Synthesis, structure and photoluminescence of [*N*-ethyl-4,4′-bipyridinium][$CdBr_4$] with *N*-ethyl-4,4′-bipyridinium generated *in situ*

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A new viologen(4,4′-bipyridinium)-based complex [*N*-ethyl-4,4′-bipyridinium][$CdBr_4$], in which *N*-ethyl-4,4′-bipyridinium (EQ^{2+}) has been generated *in situ*, has been synthesised via hydrothermal reaction and structurally characterised by single-crystal X-ray diffraction. [*N*-ethyl-4,4′-bipyridinium][$CdBr_4$] features an isolated structure, based on an *N*-ethyl-4,4′-bipyridinium moiety and a cadmium atom terminally bound by four bromine atoms. Photoluminescence investigation reveals a broad and intense emission in blue region, which may originated from $\pi \rightarrow \pi^*$ charge-transfer interaction of the *N*-ethyl-4,4′-bipyridinium moiety.

Keywords: bipyridine, *N*-ethyl-4,4′-bipyridinium cadmium, photoluminescence

In the past decade, metal/ligand reactions under hydro (solvo)thermal conditions have attracted increasing attention, due to *in situ* ligand syntheses leading to the formation of novel coordination complexes with structural diversity or interesting properties for various potential applications.[1–3] Recently a variety of novel coordination complexes synthesised *in situ* has been reported, amongst which are many transition metal complexes that play a very important role in many areas of chemistry and biology.[4–6] Metal complexes containing group 12 (IIB) elements are particularly attractive for many reasons, such as, the variety of coordination numbers and geometries provided by the d^{10} configuration of the IIB metal ions, photoelectric properties, and fluorescent properties, *etc*. Fluorescent materials, particularly blue fluorescent materials, have been of intense interest because blue fluorescence is one of the key colour components required for full-colour EL displays. Our recent efforts in synthesising novel group IIB-based complexes have focused largely on systems with blue fluorescence. Herein, we report the synthesis, structure, and photoluminescence of [*N*-ethyl-4,4′-bipyridinium][$CdBr_4$] (**1**) with *N*-ethyl-4,4′-bipyridinium generated *in situ* for the first time.

Experimental

All reactants of A.R. grade were obtained commercially and used without further purification. The fluorescent data were collected at room temperature on a computer-controlled JY FluoroMax-3 spectrometer.

*[N-ethyl-4,4′-bipyridinium][$CdBr_4$](**1**):* $CdBr_2$ (1 mmol, 272 mg), 4,4′-bipyridine (1 mmol, 156 mg), concentrated HBr acid (1 mL), ethanol (2 mL) were mixed with distilled water (7 mL) in a 25 mL Teflon-lined stainless steel autoclave and heated at 200 °C for 10 days. After slowly cooling the resulting solution to room temperature at 6 °C/h, yellow crystals suitable for X-ray analysis were obtained. The yield was 86% (based on cadmium).

X-ray structure determination

The intensity data set was collected on a Rigaku Mercury CCD X-ray diffractometer with graphite monochromated Mo-$K\alpha$ radiation (λ = 0.71073 Å) by using an ω scan technique. CrystalClear software was used for data reduction and empirical absorption corrections.[7] The structure was solved by the direct method using the Siemens SHELXTL™ Version 5 package of crystallographic software.[8] Difference Fourier maps based on the atomic positions yielded all non-hydrogen atoms. The hydrogen atom positions were generated theoretically and allowed to ride on their respective parent atoms and included in the structure factor calculations with assigned isotropic thermal parameters but were not refined. The structure was refined using a full-matrix least-squares refinement on F^2. All non-hydrogen atoms were refined anisotropically. The summary of crystallographic data and structure analysis is given in Table 1. The selected bond lengths and bond angles are listed in Table 2. Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 687257. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. Fax: (44) 1223 336-033; E-mail: deposit@ccdc.cam.ac.uk

