Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Ethylenedipyridinium dibromidodichloridocadmate(II)

Xiu-Cun Liu,[a] Xin-Cheng Liao,[a] Chun-Ling Ran,[a] Yun-Yin Niu[a] and Seik Weng Ng[b]*

[a]Department of Chemistry, Zhengzhou University, Zhengzhou 450052, People's Republic of China, and [b]Department of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia
Correspondence e-mail: seikweng@um.edu.my

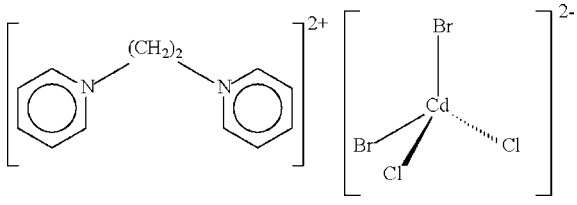
Received 8 May 2007; accepted 25 May 2007

Key indicators: single-crystal X-ray study; T = 295 K; mean σ(C–C) = 0.014 Å; disorder in main residue; R factor = 0.057; wR factor = 0.179; data-to-parameter ratio = 19.8.

The Cd atom in the title compound, $(C_{12}H_{14}N_2)[CdBr_2Cl_2]$, is coordinated by four halogen atoms in a tetrahedral geometry. The cation lies on a centre of inversion and the anion about a mirror plane. The halogen atoms on the mirror plane are both disordered between Br and Cl in a ratio of 0.75:0.25. The halogen atom in the general position is disordered between Br and Cl in a ratio of 0.25:0.75.

Related literature

For related literature, see: Allen (2002); Kallel *et al.* (1981); Sato *et al.* (1986).



Experimental

Crystal data

$(C_{12}H_{14}N_2)[CdBr_2Cl_2]$
M_r = 529.37
Orthorhombic, *Pnma*
a = 17.955 (2) Å
b = 14.338 (1) Å
c = 6.6437 (6) Å
V = 1710.4 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 6.25 mm^{-1}
T = 295 (2) K
0.20 × 0.20 × 0.10 mm

Data collection

Bruker APEX area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.147, T_{max} = 0.574
(expected range = 0.137–0.535)
8939 measured reflections
1564 independent reflections
1415 reflections with $I > 2\sigma(I)$
R_{int} = 0.025

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.057
$wR(F^2)$ = 0.179
S = 1.06
1564 reflections
79 parameters
44 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.77 e Å^{-3}
$\Delta\rho_{min}$ = −1.30 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Disordered halogen atoms are arbitrarily labelled as Br.

Cd1—Br1	2.470 (2)	Cd1—Br3	2.558 (2)
Cd1—Br2	2.535 (2)		
Br1—Cd1—Br1^{i}	116.4 (1)	Br1—Cd1—Br3	105.3 (1)
Br1—Cd1—Br2	106.7 (1)	Br2—Cd1—Br3	116.8 (1)

Symmetry code: (i) $x, -y+\frac{3}{2}, z$.

Data collection: *SMART* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *publCIF* (Westrip, 2007).

The authors thank the National Natural Science Foundation of China (grant No. 20671083), the Henan Province Excellent Young Foundation (grant No. 0612002800), Zhengzhou University and the University of Malaya for supporting this work. We thank Central China Normal University for the diffraction measurements.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WN2141).

