N(1)—Mn—N(2)	89.99 (9)	C(*b*3)—C(*b*4)—C(*a*4)	107.2 (3)
N(1)—Mn—N(3)	171.04 (9)	C(*b*6)—C(*b*5)—C(*a*5)	106.9 (2)
N(1)—Mn—N(4)	89.55 (9)	C(*b*5)—C(*b*6)—C(*a*6)	107.0 (2)
N(2)—Mn—N(3)	89.32 (9)	C(*b*8)—C(*b*7)—C(*a*7)	107.1 (2)
N(2)—Mn—N(4)	170.11 (9)	C(*b*7)—C(*b*8)—C(*a*8)	106.8 (2)
N(3)—Mn—N(4)	89.60 (9)	C(*a*1)—C(*b*1)—C11	125.1 (3)
N(1)—Mn—O(1)	93.14 (9)	C(*a*2)—C(*b*2)—C21	124.8 (3)
N(2)—Mn—O(1)	95.01 (10)	C(*a*3)—C(*b*3)—C31	125.1 (3)
N(3)—Mn—O(1)	95.82 (9)	C(*a*4)—C(*b*4)—C41	124.6 (3)
N(4)—Mn—O(1)	94.88 (10)	C(*a*5)—C(*b*5)—C51	124.5 (3)
C(*a*1)—N(1)—Mn	126.8 (2)	C(*a*6)—C(*b*6)—C61	124.9 (3)
C(*a*2)—N(1)—Mn	127.2 (2)	C(*a*7)—C(*b*7)—C71	124.6 (2)
C(*a*3)—N(2)—Mn	127.4 (2)	C(*a*8)—C(*b*8)—C81	126.0 (2)
C(*a*4)—N(2)—Mn	126.4 (2)	C(*b*1)—C(*b*2)—C21	128.1 (3)
C(*a*5)—N(3)—Mn	126.4 (2)	C(*b*2)—C(*b*1)—C11	128.0 (3)
C(*a*6)—N(3)—Mn	127.7 (2)	C(*b*3)—C(*b*4)—C41	128.2 (3)
C(*a*7)—N(4)—Mn	127.5 (2)	C(*b*4)—C(*b*3)—C31	128.0 (3)
C(*a*8)—N(4)—Mn	126.9 (2)	C(*b*5)—C(*b*6)—C61	128.1 (3)
C(*a*1)—N(1)—C(*a*2)	105.7 (2)	C(*b*6)—C(*b*5)—C51	128.6 (3)
C(*a*3)—N(2)—C(*a*4)	105.9 (2)	C(*b*7)—C(*b*8)—C81	127.1 (3)
C(*a*5)—N(3)—C(*a*6)	105.5 (2)	C(*b*8)—C(*b*7)—C71	128.2 (3)
C(*a*7)—N(4)—C(*a*8)	105.4 (2)	C(*a*2)—C(*m*1)—C(*a*3)	125.4 (3)
N(1)—C(*a*1)—C(*b*1)	109.9 (2)	C(*a*4)—C(*m*2)—C(*a*5)	125.5 (3)
N(1)—C(*a*2)—C(*b*2)	110.5 (2)	C(*a*6)—C(*m*3)—C(*a*7)	125.5 (2)
N(2)—C(*a*3)—C(*b*3)	110.2 (2)	C(*a*8)—C(*m*4)—C(*a*1)	125.6 (2)
