_2CMe)_6]$[9] and $[Co_4O(C_7H_5N_2)_6]$[8] in that the central oxygen atom is tetrahedrally surrounded by four metal atoms. If the Zn··· Zn contacts are ignored, the local stereochemistry of the ZnN_3O chromophore is tetrahedral with the 7-azaindolate ion serving as a bridging ligand. The measured intramolecular Zn··· Zn separations of 3.147(2)–3.209(2) Å and Zn–O distances of 1.903(8)–1.975(8) Å are close to the values reported for $[Zn_4O(O_2CMe)_6]$ (Zn–O 1.97, Zn··· Zn 3.20 Å).[9]

Fig. 2 shows the UV/VIS absorption spectrum of the complex in acetonitrile at room temperature. It features intense bands centred at 223 and at 288–294 nm and a broad shoulder at around 330 nm. The bands at 288–294 nm, which are absent in the spectrum of $[Zn_4O(O_2CMe)_6]$[4d] but present for the free 7-azaindole ligand, are assigned to the spin-allowed intraligand $\pi \longrightarrow \pi^*$ transitions. The nature of the band at 223 nm is difficult to acertain, since a similar band at 219 nm is also present for the free ligand. For a tetrameric zinc(II) system of the type $Zn_4O(L)_6$ where L is a bridging ligand the highest occupied molecular orbital (HOMO) is likely to be a hybrid of the p_π orbitals of the central oxygen atom and ligand L, whereas the lowest unoccupied molecular orbital (LUMO) $4S_\sigma$ comes from the symmetric combination of the four zinc(II) 4s orbitals.[4d] Thus, other than the possible intraligand $\pi \longrightarrow \pi^*$ transition of L, the ligand-to-metal charge-transfer (l.m.c.t.) transition $p_\pi(O^{2-},L) \longrightarrow 4S_\sigma$ would also exist. For the $[Zn_4O(O_2CMe)_6]$ system the l.m.c.t. band occurs at around 216 nm. Because p_{π^*} of 7-azaindolate ion is lower in energy than that of $MeCO_2$ and that the 4s orbital may also mix with the π^* of L, the analogous l.m.c.t. band of $[Zn_4O(C_7H_5N_2)_6]$ is expected to occur at a much lower energy than that at 216 nm for $[Zn_4O(O_2CMe)_6]$. The broad shoulder at 330 nm in Fig. 2 may be due to such an electronic transition. For comparison, the analogous $p_\pi(O^{2-}) \longrightarrow 4s\ (Zn^{II})$ transition of molecular ZnO occurs at $\lambda < 365$ nm, depending on the particle size.[10]

The complex exhibits intense photoluminescence both in the solid state and in fluid solutions. Fig. 3 shows the excitation and emission spectra measured in degassed acetonitrile at room temperature. The excitation spectrum is similar to the absorption spectrum. Cooling the solid sample down to 77 K leads to an enhancement of the emission intensity but without any observable vibronic feature as shown in Fig. 4. In degassed acetonitrile the lifetime and quantum yield of the emission are 0.1 μs and 0.17 respectively. The long measured lifetime suggests

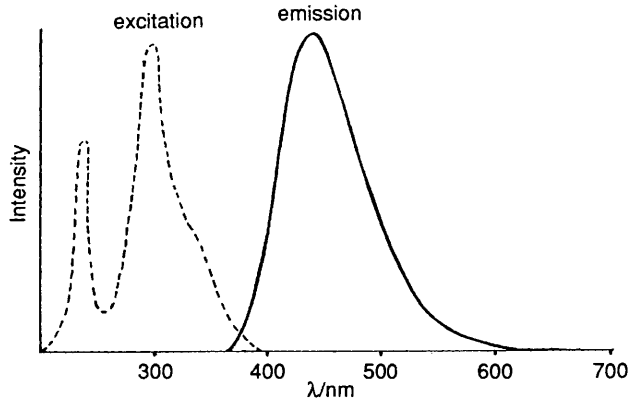

Fig. 3 Excitation and emission spectra of $[Zn_4O(C_7H_5N_2)_6]$ (*ca.* 10^{-4}–10^{-5} mol dm^{-3}) in degassed acetonitrile at room temperature

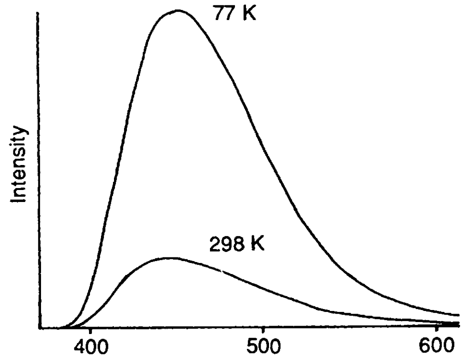

Fig. 4 Emission spectra of a solid sample of $[Zn_4O(C_7H_5N_2)_6]$ at 298 and 77 K

that the emission comes from a spin-forbidden transition. We assign it to the spin-forbidden $4S_\sigma \longrightarrow p_\pi$ (O^{2-},L) transition. Unlike the case of $[\{Cu(py)I\}_4]$ (py = pyridine) where there is a large red shift in emission energy from the solid to solution,[3a] the reverse is true for the present complex (solid, 448; acetonitrile, 425 nm). This is understandable because in the copper system the emitting electronic excited state is metal-centred and has a stronger metal–metal interaction than in the ground state. In the present zinc(II) system the orbitals involved in the electronic transition do not come from metal–metal bonding interaction which is anticipated to be insignificant for Zn^{II}.

The $[Zn_4O(C_7H_5N_2)_6]$ complex represents a new zinc(II) cluster having an electronic excited-state lifetime 10 times longer than that for $[Zn_4O(O_2CMe)_6]$. From the low-temperature emission spectrum, the 0–0 energy of the long-lived excited-state molecule is estimated to be around 400 nm (3.2 eV, *ca.* 5×10^{-19} J). Such a high energy and long-lived excited-state molecule is uncommon in the chemistry of luminescent metal clusters and may be a potential sensitizer for photochemical energy-transfer processes.

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