Table 1 Summary of crystallographic data and structure analysis for **1**

Formula	$C_{12}H_{13}Br_4CdN_2$
Formula weight	617.28
Colour	Yellow
Crystal size/mm³	0.21 0.14 0.12
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	8.415(5)
b (Å)	23.217(3)
c (Å)	9.251(5)
β (°)	105.603(8)
V (Å³)	1741(1)
Z	4
$2\theta_{max}$ (°)	50.06
Index ranges	$-10 \le h \le 10$, $-27 \le k \le 27$, $-10 \le l \le 11$
Reflections collected	10366
Independent, observed reflections (R_{int})	3036, 2297 (0.0346)
$d_{calcd.}$ (g/cm³)	2.355
μ (mm⁻¹)	10.424
T (K)	293(2)
F(000)	1148
$R1$, $wR2$	0.0310, 0.0615
S	1.030
Largest and Mean Δ/σ	0.001, 0
$\Delta\rho$(max/min) (e/Å³)	0.612/–0.489

Table 2 Selected bond lengths and bond angles

Bond	Length/Å	Bond	Length/Å
Cd(1)–Br(1)	2.566(2)	Cd(1)–Br(3)	2.592(1)
Cd(1)–Br(2)	2.5887(9)	Cd(1)–Br(4)	2.5803(8)
Angle	**(°)**	**Angle**	**(°)**
Br(1)-Cd(1)–Br(2)	112.75(3)	Br(2)-Cd(1)–Br(3)	103.93(4)
Br(1)-Cd(1)–Br(3)	113.48(4)	Br(4)-Cd(1)–Br(2)	108.30(4)
Br(1)-Cd(1)–Br(4)	107.68(2)	Br(4)-Cd(1)–Br(3)	110.60(3)

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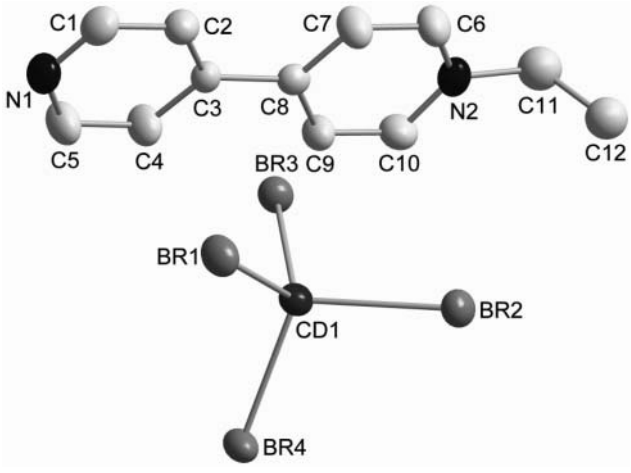

Fig. 1 ORTEP drawing of **1** with 35% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

Results and discussion

X-ray diffraction analysis reveals that, as shown in Fig. 1, the structure of the title complex consists of an *N*-ethyl-4,4′-bipyridinium moiety and a cadmium atom terminally bound by four bromine atoms with the bond lengths of Cd(1)–Br(1), Cd(1)–Br(2), Cd(1)–Br(3) and Cd(1)–Br(4) being 2.566(2), 2.5887(9), 2.592(1) and 2.5803(8) Å, respectively, which are normal and comparable with counterparts found in the literature.[9–11] The bond angles of Br–Cd–Br are in the range of 103.93(4)–113.48(4)°, which are close to those in a regular tetrahedron. The two pyridyl rings of the *N*-ethyl-4,4′-bipyridinium moiety are slightly twisted with a dihedral angle of *ca* 5.15°, which is comparable with that previously documented.[12–14] For the title complex, no π…π stacking interactions were found between the *N*-ethyl-4,4′-bipyridinium moieties. The *N*-ethyl-4,4′-bipyridinium moieties and $[CdBr_4]^{2-}$ dianions are linked via Br...C and Br...N hydrogen bonds to yield a zigzag chain running along the [2, 0, 1] direction. The hydrogen bonds and electrostatic interactions among the *N*-ethyl-4,4′-bipyridinium moieties and $[CdBr_4]^{2-}$ dianions contribute to the stabilisation of the crystal packing of **1** (Fig. 2). Results of bond valence calculations indicate that the cadmium atom is in the +2 oxidation state (Cd1: 2.14).[15] Since all the bromine atoms are in the –1 oxidation state, for the requirement of charge balance, the nitrogen atoms of the *N*-ethyl-4,4′-bipyridinium moiety must be protonated (the N-H bond lengths are 0.86 Å and 0.91 Å, respectively), as found in other complexes.[16–18] To our knowledge, complex **1** is the first EQ^{2+}-containing metal complex, although one EQ^{+}-containing complex in which the bipy is mono-protonated[19] and many EV^{2+}-containing complexes have been documented [20,21] (EQ^{2+} = *N*-ethyl-4,4′-bipyridinium, EQ^{+} = *N*-ethyl-4,4′-pyridinium, EV^{2+} = *N*, *N*′-diethyl-4,4′-bipyridinium).