N(2)—C(*a*4)—C(*b*4)	109.8 (3)	C(*b*1)—C11—C12	113.7 (3)
N(3)—C(*a*5)—C(*b*5)	110.2 (2)	C(*b*2)—C21—C22	113.4 (3)
N(3)—C(*a*6)—C(*b*6)	110.3 (2)	C(*b*3)—C31—C32	113.5 (3)
N(4)—C(*a*7)—C(*b*7)	110.3 (2)	C(*b*4)—C41—C42	114.0 (4)
N(4)—C(*a*8)—C(*b*8)	110.3 (2)	C(*b*5)—C51—C52	113.9 (3)
N(1)—C(*a*1)—C(*m*4)	124.8 (2)	C(*b*6)—C61—C62	112.6 (3)
N(1)—C(*a*2)—C(*m*1)	125.1 (2)	C(*b*7)—C71—C72	111.6 (3)
N(2)—C(*a*3)—C(*m*1)	124.7 (2)	C(*b*8)—C81—C82	114.1 (3)
N(2)—C(*a*4)—C(*m*2)	125.2 (3)	C(1*a*)—O(1)—Mn	127.8 (3)
N(3)—C(*a*5)—C(*m*2)	124.7 (2)	C(1*b*)—O(1)—Mn	126.1 (5)
N(3)—C(*a*6)—C(*m*3)	124.5 (2)	O(1)—C(1*a*)—C(2)	120.5 (8)
N(4)—C(*a*7)—C(*m*3)	125.1 (2)	O(1)—C(1*b*)—C(2)	118.5 (12)
N(4)—C(*a*8)—C(*m*4)	124.2 (2)	O(2*a*)—Cl—O(3*a*)	108.9 (5)
C(*m*4)—C(*a*1)—C(*b*1)	125.3 (2)	O(2*a*)—Cl—O(4*a*)	102.0 (4)
C(*m*1)—C(*a*2)—C(*b*2)	124.4 (3)	O(2*a*)—Cl—O(5*a*)	113.7 (9)
C(*m*1)—C(*a*3)—C(*b*3)	125.0 (3)	O(3*a*)—Cl—O(4*a*)	103.5 (6)
C(*m*2)—C(*a*4)—C(*b*4)	124.9 (3)	O(3*a*)—Cl—O(5*a*)	119.7 (6)
C(*m*2)—C(*a*5)—C(*b*5)	125.0 (3)	O(4*a*)—Cl—O(5*a*)	107.0 (9)
C(*m*3)—C(*a*6)—C(*b*6)	125.1 (2)	O(2*b*)—Cl—O(3*b*)	120.0 (17)
C(*m*3)—C(*a*7)—C(*b*7)	124.6 (2)	O(2*b*)—Cl—O(4*b*)	91.0 (12)
C(*m*4)—C(*a*8)—C(*b*8)	125.4 (2)	O(2*b*)—Cl—O(5*b*)	93.2 (15)
C(*b*2)—C(*b*1)—C(*a*1)	106.9 (2)	O(3*b*)—Cl—O(4*b*)	98.2 (11)
C(*b*1)—C(*b*2)—C(*a*2)	107.0 (2)	O(3*b*)—Cl—O(5*b*)	138.8 (14)
C(*b*4)—C(*b*3)—C(*a*3)	106.9 (3)	O(4*b*)—Cl—O(5*b*)	105.3 (11)

