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Luminescence characteristics and X-ray crystal structure of $[Cd(bipy)_3][PF_6]_2$ (bipy = 2,2′-bipyridine)

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The photoluminescence characteristics of the $[Cd(bipy)_3][PF_6]_2$ complex are reported. A moderately large quantum yield (φ) of 1.07×10^{-2} is exhibited in acetonitrile solution at 298 K. Crystallography shows the dication to have a distorted octahedral geometry and the crystal structure to be stabilized by C–H···π and C–H···F interactions. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: cadmium(II); 2,2′-bipyridine; luminescence; crystal structure

INTRODUCTION

Zinc(II) and cadmium(II) ions, are very attractive luminescent centres owing to their high colour purity and luminescence efficiency.[1–4] However, the luminescence intensity of coordinated cadmium(II) ions is not always strong. In order to overcome this characteristic, chelation of the cadmium(II) ion with appropriate ligands, which themselves have broad intense absorption bands, can greatly enhance the emission intensity. One such ligand, 2,2′-bipyridine (bipy), which has a large conjugated π-electron system, is a good activator of luminescence.[5] Herein, the luminescence characteristics of $[Cd(bipy)_3][PF_6]_2$, which show enhanced emission due to complexation, are reported as well as its crystal and molecular structure.

RESULTS AND DISCUSSION

The $[Cd(bipy)_3][PF_6]_2$ complex was prepared from the reaction between $Cd(NO_3)_2 \cdot 4H_2O$ and 2,2′-bipyridine in 1 : 3 mol ratio. The pink crystals were isolated as a PF_6 salt in very high yield. The molecular structure was established by X-ray crystallography. The crystallographic asymmetric unit, i.e. one $[Cd(bipy)_3]$ dication and two $[PF_6]$ anions, is represented in Fig. 1 and selected geometric parameters are collected in Table 1; the structure is isomorphous with the manganese(II)[6] and ruthenium(II)[7] analogues. The cadmium(II) centre exists in a distorted octahedral geometry defined by an N_6 donor set derived from three chelating bipy ligands. The range of Cd–N bond distances is relatively large at 2.308(5)–2.355(5) Å, but this reflects the disparity in Cd–N bond distances formed by only one of the bipy ligands, i.e. containing the N5 and N6 atoms, which is rather asymmetric in its mode of coordination. By contrast, the ligand containing the N3 and N4 atoms coordinates forms experimentally equivalent Cd–N distances while the remaining bipy ligand coordinates in a fashion intermediate between the two extremes just mentioned. The bipy ligands are not perfectly planar, with twists apparent in the N/C/C/N portions of the molecules, as manifested in the values of the respective torsion angles of −15.0(8), −6.2(9) and 20.9(6)°. These angles correlate with the degree of asymmetry of the Cd–N bonds in that the smallest deviation from planarity is associated with the ligand forming the symmetric Cd–N bonds. The greatest deviation from the ideal octahedral geometry is evident in the N–Cd–N chelate angles that range from 71.36(15) to 71.71(17)°. The geometries of the PF_6 anions, with effectively octahedral phosphorus atom geometries, are as expected and are not discussed further. Cohesive C–H···π and P–F···H interactions dominate the crystal packing. The $[Cd(bipy)_3]$ dications are aligned along the crystallographic 3_1 axis via C18–H···π interactions so that the C18–H··· ring centroid

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Table 1. Selected bond distances (Å) and angles (°) for $[Cd(bipy)_3][PF_6]_2$

Cd–N1	2.345(4)	Cd–N2	2.320(4)
Cd–N3	2.339(5)	Cd–N4	2.341(4)
Cd–N5	2.308(5)	Cd–N6	2.355(5)
N1–Cd–N2	71.36(15)	N1–Cd–N3	93.51(15)
N1–Cd–N4	162.14(14)	N1–Cd–N5	97.63(16)
N1–Cd–N6	100.97(15)	N2–Cd–N3	98.54(16)
N2–Cd–N4	100.73(15)	N2–Cd–N5	160.21(15)
N2–Cd–N6	93.80(15)	N3–Cd–N4	71.43(16)
N3–Cd–N5	98.51(18)	N3–Cd–N6	163.39(15)
N4–Cd–N5	94.16(16)	N4–Cd–N6	95.43(16)
N5–Cd–N6	71.71(17)	Cd–N1–C1	123.9(4)
Cd–N1–C5	115.3(3)	Cd–N2–C6	116.5(4)
Cd–N2–C10	123.7(3)	Cd–N3–C11	124.7(4)
Cd–N3–C15	117.1(4)	Cd–N4–C16	117.1(4)
Cd–N4–C20	123.3(4)	Cd–N5–C21	122.7(4)
Cd–N5–C25	117.2(4)	Cd–N6–C26	114.4(3)
Cd–N6–C30	125.2(4)		