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Barbour, L. J. (2001). *J. Supramol. Chem.* **1**, 189–191.
Bruker (2004). *SAINT* (Version 6.45a) and *SMART* (Version 6.45a). Bruker AXS Inc., Madison, Wisconsin, USA.
Kallel, A., Bats, J. W. & Daoud, A. (1981). *Acta Cryst.* B**37**, 676–677.
Sato, S., Ikeda, R. & Nakamura, D. (1986). *Bull. Chem. Soc. Jpn*, **59**, 1981–1989.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Westrip, S. P. (2007). *publCIF*. In preparation.

  doi:10.1107/S1600536807025585

supplementary materials

Acta Cryst. (2007). E**63**, m1780 [**doi:10.1107/S1600536807025585**]

Ethylenedipyridinium dibromidodichloridocadmate(II)

X.-C. Liu, X.-C. Liao, C.-L. Ran, Y.-Y. Niu and S. W. Ng

Comment

The discrete tetrahedral tetrahalidocadmate(II) dianion has been characterized in a number of salts (Cambridge Structural Database, Version 5.28; Allen, 2002); examples of the ammonium salts include, for example, bis(tetramethylammonium) tetrachloridocadmate, bis(tetramethylammonium) tetrabromidomercurate (Sato *et al.*, 1986) and bis(tetramethylammonium) tetraiodidocadmate (Kallel *et al.*, 1981). In the 1,2-ethanedipyridinium salt of the mixed-halogen cadmate, the metal atom is coordinated by four halogen atoms in a tetrahedral geometry; the halogen atoms are disordered (Fig. 1). The cations and anions do not have signification interactions with each other.

Experimental

The salt was synthesized from the reaction of ethane-1,2-dipyridinium dibromide (0.035 g, 0.1 mmol) in methanol (5 ml) and cadmium dichloride (0.037 g, 0.2 mmol) in DMF (10 ml). The mixture was set aside for the formation of colourless block-shaped crystals in 40% yield after several days. CH&N elemental analysis: Calc. C 27.22, H 2.67, N 5.29%. Found C 27.89, H 2.49, N 5.36%.

Refinement

Of the three halogens in the asymmetric unit, one lies in a general position and the other two on a mirror plane. Initial attempts to refine the structure with either three chlorines or three bromines gave unacceptably high *R*-indices (and large peaks/holes). The three halogen atoms were then refined as three (Br+Cl) mixtures; in one attempt the components had only the same displacement parameters. A second attempt allowed the mixtures to have the same displacement parameters as well as sharing the same site. The second led to a formulation consisting of approximately two Br and two Cl atoms. The use of a special restraint command that fixed the number of Br and Cl atoms as both being exactly two led to the occupancy of Br1 as nearly 0.25 and that of Br2 and Br3 as both nearly 0.75. In the best disorder model, the halogen in the general position was set to (0.25Br + 0.75 C l); those in the special position were both set to (0.75Br + 0.25 C l)·The anion is $[CdBr_2Cl_2]^{2-}$, a formulation that is supported by CH&N elemental analysis. Other formulations led to much larger peaks/holes.

Disorder also affected the cation; the pyridyl ring was refined as a rigid hexagon of 1.39 Å sides. The C—C distance was restrained to 1.50±0.01 Å, and the N···C distance to 2.45±0.01 Å. The displacement parameters of atoms of the cation were restrained to be nearly isotropic. Carbon-bound H atoms were positioned geometrically (C–H 0.93 and 0.97 Å), and were included in the refinement in the riding model approximation, with $U_{iso}(H) = 1.2U_{eq}(C)$.

In the final difference Fourier map the largest peak was 0.9 Å from C6 and the deepest hole at 0.6 Å from Cl3.

Figures

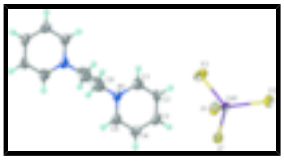


Fig. 1. The structure of $[C_{12}H_{14}N_2][CdBr_2Cl_2]$, with displacement ellipsoids drawn at the 50% probability level. The bromine and chlorine atoms are disordered; the halogen atom on the general position is labelled X1 (and the symmetry-related $X1^i$); those on the special position are labelled X2 and X3. Hydrogen atoms are drawn as spheres of arbitrary radius. [Symmetry code: i = x, 3/2 – y, z.] Unlabelled atoms in the cation are related to labelled atoms by (1 – x, 1 – y, 1 – z).