Cell determination and intensity data collection were performed on an Enraf–Nonius FAST area-detector diffractometer with an Mo rotating anode source. Our detailed methods and procedures for small-molecule X-ray data collection with the FAST system have been described previously (Scheidt & Turowska-Tyrk, 1994). All reflections were used in least-squares refinement, including negative intensities.

Both the ethanol ligand and the perchlorate anion were found to be disordered. For the ethanol ligand, two positions [C(1*a*) and C(1*b*)] are found for the C atom bonded to the O atom, with a separation of 1.22 Å, and refined occupancies of 0.531 (14) and 0.469 (14), respectively. The terminal C atom of the ethanol ligand is essentially disordered; however, we were unable to resolve it with the room-temperature data. For the perchlorate anion, the Cl atom has full occupancy, while the O atoms are disordered and have been resolved into two fragments (a and *b*) with different orientations. Group occupancies were applied and the refined values are 0.668 (8) and 0.332 (8), respectively. All the H atoms were idealized using riding models.

Data collection: *MADNES* (Messerschmitt & Pflugrath, 1987). Cell refinement: *MADNES*. Data reduction: *MADNES*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

We thank the National Institutes of Health for support of this research under grant GM-38401. Funds for the purchase of the FAST area-detector diffractometer were provided through NIH grant RR-06709. BC acknowledges the J. Peter Grace Prize Fellowship through the University of Notre Dame.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1159). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Cheng, B. & Scheidt, W. R. (1995). *Acta Cryst.* C**51**, 825–828.
Cheng, B., Cukiernik, F., Fries, P. H., Marchon, J.-C. & Scheidt, W. R. (1995). *Inorg. Chem.* **34**, 4627–4639.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Messerschmitt, A. & Pflugrath, J. W. (1987). *J. Appl. Cryst.* **20**, 306–315.
Scheidt, W. R. & Lee, Y. J. (1987). *Struct. Bonding*, **64**, 1–70.
Scheidt, W. R. & Turowska-Tyrk, I. (1994). *Inorg. Chem.* **33**, 1314–1318.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1994). *SHELXL*93. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158–166.
Williamson, M. M. & Hill, C. L. (1986). *Inorg. Chem.* **25**, 4668–4671.
Williamson, M. M. & Hill, C. L. (1987). *Inorg. Chem.* **26**, 4155–4160.

Acta Cryst. (1996). C**52**, 588–591

Bis(2-methyl-4-nitroanilinium) Tetrachlorocadmate

Reiko Azumi, Kazumasa Honda, Midori Goto, Junji Akimoto, Yoshinao Oosawa, Hiroaki Tachibana, Motoo Tanaka and Mutsuyoshi Matsumoto

National Institute of Materials and Chemical Research, Higashi, Tsukuba, Ibaraki 305, Japan. E-mail: azumi@ccmail.nimc.go.jp

(*Received 26 May 1995; accepted 18 September 1995*)

Abstract

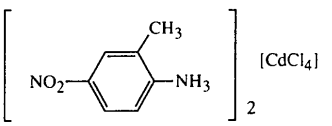
The crystal structure of bis(2-methyl-4-nitroanilinium) tetrachlorocadmate, $(C_7H_9N_2O_2)_2[CdCl_4]$, has been determined by X-ray diffraction at room temperature. The

crystal has a layered structure in which the organic bilayer is sandwiched between the inorganic sheets. The Cd ion and Cl anions form distorted four-coordinate tetrahedra.

Comment

Organic ammonium-based layered halide compounds [general formula $(RNH_3)_2MX_4$] have been investigated extensively over the past two decades (Chapuis, 1978; Kind *et al.*, 1979; Dolzhenko, Inabe & Maruyama, 1986; Jurga, Jurga, Reynhardt & Katowski, 1993). Most of these compounds have perovskite-type structures in which halogen anions form corner-sharing octahedra centred by divalent metal atoms. Alkylammonium bilayers are sandwiched between the inorganic sheets. The exceptions reported so far are Zn compounds, where $ZnCl_4^{2-}$ moieties form four-coordinate tetrahedra and alkylammonium portions form interdigitated bilayers (Zuniga & Chapuis, 1985).

We have reported that bis(4-nitroanilinium) tetrachlorocadmate crystallizes with a perovskite-type layered structure, which resembles those of alkylammonium compounds (Azumi *et al.*, 1995). We report here on the formation of a distorted perovskite-type structure of the chlorocadmate moiety using 2-methyl-4-nitroaniline instead of 4-nitroaniline, (I).



(I)

The X-ray diffraction analysis of a single crystal of the title compound (Fig. 1) revealed that the crystal has a layered structure in which the inorganic and organic parts are arranged in alternate sheets (Fig. 2). 2-Methyl-4-nitroanilinium molecules form a 'tail-to-tail' bilayer with the nitro groups of the molecules positioned in the central portion of the organic layer. The benzene ring is almost planar with all the skeletal torsion angles having values within 2°. The N atom of the ammonium group is bonded to Cl atoms through hydrogen bonds. The structure of the organic portion is similar to that reported for the 4-nitroanilinium compound (Azumi *et al.*, 1995).