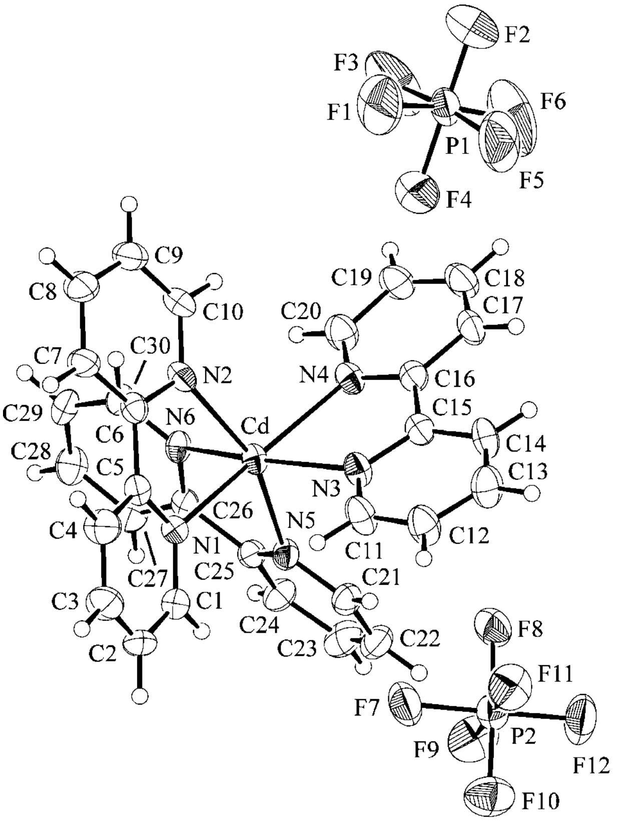

Figure 1. Molecular structures of the cation and anions in $[Cd(bipy)_3][PF_6]_2$ showing the crystallographic numbering scheme employed.

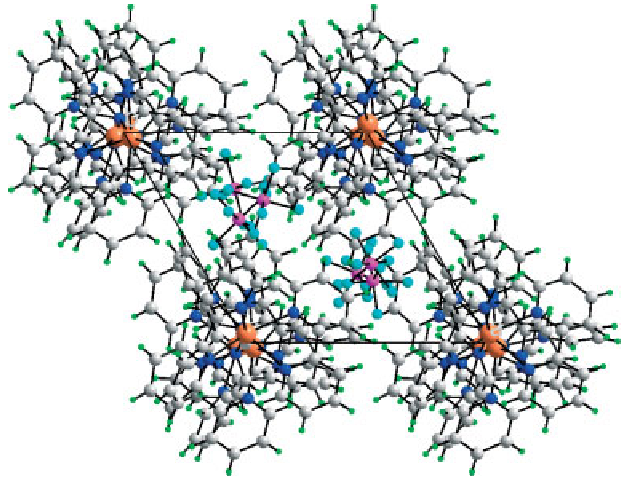

Figure 2. View, down the *c*-axis, of the crystal packing in $[Cd(bipy)_3][PF_6]_2$.

of N6-pyridine is 2.85 Å and the angle at H18 is 149° for symmetry operation *i*: $-x+y$, $-x$, $-1/3+z$. There are a myriad P–F···H interactions operating in the structure, and these serve to stabilize the aforementioned chains by forming links between successive dications as well as linking adjacent chains. Indeed, the shortest and most directional P–F···H interaction formed by each PF_6 anion is an interchain contact. Thus, for the first anion C14–H···F3^{ii} is 2.44 Å, C14···F3^{ii} is 3.305(12) Å and the angle at H14 is 154°, and for the second anion, C24–H···F10^{iii} is 2.36 Å, C24···F10^{iii} is 3.215(8) Å and the angle at H24 is 152°; symmetry operations *ii*: x, $1+y$, z and *iii*: x,$-1+y$, z. A view of the unit cell contents is shown in Fig. 2.

