(4-Ethyl-4,4′-bipyridinium-$\kappa N^{4'}$)triiodocadmium(II)

Hong-Xu Guo,[a]* **Jian-Xin Chen,**[b] **Liu-Ming Yang**[a] **and Zhi-Xing Lin**[a]

[a]Department of Chemistry and Environmental Science, Zhangzhou Normal University, Zhangzhou, Fujian 363000, People's Republic of China, and [b]Department of Chemistry, Fujian Normal University, Fuzhou, Fujian 350001, People's Republic of China

Correspondence e-mail:
guohongxu919@yahoo.com.cn

In the title compound, $[CdI_3(C_{12}H_{13}N_2)]$, the Cd^{2+} ion is coordinated by three I^- ions and by one N atom from an N-ethyl-4,4′-bipyridinium (EP) ligand in a distorted tetrahedral arrangement, with Cd—I bond lengths in the range 2.708 (1)–2.742 (1) Å. In the EP ligand, the dihedral angle between the two pyridyl planes is 38.9 (4)°.

Comment

In the last few years, the design and synthesis of inorganic–organic hybrid materials have been increasingly developed (Zhang *et al.*, 2006). In this field, the halogens are a common terminal or bridging ligand for preparing a large range of complexes with rich coordination environments (Lobana & Hundal, 2002). Many halogen-coordinated complexes containing Cu, Zn, Co and Mn have been reported (Li *et al.*, 2004; Schneider *et al.*, 2000; Espallargas *et al.*, 2006; Eichhofer *et al.*, 1997). As a heavy metal ion with a d^{10} configuration, Cd also exhibits a rich coordination chemistry. In Cd–I–N systems, although the $[CdI_2N_4]$ (Hu *et al.*, 2003), $[CdI_2N_3]$ (Wang *et al.*, 2005) and $[CdI_2N_2]$ (Amoedo-Portela *et al.*, 2003) polyhedra have been extensively studied, the $[CdI_3N]$ tetrahedron is unreported, except for the compound (DMAPM)[Cd-(DMAP)I$_3$] [DMAPM = 4-(N,N-dimethylamino)-1-methyl-pyridinium and DMAP = 4-(N,N-dimethylamino)pyridine; Ren *et al.*, 2003]. We report here the structure of the title Cd-coordinated complex, (I), with the Cd atom linked to three I atoms and one bipyridyl N atom.

(I)
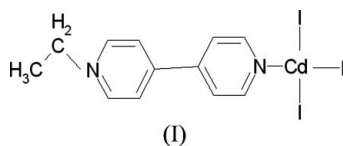
The asymmetric unit of (I) consits of a mononuclear Cd^{II} complex, in which the Cd site is tetracoordinated by three I^- ions and by one N atom from an N-ethyl-4,4′-bipyridinium (EP) ligand (Fig. 1). The Cd—I bond lengths [2.708 (1)–2.742 (1) Å] are normal and comparable with those in $[Ni(C_6H_{24}N_6)][CdI_4]$ (Sohail *et al.*, 2006), whereas the Cd—N bond distance [2.338 (9) Å] is slightly longer than that in $[Cd(DMAP)I_3]^-$ [2.288 (15) Å; Ren *et al.*, 2003] (Table 1). In the EP ligand, the dihedral angle between the two pyridyl planes is 38.9 (4)°.

Experimental

A mixture of $H_3PO_4.12MoO_3.30H_2O$ (2.3657 g, 1 mmol), CdI_2 (0.4028 g, 1.1 mmol), 4,4′-bipyridine (0.1874 g, 1.2 mmol), ethanol

(10 ml) and H_2O (10 ml) was heated at 423 K for 5 d. The autoclave was then cooled at a rate of 5 K h^{-1} to room temperature. Prismatic black crystals were isolated manually (yield 18.3% based on Cd), washed with water and ethanol, and dried at room temperature. The ligand EP in (I) is formed by 4,4′-bipyridyl and ethanol in an acid medium through ethylation; we believe this to be the first example of such a reaction. Analysis, calculated for $C_{12}H_{13}CdI_3N_2$: C 21.22, H 1.92, N 4.13%; found: C 21.29, H 2.01, N 4.16%.