The $CdCl_4$ portion, on the other hand, has a distorted four-coordinate tetrahedral arrangement, which is quite different from the case of bis(4-nitroanilinium) tetrachlorocadmate or bis(alkylammonium) tetrachlorocadmate (Chapuis, 1978; Kind *et al.*, 1979). This structure is formed by the addition of a methyl group to the benzene ring, which makes the organic component bulkier. Fig. 3 shows a projection along the *b* axis, *i.e.* along the layer normal. The lattice constants of the layer plane are 8.266 (2) × 8.334 (1) Å, which are

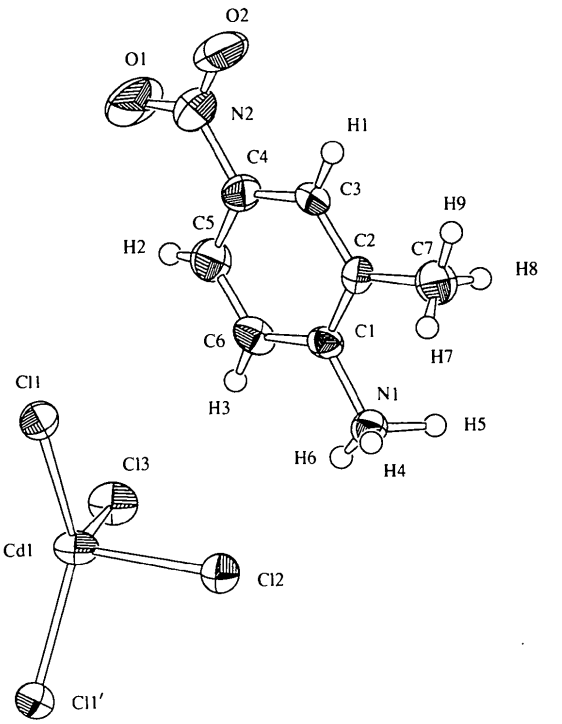


Fig. 1. Perspective view of the title compound with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

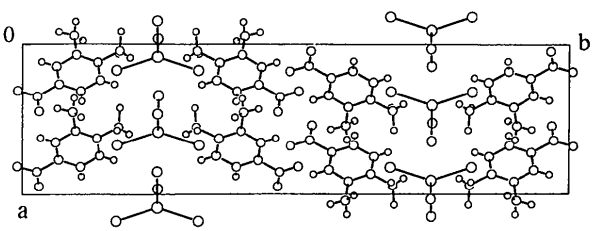


Fig. 2. Molecular packing viewed from the [001] axis.

larger than those for bis(4-nitroanilinium) tetrachlorocadmate [7.792 (1) × 7.256 (1) Å; Azumi *et al.*, 1995] or bis(*n*-propylammonium) tetrachlorocadmate in a room-temperature phase [7.609 (5) × 7.367 (3) Å; Chapuis, 1978]. The ammonium moiety is inserted between the halide tetrahedra. The Cd—Cl distances in a tetrahedral unit are 2.458 (2), 2.474 (3) and 2.565 (3) Å, while the distance between the Cd atom and the nearest Cl anion of a neighbouring unit is 3.345 (3) Å. Although this distance is too far for the coordination of a metal and a halide, the features detailed below suggest that this structure has a distorted perovskite-type layered structure. The tetrahedron is considered to form through the distortion of an octahedron. The Cl1—Cd—Cl1^{i} angle is 135.79 (9)° [symmetry code: (i) x, $\frac{1}{2}-y$, z], which is significantly larger than the standard angle of a tetrahedron. Furthermore, two of the Cd—Cl bonds in a $CdCl_4$