Emission spectra were recorded on a Perkin–Elmer LS55 luminescence spectrometer. The quantum yield (φ) of the $[Cd(bipy)_3][PF_6]_2$ complex at room temperature in acetonitrile solution was determined by a relative method using an organic compound (a cyclohexane solution of aniline) as the standard. The data obtained were used to calculate φ using the relationship:[8]

$$\varphi = \varphi_{std}(A_{std}/A)(\mathrm{I}/\mathrm{I}_{std})(\eta^2/\eta^2_{std})$$

where φ and φ_{std} are the quantum yields of unknown and standard samples, A and A_{std} are the solution absorbances at the excitation wavelength (λ_{ex}), I and I_{std} are the integrated emission intensities, and η and η_{std} are the refractive indices of the solvents used to prepare the solutions of the unknown and standard samples, respectively. In acetonitrile solution, $[Cd(bipy)_3][PF_6]_2$ displays two intense UV-absorption bands. The free bipy ligand in the same solvent also shows two absorption maxima at 281 and 235 nm owing to $\pi-\pi^*$ transitions. In the complex, these bands are red-shifted to 295 and 243 nm, respectively, due to perturbation of these $\pi-\pi^*$ transitions by the metal centre. Excitation of $[Cd(bipy)_3][PF_6]_2$ with energy corresponding to any one of these absorption maxima gives rise to an emission at 326 nm with a quantum yield (φ) of 1.07×10^{-2}. The cadmium(II) centre in the complex plays a key role in the enhancement of fluorescent emission of free bipy ligand, which becomes more rigid on coordination to the metal centre, thus reducing the loss of energy by thermal vibrational decay.[1,9]

Luminescence properties of cadmium(II) complexes are not well documented. Only a few such studies have been reported,[9–12] and none involve quantum yield data. The $[Ru(bipy)_3]^{2+}$ complex is known as a strong fluorescence emitter with a quantum yield of 3.2×10^{-2} under identical experimental conditions employed in the present study.[13] A comparison with $[Ru(bipy)_3]^{2+}$ thus suggests that $[Cd(bipy)_3][PF_6]_2$ is a moderately strong fluorescence emitter, with a quantum yield data one third that of the $[Ru(bipy)_3]^{2+}$ dication.

EXPERIMENTAL

Materials

Cadmium nitrate tetrahydrate, 2,2′-bipyridine, and ammonium hexafluorophosphate were purchased from Aldrich. All other chemicals were commercially available and used as received. Solvents were reagent grade.

Synthesis of $[Cd(bpy)_3](PF_6)_2$

To an aqueous solution of cadmium nitrate tetrahydrate (0.15 g, 0.5 mmol) was added a solution of 2,2′-bipyridine (0.23 g, 1.5 mmol) in 20 ml of methanol. The resulting light-pink solution was stirred for 30 min and then ammonium hexafluorophosphate (0.163 g, 1.0 mmol) was added. After a further 30 min stirring, the solution was filtered and left in air for slow evaporation. After about a week, a pink crystalline compound was obtained along with X-ray diffraction quality crystals. It was filtered, washed with diethyl ether and dried *in vacuo*. Yield: 0.4 g (93%). Anal. calcd for $C_{30}H_{24}CdN_6F_{12}P_2$: C, 41.38; H, 2.75; N, 9.65. Found: C, 40.98; H, 2.72; N, 9.56%.

Crystal structure determination

Intensity data were measured for a light-pink crystal at 223 K on a Bruker AXS SMART CCD with graphite monochromatized Mo $K\alpha$ radiation (0.71069 Å) so that $\theta_{max} = 30.0°$. The structure was solved by heavy-atom methods[14] and refined[15] on F^2 with non-hydrogen atoms modelled with anisotropic displacement parameters, with hydrogen atoms in the riding model approximation and using a weighting scheme of the form $w = 1/[\sigma^2(F_o^2) + (0.047P)^2]$ where $P = (F_o^2 + 2F_c^2)/3)$. The refinement converged to final R [for 5801 reflections with $I > 2\sigma(I)$] = 0.052. $wR = 0.114$ (all 9234 data). The absolute structure was confirmed by the value of the Flack parameter,[16] i.e. −0.03(2). *Crystal data*: $C_{30}H_{24}CdN_6F_{12}P_2$, $M = 870.89$, hexagonal, space group $P3_1$, $a = 10.4528(4)$, $c = 26.541(2)$ Å, $V = 2511.4(2)$Å^3, $Z = 3$, $D_c = 1.728$ g/cm^3, $\mu = 0.848$ mm^{-1}, $F(000) = 1296$. CCDC deposition no. = 275 094. Figures 1 and 2 were drawn with ORTEP[17] and DIAMOND,[18] respectively.

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