

4,4'-Bipyridinium tetrabromo-  
cadmate(II) with strong fluorescenceWen-Tong Chen,\* Xi-Rui Zeng, Xiao-Niu Fang, Xin-Fa Li  
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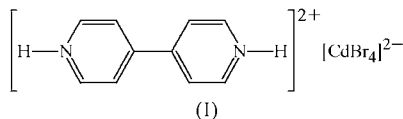
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The title compound,  $(C_{10}H_{10}N_2)[CdBr_4]$ , was synthesized *via* a hydrothermal reaction. Its structure features discrete 4,4'-bipyridinium cations and tetrahedral  $[CdBr_4]^{2-}$  anions linked into ion pairs by single  $N-H \cdots Br$  hydrogen bonds. Photoluminescent investigation reveals that the title compound displays a strong emission in the blue region, which may originate from  $\pi \rightarrow \pi^*$  charge-transfer interactions of the 4,4'-bipyridinium cations.

## Comment

The ability of bifunctional 4,4'-bipyridine (bipy) to act as a rigid rod-like organic building block in the self-assembly of coordination frameworks is well known. Bipy is found as a charge-compensating cation (Zapf *et al.*, 1997; Lu *et al.*, 2005), a pillar bonding to an inorganic skeletal backbone (Chen *et al.*, 2003; Wang, Liao *et al.*, 2005), an uncoordinated guest molecule and organic template (Prabusankar *et al.*, 2004; Biradha & Mahata, 2005), a bridge connecting two metal complex moieties (Jude *et al.*, 2005; Yang & Mao, 2005), or a ligand linking a metal and an inorganic framework (Yaghi & Li, 1996; Shi *et al.*, 2000; Wang, Zhou *et al.*, 2005). Bipy has also attracted attention in recent years because of its common characteristic of delocalized  $\pi$  electrons across the pyridyl rings, which makes it an excellent candidate in preparing light-emitting compounds with potential in various technical applications, such as chemical sensors (Vogler & Kunkely, 2001; Sun & Lees, 2002), sensitizers in solar energy conversion (Hagfeldt & Gratzel, 2000; Balzani & Juris, 2001), and emitting materials for organic light-emitting diodes (Baldo *et al.*, 1998; Gao & Bard, 2000).



Recently, many structures of metal halide–bipy materials have been reported (Lu *et al.*, 1998; Hu *et al.*, 2003). However,

among these, group 12 (IIB) metal halide–bipy materials are relatively rare. Compounds containing group 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, their photoelectric and fluorescent properties, the widespread application of IIB compounds, and the essential role of zinc in biological systems. Fluorescent materials, particularly blue fluorescent materials, are of considerable interest because blue fluorescence is one of the key colour components required for full-colour electroluminescent displays and blue fluorescent materials are still rare. While neutral 4,4'-bipy can act as a ligand, the 4,4'-H<sub>2</sub>bipy dication usually forms supramolecular frameworks through hydrogen bonding and cannot act as a ligand. Our recent efforts towards synthesizing novel group IIB-based compounds have focused largely on systems containing 4,4'-H<sub>2</sub>bipy. We describe here the hydrothermal synthesis and characterization of the title compound, namely (4,4'-H<sub>2</sub>bipy)- $[CdBr_4]$ , (I).

The structure of (I) consists of discrete 4,4'-H<sub>2</sub>bipy dications and tetrabromocadmate(II) dianions (Fig. 1). The anion has a reasonably regular tetrahedral geometry (Table 1), with Cd–Br distances in the normal range and comparable with those reported by Chesnut *et al.* (1999) and Liu *et al.* (2002). The two pyridyl rings of the cation are slightly twisted, with a small dihedral angle of  $5.53(18)^\circ$ , which is comparable with that previously documented (Lu *et al.*, 1998). There are no  $\pi \rightarrow \pi^*$  stacking interactions between the cations. Single  $N-H \cdots Br$  hydrogen bonds link the cations and anions into ion pairs (Table 2 and Fig. 1).

