Johnson, C. K. (1976). *ORTEP*II. 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-monoaqua-cadmium]

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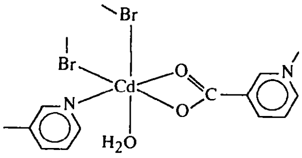
Abstract

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.

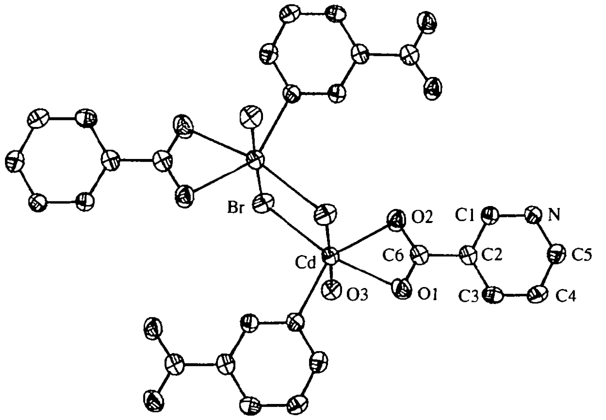


Fig. 1. The molecular structure of the title compound showing 50% probability displacement ellipsoids. H atoms are omitted for clarity.

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 complexes of nicotinate (Moore, Glick, & Baker, 1972; Prout, Marin & Hutchison, 1985). Moreover, the two Cd—O distances for the chelating carboxylate group in this structure are almost identical [2.348 (3) and 2.331 (3) Å], but in the structures of the Pb^{II} complexes quoted above, one coordination bond of the chelating carboxylate group is always much longer than the other. Bond angles around the Cd^{II} atom are also interesting. The Cd—O1 bond is essentially perpendicular to the Cd—N(x, $1+y$, z) bond, though the O1—Cd—O2 angle is much smaller than 90°. On the other hand, the Br atom is located approximately on the bisector of the O2—Cd—N(x, $1+y$, z) angle.

The pyridine ring and the carboxylate group are not coplanar, the dihedral angle between their planes being 14.7°. This is in agreement with the value found in a Cd^{II} complex of isonicotinate (Biagini, Gaetani, Guastini, Mussati & Nardelli, 1971) and implies that there is no conjugation between the pyridine ring and the carboxylate group.

The crystal consists of polymeric molecules. The terminal carboxylate group and the pyridine N atom of the nicotinate anion bridge the Cd^{II} atoms to form zigzag chains along the b axis, and the Br atoms further link adjacent chains to form di-*catena* polymers, as illustrated in Fig. 2. In the di-*catena* polymeric molecule, a hydrogen bond exists between atoms O3 and O2($1-x$, $1-y$, $-z$), and short van der Waals contacts of 3.393 (6) [C2···C4($2-x$, $1-y$, $1-z$)] and 3.402 (8) Å [C3···C3($1-x$, $1-y$, $1-z$)] are found between adjacent di-*catena* polymeric molecules.

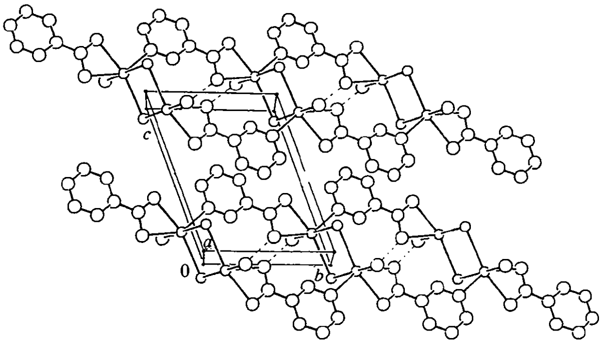


Fig. 2. A packing diagram of the title compound showing the hydrogen-bonding network.

Experimental

The title complex was prepared by dissolving $CdSO_4.\frac{8}{3}H_2O$ (10 mmol) and KBr (20 mmol) in hot water, and then dropping an aqueous solution of sodium nicotinate (10 mmol) into the stirred solution at 333 K. Crystals were grown by slow evaporation at room temperature.