Ethylenedipyridinium dibromidodichloridocadmate(II)

Crystal data

$(C_{12}H_{14}N_2)[CdBr_2Cl_2]$	F_{000} = 1008
M_r = 529.37	D_x = 2.056 Mg m^{-3}
Orthorhombic, *Pnma*	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: -P 2ac 2n	Cell parameters from 4134 reflections
a = 17.955 (2) Å	θ = 2.3–27.4º
b = 14.338 (1) Å	μ = 6.25 mm^{-1}
c = 6.6437 (6) Å	T = 295 (2) K
V = 1710.4 (3) Å^3	Block, colourless
Z = 4	0.20 × 0.20 × 0.10 mm

Data collection

Bruker APEX area-detector diffractometer	1564 independent reflections
Radiation source: fine-focus sealed tube	1415 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.025
T = 298(2) K	θ_{max} = 25.0º
φ and ω scans	θ_{min} = 2.3º
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	h = −17→21
T_{min} = 0.147, T_{max} = 0.574	k = −15→17
8939 measured reflections	l = −7→7

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.057	H-atom parameters constrained
$wR(F^2)$ = 0.179	$w = 1/[\sigma^2(F_o^2) + (0.1162P)^2 + 9.0378P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.06	$(\Delta/\sigma)_{max}$ = 0.001
1564 reflections	$\Delta\rho_{max}$ = 1.77 e Å^{-3}

79 parameters	$\Delta\rho_{min} = -1.30$ e Å^{-3}
44 restraints	Extinction correction: none
Primary atom site location: structure-invariant direct methods	

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Cd1	0.92879 (4)	0.7500	0.64150 (12)	0.0371 (3)	
Br1	0.91363 (10)	0.60359 (14)	0.4500 (3)	0.0702 (6)	0.25
Br2	0.82923 (11)	0.7500	0.9121 (3)	0.0760 (6)	0.75
Br3	1.06428 (9)	0.7500	0.7605 (3)	0.0720 (6)	0.75
Cl1	0.91363 (10)	0.60359 (14)	0.4500 (3)	0.0702 (6)	0.75
Cl2	0.82923 (11)	0.7500	0.9121 (3)	0.0760 (6)	0.25
Cl3	1.06428 (9)	0.7500	0.7605 (3)	0.0720 (6)	0.25
N1	0.5912 (2)	0.5361 (5)	0.4128 (9)	0.069 (2)	
C1	0.6503 (3)	0.5331 (5)	0.5477 (8)	0.075 (3)	
C2	0.7163 (2)	0.5795 (5)	0.5034 (8)	0.056 (2)	
C3	0.7231 (2)	0.6288 (4)	0.3243 (8)	0.055 (2)	
C4	0.6640 (3)	0.6318 (4)	0.1894 (7)	0.053 (2)	
C5	0.5980 (2)	0.5854 (4)	0.2336 (7)	0.055 (2)	
C6	0.5283 (5)	0.4733 (7)	0.4383 (15)	0.080 (3)	
H1	0.6457	0.5001	0.6675	0.090*	
H2	0.7558	0.5775	0.5937	0.067*	
H3	0.7673	0.6599	0.2947	0.067*	
H4	0.6686	0.6648	0.0695	0.064*	
H5	0.5585	0.5874	0.1434	0.066*	
H6a	0.5436	0.4170	0.5081	0.096*	
H6b	0.5076	0.4561	0.3087	0.096*	