The structures of several analogous salts have already been documented (Gillon *et al.*, 1999, 2000), of which five are isomorphous with the title compound, namely (4,4'-H<sub>2</sub>bipy) $[ZnCl_4]$ , (II), (4,4'-H<sub>2</sub>bipy) $[ZnBr_4]$ , (III), (4,4'-H<sub>2</sub>bipy)-

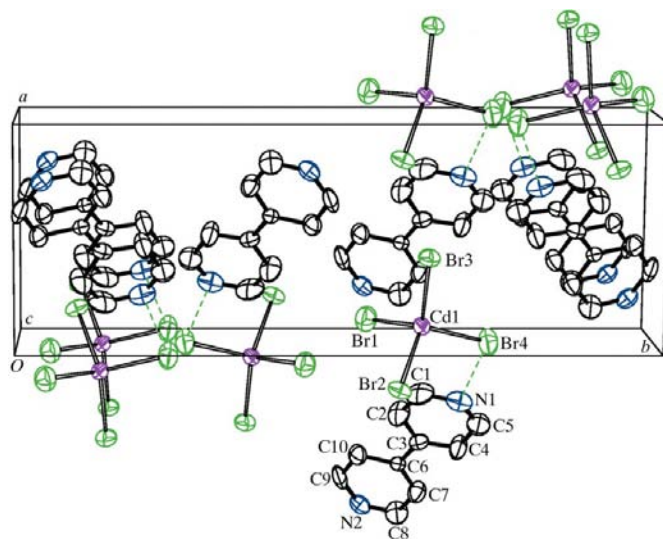


Figure 1

A packing diagram for (I), showing the atom-labelling scheme. Dashed lines represent  $N-H \cdots Br$  hydrogen bonds. Displacement ellipsoids are drawn at the 35% probability level and H atoms have been omitted for clarity.

[HgCl<sub>4</sub>], (IV), and (4,4'-H<sub>2</sub>bipy)[CoCl<sub>4</sub>] and (4,4'-H<sub>2</sub>bipy)-[CoBr<sub>4</sub>]. Salts (II)–(IV) are group IIB metal halides with 4,4'-H<sub>2</sub>bipy. The tetrachloro analogue of the title compound, (4,4'-H<sub>2</sub>bipy)[CdCl<sub>4</sub>], (V), features a hydrogen-bonded two-dimensional sheet motif in which the tetrachlorometallate anions polymerize to form a one-dimensional chain; this motif is very different from the discrete anions found in (I). This difference may be attributable to the different halide anions and the different number of hydrogen bonds. For the analogues mentioned above, besides the structural motif exhibited by compound (V) (motif *A*), there are two other motifs, namely *B*, a hydrogen-bonded polymeric ribbon structure, and *C*, a hydrogen-bonded dimeric ring motif.

Compound (II) exhibits motif *C*, in which both bipy N atoms are donors for hydrogen bonds. Although the title compound is essentially isostructural with (II)–(IV), there is only one classical hydrogen bond that links the dication and dianion together, and no hydrogen-bonded dimeric ring motif can be formed because the second hydrogen bond is 'missing'. Actually, the missing hydrogen bond is present in principle, but the N2...Br1<sup>i</sup> [symmetry code: (i)  $-1 - x, 1 - y, 1 - z$ ] distance of 3.434 (3) Å is slightly longer than what might be considered a true interaction, and the N2–H2B...Br1<sup>i</sup> angle of 97.7° is smaller than 110°. Therefore, the structural motif of the title compound may be classified as a fourth type, *D*, where the missing hydrogen bond is not considered as a true hydrogen bond.

The small difference between the structural motifs displayed by (I) and isomorphous compounds (II)–(IV) may be caused by the different metal halides. That compounds (I) and (V) are both Cd<sup>II</sup> salts yet adopt very different structural motifs indicates that the halide atoms play a vital role in the structural motifs. However, this is not always true, because isostructural compounds (II) and (III) both contain Zn<sup>II</sup> but different halide atoms, which poses the question of why this is

the case. We reason that the ability of Cd to adopt an octahedral coordination is larger than that of Zn. Therefore, the numbers of hydrogen bonds, metal centres and halide atoms are three key factors in forming structural motifs.

The solid-state emission spectrum of (I) was investigated at room temperature (Fig. 2). The fluorescence spectrum shows a broad and strong emission with a maximum wavelength of 426 nm upon photo-excitation at 325 nm. The emission should probably be assigned to the  $\pi \rightarrow \pi^*$  charge-transfer interaction of the 4,4'-H<sub>2</sub>bipy cations. Thus, this compound may be a candidate for blue-light luminescent materials and it is believed that more IIB metal halide–bipy compounds with good luminescent properties can be developed.

## Experimental

CdBr<sub>2</sub>·4H<sub>2</sub>O (0.3 mmol, 103 mg), 4,4'-bipyridine (0.2 mmol, 31 mg) and distilled water (3 ml) were loaded into a Teflon-lined stainless steel autoclave (25 ml) and kept at 373 K for 3 d. After being slowly cooled to room temperature at a rate of 6 K h<sup>-1</sup>, yellow crystals of (I) suitable for X-ray analysis were obtained (yield 20%, based on Cd).