Crystal data

[$CdBr(C_6H_4NO_2)(H_2O)$]
$M_r = 332.43$
Triclinic
$P\bar{1}$
$a = 7.046 (1)$ Å
$b = 7.9939 (9)$ Å
$c = 9.100 (3)$ Å
$\alpha = 106.81 (2)°$
$\beta = 89.00 (3)°$
$\gamma = 114.74 (1)°$
$V = 442.4 (3)$ Å^3
$Z = 2$
$D_x = 2.50$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10.2–14.9°$
$\mu = 6.899$ mm^{-1}
$T = 296$ K
Prism
0.20 × 0.15 × 0.13 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scans (*TEXSAN*; Molecular Structure Corporation, 1989)
$T_{\min} = 0.585$, $T_{\max} = 1.000$
2300 measured reflections
2129 independent reflections

1848 observed reflections [$I > 3\sigma(I)$]
$R_{\rm int} = 0.024$
$\theta_{\max} = 28°$
$h = 0 \rightarrow 9$
$k = -10 \rightarrow 9$
$l = -12 \rightarrow 11$
3 standard reflections monitored every 300 reflections
intensity decay: 0.5%

Refinement

Refinement on F
$R = 0.027$
$wR = 0.038$
$S = 1.13$
1848 reflections
109 parameters
H-atom parameters not refined

Weighting scheme based on measured e.s.d.'s
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.64$ e Å^{-3}
$\Delta\rho_{\min} = -0.84$ e Å^{-3}
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)*

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

	x	y	z	$U_{\rm eq}$
Cd	0.80074 (5)	0.89320 (4)	0.13465 (3)	0.0316 (1)
Br	0.76390 (7)	0.91792 (6)	−0.14873 (5)	0.0369 (2)
O1	0.8057 (6)	0.7802 (4)	0.3451 (5)	0.044 (1)
O2	0.7892 (5)	0.5908 (4)	0.1114 (3)	0.039 (1)
O3	0.4288 (5)	0.7439 (5)	0.1251 (4)	0.038 (1)
N	0.7822 (5)	0.1636 (4)	0.2910 (4)	0.029 (1)
C1	0.8025 (6)	0.3089 (5)	0.2368 (4)	0.028 (2)
C2	0.7771 (6)	0.4703 (5)	0.3245 (4)	0.028 (1)
C3	0.7311 (6)	0.4817 (6)	0.4748 (5)	0.031 (2)
C4	0.7092 (7)	0.3327 (6)	0.5306 (5)	0.036 (2)
C5	0.7358 (7)	0.1760 (6)	0.4357 (5)	0.034 (2)
C6	0.7929 (6)	0.6237 (5)	0.2572 (5)	0.031 (2)

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

Cd—Br	2.6678 (9)	N—C1	1.343 (5)
Cd—Br^{i}	2.7804 (8)	N—C5	1.337 (5)
Cd—O1	2.348 (3)	C1—C2	1.388 (5)
Cd—O2	2.331 (3)	C2—C3	1.386 (6)
Cd—O3	2.373 (3)	C2—C6	1.486 (5)
Cd—N^{ii}	2.272 (3)	C3—C4	1.376 (6)
O1—C6	1.242 (5)	C4—C5	1.384 (6)
O2—C6	1.274 (5)	O3···O2^{iii}	2.738 (5)
Br—Cd—Br^{i}	89.52 (3)	Cd—O1—C6	91.2 (3)
Br—Cd—O1	163.95 (7)	Cd—O2—C6	91.1 (2)
Br—Cd—O2	108.29 (7)	Cd—N^{ii}—C1^{ii}	120.7 (3)

Br—Cd—O3	90.10 (9)	Cd—N^{ii}—C5^{ii}	120.8 (3)
Br—Cd—N^{ii}	103.66 (8)	C1—N—C5	118.2 (3)
Br^{i}—Cd—O1	95.0 (1)	N—C1—C2	122.8 (4)
Br^{i}—Cd—O2	95.32 (8)	C1—C2—C3	118.2 (3)
Br^{i}—Cd—O3	177.8 (1)	C1—C2—C6	120.7 (4)
Br^{i}—Cd—N^{ii}	92.47 (9)	C3—C2—C6	121.1 (3)
O1—Cd—O2	56.0 (1)	C2—C3—C4	119.2 (4)
O1—Cd—O3	85.9 (1)	C3—C4—C5	119.2 (4)
O1—Cd—N^{ii}	91.5 (1)	N—C5—C4	122.4 (4)
O2—Cd—O3	86.9 (1)	O1—C6—O2	121.7 (4)
O2—Cd—N^{ii}	147.1 (1)	O1—C6—C2	118.7 (4)
O3—Cd—N^{ii}	85.5 (1)	O2—C6—C2	119.6 (3)
Cd—Br—Cd^{i}	90.48 (3)		

Symmetry codes: (i) $2-x, 2-y, -z$; (ii) $x, 1+y, z$; (iii) $1-x, 1-y, -z$.