A search from the Cambridge Crystallographic Data Centre (CCDC) shows that there are dozens of complexes containing isolated $[CdBr_4]^{2-}$ dianions.[22,23] However, in these complexes the counterpart cations are various but none of them is the *N*-ethyl-4,4′-bipyridinium dication. Therefore, complex **1** is the first example of an $[CdBr_4]^{2-}$-containing complex with *N*-ethyl-4,4′-bipyridinium as a counter ion.

Unlike the syntheses of other viologen-based complexes, in which the viologen cation was derived from the starting reagent,[25,25] the preparation of **1** resulted in the *in situ* generation of the EQ^{2+} dication. This provides a route for the synthesis of viologen-based complexes, and makes the synthesis of viologen comparatively less toxic and more efficient. To our knowledge, this is the first example of the *in situ* generation of the EQ^{2+} dication, although an unprecedented *in situ* generation of the EV^{2+} dication was reported before.[26]

The solid-state emission spectra of **1** were investigated at room temperature. and the emission spectrum of **1** is given in Fig. 3. The fluorescent spectral study shows that **1** exhibits a broad and strong blue-light emission band with a maximum wavelength of 428 nm upon photo-excitation at 345 nm. To understand the nature of the luminescence of **1**, the luminescent spectra of pure bipy were also measured under the same conditions. For pure bipy, the emission spectra show one intense emission band in the blue region with a maximum wavelength of 438 nm upon photo-excitation at 357 nm (inner plot of Fig. 3). The similarity of the luminescent spectrum of **1** and pure bipy suggests that the emission spectrum of **1** should be assigned as an intraligand $\pi \rightarrow \pi^*$ transition of the *N*-ethyl-4,4′-bipyridinium moiety.

In summary, a novel viologen-based complex [*N*-ethyl-4,4′-bipyridinium][$CdBr_4$] (**1**), in which the *N*-ethyl-4,4′-bipyridinium was generated *in situ* for the first time, has been synthesised *via* a hydrothermal reaction. The crystal structure features an isolated structure, based on a *N*-ethyl-4,4′-bipyridinium moiety and a cadmium atom terminally bound by four bromine atoms. Complex **1** exhibits a strong blue fluorescent emission band.