Crystal data

$[CdI_3(C_{12}H_{13}N_2)]$	$Z = 4$
$M_r = 678.35$	$D_x = 2.451$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 7.5768$ (3) Å	$\mu = 6.21$ mm^{-1}
$b = 12.9594$ (3) Å	$T = 293$ (2) K
$c = 18.9013$ (4) Å	Prism, black
$\beta = 97.960$ (4)°	$0.25 \times 0.15 \times 0.10$ mm
$V = 1838.05$ (9) Å^3	

Data collection

Siemens SMART CCD area-detector diffractometer	8924 measured reflections
ω scans	4026 independent reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)	2801 reflections with $I > 2\sigma(I)$
$T_{min} = 0.316$, $T_{max} = 0.893$	$R_{int} = 0.033$
(expected range = 0.190–0.537)	$\theta_{max} = 27.1°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0252P)^2 + 20.1922P]$
$R[F^2 > 2\sigma(F^2)] = 0.069$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.124$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.06$	$\Delta\rho_{max} = 1.93$ e Å^{-3}
4026 reflections	$\Delta\rho_{min} = -1.30$ e Å^{-3}
163 parameters	
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Cd1—N1	2.338 (9)	Cd1—I3	2.7165 (12)
Cd1—I1	2.7077 (12)	Cd1—I2	2.7415 (12)
N1—Cd1—I1	101.3 (2)	N1—Cd1—I2	98.6 (2)
N1—Cd1—I3	108.4 (2)	I1—Cd1—I2	120.77 (4)
I1—Cd1—I3	115.86 (4)	I3—Cd1—I2	109.27 (4)

Carbon-bound H atoms were positioned geometrically, with C—H = 0.93, 0.97 and 0.96 Å for aromatic, methylene and methyl H atoms, respectively, and included in the refinement in the riding-model approximation, with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(C)$ for aromatic/methine and methylene H atoms, respectively. In the final difference Fourier synthesis, seven residual peaks in the range 0.85–1.93 e Å^{-3}
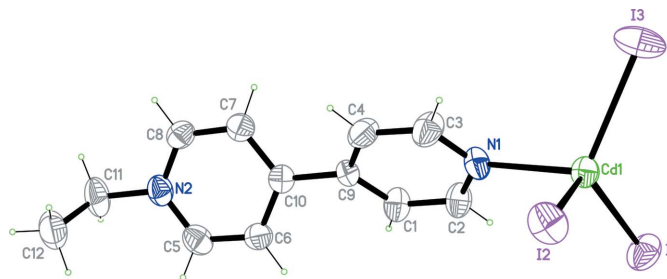

Figure 1
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 35% probability level.

were observed within 0.98 Å of atom I3. The deepest hole was located 0.91 Å from this atom.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXL97*; software used to prepare material for publication: *SHELXL97*.

References

Amoedo-Portela, A., Carballo, R., Casas, J. S., Garciá-Martinez, E., Sanchez-Gonzaléz, A., Sordo, J. & Vazquez-López, E. M. (2003). *Polyhedron*, **22**, 1077–1083.
Bruker (1999). *SMART* (Version 5.624), *SAINT* (Version 6.02a) and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Eichhofer, A., Fenske, D. & Fuhr, O. (1997). *Z. Anorg. Allg. Chem.* **623**, 762–768.
Espallargas, G. M., Brammer, L. & Sherwood, D. (2006). *Angew. Chem. Int. Ed.* **45**, 435–440.
Hu, C. H., Li, Q. & Englert, U. (2003). *CrystEngComm*, **5**, 519–529.
Li, G. H., Shi, Z., Liu, X. M., Dai, Z. M. & Feng, S. H. (2004). *Inorg. Chem.* **43**, 6884–6886.
Lobana, T. S. & Hundal, G. (2002). *J. Chem. Soc. Dalton Trans.* pp. 2203–2206.
Ren, P., Qin, J. G., Du, F. Y. & Liu, T. (2003). *Inorg. Chem. Commun.* **6**, 1375–1377.
Schneider, O., Geratner, E., Weller, F. & Dehnicke, K. (2000). *Z. Anorg. Allg. Chem.* **626**, 827–829.
Sheldrick, G. M. (1997). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.
Sohail, M., Molloy, K. C., Mazhar, M., Kociok-Köhn, G. & Khosa, M. K. (2006). *Acta Cryst.* E**62**, m394–m396.
Wang, Y. T., Tong, M. L., Fan, H. H., Wang, H. Z. & Chen, X. M. (2005). *Dalton Trans.* pp. 424–426.
Zhang, L. Y., Zhang, J. P., Lin, Y. Y. & Chen, X. M. (2006). *Cryst. Growth Des.* **6**, 1684–1869.