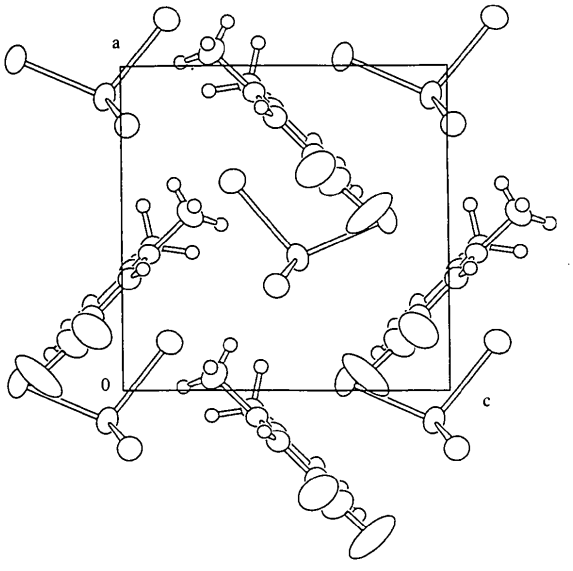


Fig. 3. Projection along the [010] axis.

unit (Cd—Cl2 and Cd—Cl3) lie in the *ac* plane. These features suggest that a weak network structure still remains between neighbouring $CdCl_4$ units, in contrast to the case of $(C_nH_{2n+1}NH_3)_2[ZnCl_4]$ compounds where the $ZnCl_4$ portions are completely isolated from their neighbours (Zuniga & Chapuis, 1985).

Experimental

Crystals of the title compound were obtained by slow evaporation of a 2:1 mixture of 2-methyl-4-nitroaniline and cadmium chloride ($CdCl_2$) in a mixed solvent of aqueous HCl and ethanol.

Crystal data

$(C_7H_9N_2O_2)_2[CdCl_4]$
$M_r = 560.54$
Orthorhombic
Pnma
$a = 8.266\,(2)$ Å
$b = 30.465\,(5)$ Å
$c = 8.334\,(1)$ Å
$V = 2098.7\,(7)$ Å^3
$Z = 4$
$D_x = 1.774$ Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 9$–$13°$
$\mu = 1.577$ mm^{-1}
$T = 293$ K
Block
0.23 × 0.20 × 0.07 mm
Pale yellow

Data collection

Rigaku AFC-5*S* diffractometer
ω scans
Absorption correction: none
3527 measured reflections
3527 independent reflections
1298 observed reflections $[I > 3\sigma(I)]$
$\theta_{max} = 30°$
$h = 0 \rightarrow 11$
$k = -42 \rightarrow 0$
$l = 0 \rightarrow 11$
3 standard reflections monitored every 50 reflections
intensity decay: 1.1%

Refinement

Refinement on F
$R = 0.043$
$wR = 0.042$
$S = 1.23$
1298 reflections
127 parameters
All H atoms were found in a difference Fourier map and their parameters not refined
$w = 1/[\sigma^2(F) + 0.000196F^2]$
$(\Delta/\sigma)_{max} = 0.004$
$\Delta\rho_{max} = 0.288$ e Å^{-3}
$\Delta\rho_{min} = -0.308$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
Cd1	0.5904 (1)	1/4	0.45638 (9)	0.0375 (3)
Cl1	0.6795 (2)	0.17525 (5)	0.5235 (2)	0.0393 (5)
Cl2	0.3508 (3)	1/4	0.6519 (3)	0.0421 (8)
Cl3	0.4691 (3)	1/4	0.1850 (3)	0.0458 (8)
O1	0.4524 (9)	0.0311 (2)	0.242 (1)	0.1126 (3)
O2	0.3179 (8)	−0.0079 (2)	0.4056 (8)	0.0802 (3)
N1	0.0569 (6)	0.1793 (2)	0.5989 (6)	0.0343 (1)
N2	0.3547 (8)	0.0274 (2)	0.3473 (9)	0.0587 (3)
C1	0.1307 (8)	0.1390 (2)	0.5289 (8)	0.0312 (1)
C2	0.0813 (8)	0.0987 (2)	0.5875 (7)	0.0319 (1)
C3	0.1582 (8)	0.0621 (2)	0.5247 (8)	0.0325 (1)
C4	0.2751 (9)	0.0673 (2)	0.4096 (8)	0.0389 (3)
C5	0.3206 (9)	0.1076 (3)	0.3509 (9)	0.0474 (3)
C6	0.2463 (9)	0.1440 (2)	0.4107 (7)	0.0366 (3)
C7	−0.0457 (9)	0.0938 (2)	0.7154 (9)	0.0474 (3)