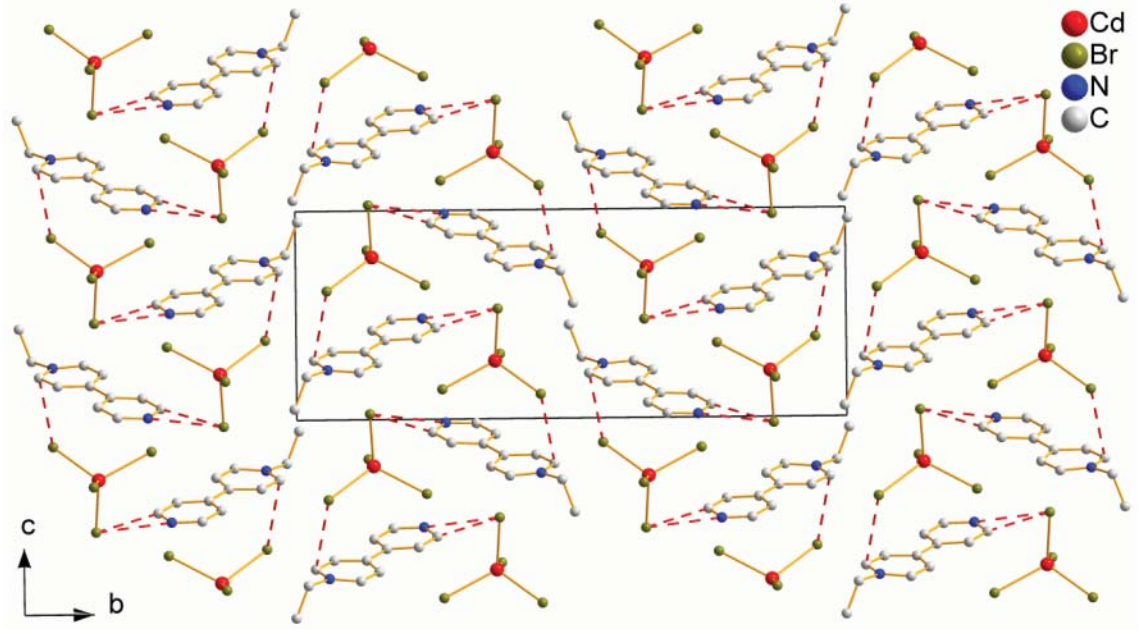

Fig. 2 Packing diagram of **1** with the dashed lines representing hydrogen bonds (Å): Br2...C6(1+*x*, *y*, 1+*z*) 3.483(6), Br3...N1(*x*, 3/2–*y*, 1/2+*z*) 3.379(5) and Br3...C5(*x*, 3/2–*y*, 1/2+*z*) 3.497(6).

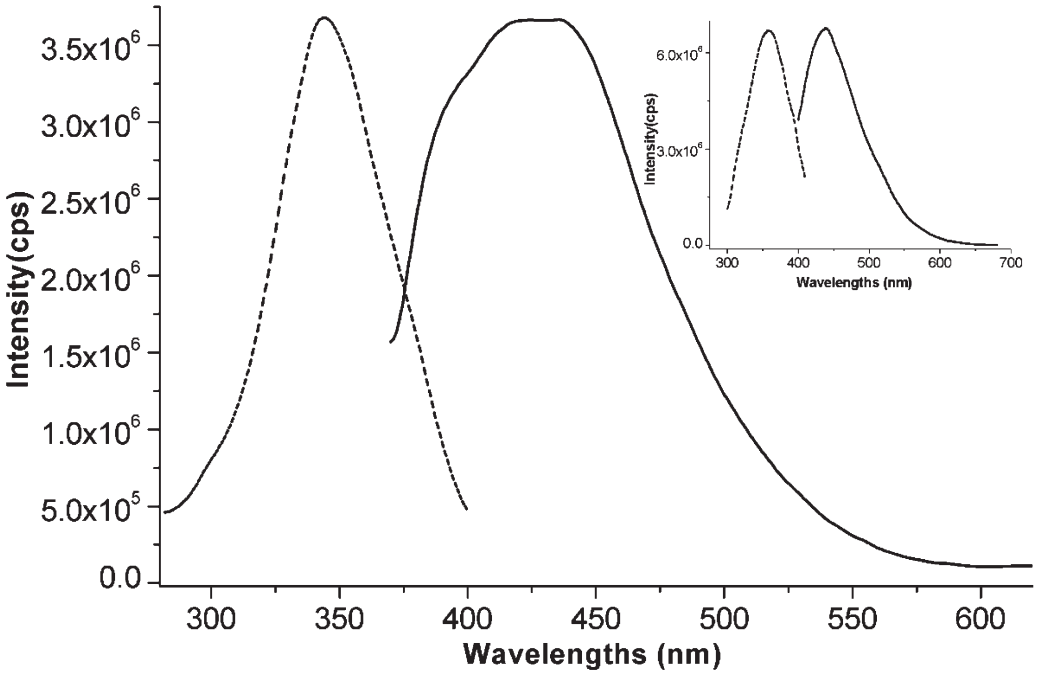

Fig. 3 Solid-state emission and excitation spectra of **1** at room temperature (inset plot: pure bipy ligand). Solid line: emission spectrum; dashed line: excitation spectrum.

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