The structure was solved by the heavy-atom method and refined anisotropically for all non-H atoms. The H-atom sites were obtained from a difference Fourier synthesis and not refined. All computations were performed on a MicroVAX 3100 computer.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1989). Program(s) used to solve structure: *TEXSAN*. Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and least-squares-planes data have been deposited with the IUCr (Reference: AS1203). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Biagini, C. M., Chiesi, V. A., Guastini, C. & Viterbo, D. (1974). *Gazz. Chim. Ital.* **104**, 1087–1093.

Biagini, C. M., Gaetani, M. A., Guastini, C. & Mussati, A. (1975). *Gazz. Chim. Ital.* **105**, 117–123.

Biagini, C. M., Gaetani, M. A., Guastini, C., Mussati, A. & Nardelli, M. (1971). *Gazz. Chim. Ital.* **101**, 815–824.

Biagini, C. M., Gaetani, M. A., Guastini, C. & Nardelli, M. (1972). *Gazz. Chim. Ital.* **102**, 1034–1039.

Cariati, F., Naldini, L. & Panzanelli, A. (1983). *Inorg. Chim. Acta*, **69**, 117–122.

Chen, Z., Lin, S., Qiu, J., Wang, Z., Huang, J. & Tang, W. (1994). *J. Chem. Soc. Dalton Trans.* pp. 2989–2993.

Chen, C., Xu, D., Xu, Y., Cheng, C. & Ling, R. (1992). *Acta Cryst.* **C48**, 1231–1233.

Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5. Enraf–Nonius, Delft, The Netherlands.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Molecular Structure Corporation (1989). *TEXSAN. Single Crystal Structure Analysis Software*. Version 5.0. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Moore, J. W., Glick, M. D. & Baker, W. A. (1972). *J. Am. Chem. Soc.* **94**, 1858–1865.

Prout, K., Marin, J. M. & Hutchison, C. A. (1985). *Acta Cryst.* **C41**, 201–204.

Xu, D., Chen, C., Xu, Y., Cheng, C., Chen, J. & Tang, W. (1991). *Acta Cryst.* **C47**, 72–75.

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Poly[bis(p-nitrosalicylato-O:O')disilver(I)-O^3:Ag';Ag:$O^{3'}$]

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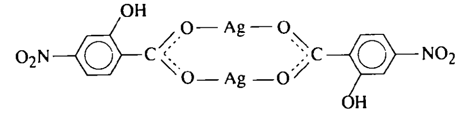
Abstract

The structure of the title compound, $[Ag_2(C_7H_4NO_5)_2]_n$, consists of polymeric networks made up of centrosymmetric bis(carboxylato-O,O')-bridged Ag dimers, which are cross-linked *via* Ag—OH bonds [2.47 (1) Å]. The distances in the chelate ring are Ag—O 2.20 (1) and 2.16 (1), and Ag···Ag 2.796 (2) Å.

Comment

Several silver(I) carboxylate complexes have been reported previously. The majority of these structures consist of discrete centrosymmetric carboxylate-bridged Ag dimers, such as silver(I) benzoate and silver(I) 4-hydroxybenzoate (Usubaliev *et al.*, 1981), and silver(I) 2,6-dihydroxybenzoate (Smith, Kennard & Mak, 1988). Carboxylate-bridged Ag dimers are also known to cross-link *via* Ag—OH bonds forming polymeric sheets, as observed in silver(I) 2,6-dihydroxybenzoate (Mak, Smith & Kennard, 1993). The structure of poly[bis(p-nitrosalicylato-O,O')disilver(I)-O^3:Ag';Ag:$O^{3'}$], (I), reported here, also has polymeric bands of OH-cross-linked centrosymmetric Ag dimers.



(I)

The p-nitrosalicylato ligand is approximately planar, as can be seen from the torsion angles C2—C1—C7—O2 and O5—N1—C4—C5 of −8 (3) and 8 (3)°, respectively. There is also an intraligand hydrogen bond present [O3—H···O2 2.49 (1) Å; Fig. 1]. The ring planes are parallel to the (100) face, while the Ag—OH bonds lie approximately along the diagonal of the same face of the unit cell (Fig. 2). Bond lengths and angles are comparable with those found for analogous complexes.