### Crystal data

(C <sub>10</sub> H <sub>10</sub> N <sub>2</sub> )[CdBr <sub>4</sub> ]	<i>Z</i> = 4
<i>M<sub>r</sub></i> = 590.24	<i>D<sub>x</sub></i> = 2.510 Mg m <sup>-3</sup>
Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>c</i>	Mo <i>K</i> α radiation
<i>a</i> = 7.852 (2) Å	$\mu$ = 11.61 mm <sup>-1</sup>
<i>b</i> = 20.795 (2) Å	<i>T</i> = 293 (2) K
<i>c</i> = 9.987 (3) Å	Block, yellow
$\beta$ = 106.684 (4)°	0.26 × 0.14 × 0.11 mm
<i>V</i> = 1562.0 (6) Å <sup>3</sup>	

### Data collection

Rigaku Mercury CCD area-detector diffractometer	9983 measured reflections
$\omega$ scans	2813 independent reflections
Absorption correction: multi-scan ( <i>SPHERE</i> ; Rigaku, 2000)	1611 reflections with <i>I</i> > 2σ( <i>I</i> )
<i>T</i> <sub>min</sub> = 0.364, <i>T</i> <sub>max</sub> = 1.000	<i>R</i> <sub>int</sub> = 0.055
(expected range = 0.101–0.279)	$\theta_{\max}$ = 25.4°

### Refinement

Refinement on <i>F</i> <sup>2</sup>	H-atom parameters constrained
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )] = 0.051	$w = 1/[\sigma^2(F_o^2) + (0.0448P)^2]$
<i>wR</i> ( <i>F</i> <sup>2</sup> ) = 0.137	where $P = (F_o^2 + 2F_c^2)/3$
<i>S</i> = 0.88	(Δ/σ) <sub>max</sub> = 0.002
2813 reflections	Δρ <sub>max</sub> = 1.10 e Å <sup>-3</sup>
154 parameters	Δρ <sub>min</sub> = -1.11 e Å <sup>-3</sup>

**Table 1**

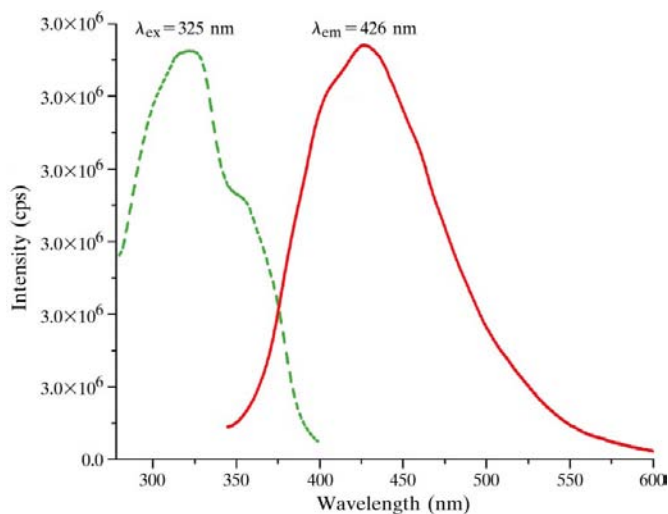
Selected geometric parameters (Å, °).

Cd1–Br1	2.5241 (7)	Cd1–Br4	2.5921 (6)
Cd1–Br3	2.5871 (8)	Cd1–Br2	2.6260 (6)
Br1–Cd1–Br3	110.769 (18)	Br1–Cd1–Br2	105.73 (2)
Br1–Cd1–Br4	105.12 (2)	Br3–Cd1–Br2	112.56 (2)
Br3–Cd1–Br4	111.031 (17)	Br4–Cd1–Br2	111.243 (19)

**Table 2**

Hydrogen-bond geometry (Å, °).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
N1–H1B...Br4	0.86	2.44	3.272 (4)	162



**Figure 2**

Solid-state emission and excitation spectra of (I) at room temperature. The solid line denotes the emission spectrum and the dashed line the excitation spectrum.

All H atoms were positioned geometrically and refined using a riding model, with C—H = 0.93 Å and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .

Data collection: *CrystalClear* (Rigaku, 2002); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXTL* (Siemens, 1994); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN3023). Services for accessing these data are described at the back of the journal.

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