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cd1	0.0328 (5)	0.0379 (5)	0.0406 (5)	0.000	0.0018 (3)	0.000
Br1	0.0544 (10)	0.0715 (12)	0.0846 (13)	−0.0025 (8)	−0.0020 (9)	−0.0256 (10)
Br2	0.0685 (11)	0.1012 (14)	0.0584 (10)	0.000	0.0344 (8)	0.000
Br3	0.0437 (9)	0.0825 (12)	0.0897 (14)	0.000	−0.0088 (8)	0.000
Cl1	0.0544 (10)	0.0715 (12)	0.0846 (13)	−0.0025 (8)	−0.0020 (9)	−0.0256 (10)
Cl2	0.0685 (11)	0.1012 (14)	0.0584 (10)	0.000	0.0344 (8)	0.000
Cl3	0.0437 (9)	0.0825 (12)	0.0897 (14)	0.000	−0.0088 (8)	0.000
N1	0.033 (3)	0.105 (6)	0.069 (4)	−0.018 (4)	−0.009 (3)	0.033 (4)
C1	0.057 (5)	0.100 (7)	0.069 (5)	−0.008 (5)	−0.006 (4)	0.034 (5)
C2	0.025 (3)	0.070 (5)	0.072 (5)	−0.002 (3)	−0.008 (3)	0.018 (4)
C3	0.032 (4)	0.061 (5)	0.073 (5)	−0.010 (4)	0.005 (4)	0.011 (4)
C4	0.050 (4)	0.054 (4)	0.055 (4)	−0.010 (4)	0.006 (4)	0.009 (4)
C5	0.036 (4)	0.069 (5)	0.059 (5)	−0.011 (4)	−0.002 (4)	0.013 (4)
C6	0.100 (7)	0.066 (5)	0.074 (6)	0.021 (5)	−0.016 (5)	−0.011 (5)

Geometric parameters (Å, °)

Cd1—Br1	2.470 (2)	C2—H2	0.9300
Cd1—Br1^{i}	2.470 (2)	C3—C4	1.3900
Cd1—Br2	2.535 (2)	C3—H3	0.9300
Cd1—Br3	2.558 (2)	C4—C5	1.3900
N1—C1	1.3900	C4—H4	0.9300
N1—C5	1.3900	C5—H5	0.9300
N1—C6	1.453 (12)	C6—C6^{ii}	1.514 (9)
C1—C2	1.3900	C6—H6A	0.9700
C1—H1	0.9300	C6—H6B	0.9700
C2—C3	1.3900		
Br1—Cd1—Br1^{i}	116.4 (1)	C4—C3—C2	120.0
Br1—Cd1—Br2	106.7 (1)	C4—C3—H3	120.0
Br1—Cd1—Br3	105.3 (1)	C2—C3—H3	120.0
Br1^{i}—Cd1—Br2	106.7 (1)	C3—C4—C5	120.0
Br1^{i}—Cd1—Br3	105.3 (1)	C3—C4—H4	120.0
Br2—Cd1—Br3	116.8 (1)	C5—C4—H4	120.0
C1—N1—C5	120.0	C4—C5—N1	120.0
C1—N1—C6	119.9 (6)	C4—C5—H5	120.0
C5—N1—C6	118.9 (6)	N1—C5—H5	120.0
N1—C1—C2	120.0	N1—C6—C6^{ii}	105.8 (10)
N1—C1—H1	120.0	N1—C6—H6A	110.6
C2—C1—H1	120.0	C6^{ii}—C6—H6A	110.6
C1—C2—C3	120.0	N1—C6—H6B	110.6
C1—C2—H2	120.0	C6^{ii}—C6—H6B	110.6
C3—C2—H2	120.0	H6A—C6—H6B	108.7
C5—N1—C1—C2	0.0	C3—C4—C5—N1	0.0
C6—N1—C1—C2	167.7 (7)	C1—N1—C5—C4	0.0
N1—C1—C2—C3	0.0	C6—N1—C5—C4	−167.8 (6)
C1—C2—C3—C4	0.0	C1—N1—C6—C6^{ii}	93.0 (11)
C2—C3—C4—C5	0.0	C5—N1—C6—C6^{ii}	−99.2 (11)

Symmetry codes: (i) *x*, −*y*+3/2, *z*; (ii) −*x*+1, −*y*+1, −*z*+1.

Fig. 1