Table 2. *Selected geometric parameters (Å, °)*

Cd1—Cl1	2.458 (2)	Cd1—Cl3	2.474 (3)
Cd1—Cl2	2.565 (3)	Cd1···Cl3^{i}	3.345 (3)
Cl1—Cd1—Cl1^{ii}	135.79 (9)	Cl1—Cd1—Cl3	109.24 (5)
Cl1—Cd1—Cl2	94.98 (5)	Cl2—Cd1—Cl3	105.54 (10)

Symmetry codes: (i) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z$; (ii) $x, \frac{1}{2} - y, z$.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1993). Program(s) used to solve structure: Patterson method using *SAPI*91 (Fan, 1991). Program(s) used to refine structure: *TEXSAN LS*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *TEXSAN FINISH*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KH1059). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Azumi, R., Honda, K., Goto, M., Akimoto, J., Oosawa, Y., Tachibana, H., Nakamura, T., Tanaka, M. & Matsumoto, M. (1995). *Acta Cryst.* C**51**, 2534–2537.
Chapuis, G. (1978). *Acta Cryst.* B**34**, 1506–1512.
Dolzhenko, Y. I., Inabe, T. & Maruyama, Y. (1986). *Bull. Chem. Soc. Jpn*, **59**, 563–567.
Fan, H.-F. (1991). *SAPI*91. *Structure Analysis Programs with Intelligent Control*. Rigaku Corporation, Tokyo, Japan.

Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Jurga, S., Jurga, K., Reynhardt, E. C. & Katowski, P. (1993). *Z. Naturforsch. Teil A*, **48**, 563–569.
Kind, R., Plesko, S., Arend, H., Blinc, R., Zeks, B., Seliger, J., Lozar, B., Slak, J., Levstik, A., Filipic, C., Zagar, V., Lahajnar, G., Millia, F. & Chapuis, G. (1979). *J. Chem. Phys.* **71**, 2118–2130.
Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Molecular Structure Corporation (1993). *TEXSAN. Single Crystal Structure Analysis Software*. Version 1.6c. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Zuniga, F. J. & Chapuis, G. (1985). *Mol. Cryst. Liq. Cryst.* **128**, 349–366.

Acta Cryst. (1996). C**52**, 591–593

The Polymeric Cadmium Complex Poly-[μ-(nicotinato-*O*,*O*′:*N*)-μ-bromo-monoaquacadmium]

CUNGEN ZHANG,[a] DUANJUN XU,[a] YUANZHI XU[a] AND XIAOYING HUANG[b]

[a]*Department of Chemistry, Zhejiang University, Hangzhou 310027, People's Republic of China, and* [b]*Fujian Institute of Research on Structure of Matter, Fuzhou 350002, People's Republic of China*

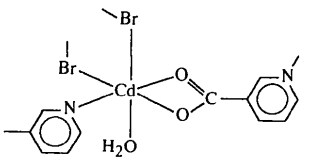
(*Received 20 June 1995; accepted 29 August 1995*)

Abstract

In the title complex, poly[aquacadmium-μ-bromo-μ-(3-pyridinecarboxylato-*O*,*O*′:*N*)], $[CdBr(C_6H_4NO_2)(H_2O)]_n$, the Cd^{II} atom is six-coordinate. The carboxylate group of the nicotinate anion coordinates to the Cd^{II} atom as a chelate, with almost identical Cd—O distances [2.348 (3) and 2.331 (3) Å] and a small chelating angle of 56.0 (1)°. Both the nicotinate and Br^- anions bridge the Cd^{II} atoms to form polymeric di-*catena* chains in the crystal.

Comment

Structural research on complexes bridged by heterocyclic aromatic molecules and their derivatives has been ongoing in our laboratory with the aim of studying the magnetic behaviour of these multinuclear complexes in relation to their spatial structures (Xu *et al.*, 1991; Chen, Xu, Xu, Cheng & Ling, 1992). As part of this research, a series of complexes bridged by a nicotinate or an isonicotinate anion were synthesized, of which the structure of the nicotinate complex (I) has been determined by means of X-ray analysis and is presented here.



(I)

The Cd^{II} atom has distorted octahedral coordination, as shown in Fig. 1. Two nicotinate anions, related by translation along the *b* axis, coordinate to the Cd^{II} atom in the equatorial plane through the terminal carboxylate group of one anion and the pyridine N atom of the other. The Cd—N(x, $1+y$, z) distance of 2.272 (3) Å is comparable to that of 2.310 (3) Å found in the Cd complex of isonicotinate (Biagini, Gaetani, Guastini, Mussati & Nardelli, 1971). Two centrosymmetric Br atoms coordinate to the Cd^{II} atom, one of which is in the equatorial plane and has the shorter Cd—Br distance of 2.6678 (9) Å, while the other is in the axial direction and has the longer Cd—Br distance of 2.7804 (8) Å. Both Cd—Br distances are significantly shorter than the sum of the radii of the individual ions. A water molecule in an axial position coordinates to the Cd^{II} atom, with a Cd—O distance of 2.373 (3) Å, to complete sixfold coordination.

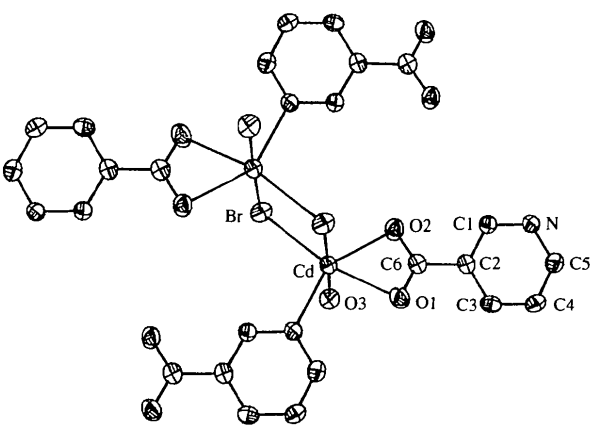


Fig. 1. The molecular structure of the title compound showing 50% probability displacement ellipsoids. H atoms are omitted for clarity.

The remarkable feature of this structure is that the carboxylate group of the nicotinate anion coordinates to the Cd^{II} atom as a chelate with quite a small O1—Cd—O2 angle of 56.0 (1)°. This is in contrast to values found in the six-coordinate complexes of nicotinate or isonicotinate reported so far (Biagini, Chiesi, Guastini & Viterbo, 1974; Cariati, Naldini & Panzanelli, 1983; Chen *et al.*, 1994), but similar to those found in complexes with a higher coordination number, for example, in the eight-coordinate Pb^{II} complex of nicotinate (Biagini, Gaetani, Guastini & Musatti, 1975), in the Pb^{II} complex of isonicotinate (Biagini, Gaetani, Guastini & Nardelli, 1972) and in the eight-coordinate lanthanide