

- Carruthers, J. R. & Watkin, D. J. (1979). *Acta Cryst.* **A35**, 698–699.
- Enraf–Nonius (1995). *DIP2000 User Manual*. Enraf–Nonius, Delft, The Netherlands.
- Jeffs, S. E., Small, R. W. H. & Worrall, I. J. (1984). *Acta Cryst.* **C40**, 1329–1331.
- Knop, O., Cameron, S. T., Adhikesavalu, D., Vincent, B. R. & Jenkins, J. A. (1987). *Can. J. Chem.* **65**, 1527–1556, and references therein.
- Leman, J. T., Roman, H. A. & Barron, A. R. (1992). *J. Chem. Soc. Dalton Trans.* pp. 2183–2191.
- Reger, D. L., Mason, S. S., Reger, L. B., Rheingold, A. L. & Ostrander, R. L. (1994). *Inorg. Chem.* **33**, 1811–1816.
- Reger, D. L., Mason, S. S., Rheingold, A. L. & Ostrander, R. L. (1994). *Inorg. Chem.* **33**, 1803–1810.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Tsapkov, V. I., Gandzii, M. V., Chumakov, Y. M., Biyushkin, V. N., Malinovskii, T. I., Bkhusam, G. & Samus, M. (1992). *Koord. Khim.* **18**, 850–858.
- Watkin, D. J., Prout, C. K., Carruthers, R. J. & Betteridge, P. (1996). *CRYSTALS*. Issue 10. Chemical Crystallography Laboratory, University of Oxford, England.
- Watkin, D. J., Prout, C. K. & Pearce, L. J. (1996). *CAMERON*. Chemical Crystallography Laboratory, University of Oxford, England.

Acta Cryst. (1996). **C52**, 2183–2185

Bis(*p*-aminobenzoic acid-*N*)dichloro-cadmium(II)

YVETTE LE FUR* AND RENÉ MASSE

Laboratoire de Cristallographie, Associé à l'Université Joseph Fourier, CNRS, BP 166, 38042 Grenoble CEDEX, France. E-mail: masse@labs.polycnrs-gre.fr

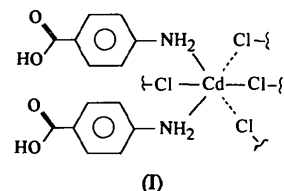
(Received 1 February 1996; accepted 14 March 1996)

Abstract

In crystals of $[\text{CdCl}_2(\text{C}_7\text{H}_7\text{NO}_2)_2]$, the Cd atom is octahedrally coordinated by four Cl atoms and two N atoms from two *p*-aminobenzoic acid ligands. Infinite zigzag chains of edge-shared octahedra run along the *a* axis. Pairs of *p*-aminobenzoic acid residues anchored onto the Cd chains form thick organic–inorganic layers parallel to the (011) plane. An N—H...Cl hydrogen-bond network maintains the packing cohesion between the layers.

Comment

Crystals of the title compound, (I), are built from infinite chains of CdCl_4N_2 octahedra interconnected in a three-dimensional manner through pairs of O—H...O hydrogen-bonded *p*-aminobenzoic acid molecules and also by N—H...Cl hydrogen bonds. The main geometrical features of this organic–inorganic assembly are summarized in Tables 2 and 3.



The carboxyl groups of the independent ($n = 1, 2$) *p*-aminobenzoic acid residues are linked by pairs of hydrogen bonds $[\text{O}(11)—\text{H}(\text{O}11)\cdots\text{O}(22')]$ and $\text{O}(21)—\text{H}(\text{O}21)\cdots\text{O}(12'')$; symmetry codes: (i) $x, y + 1, z$; (ii) $x, y - 1, z$, as is typical in assemblies formed from carboxylic acid synthons (Desiraju, 1995). The two linked carboxyl groups are not, however, related centrosymmetrically. The interatomic distances and angles are close to those observed in *p*-aminobenzoic acid (Lai & Marsh, 1967). In the two structurally distinct organic residues ($n = 1, 2$) of the asymmetric unit, the atoms of the aromatic ring are coplanar to within 0.01 Å and the angle between these planes is 3.8(9)°. The amino and carboxyl groups are displaced significantly from the aromatic plane; atoms C(*n*4), C(*n*7), O(*n*1) and O(*n*2) ($n = 1, 2$) of the carboxyl groups are coplanar to within 0.01 Å, but these groups are rotated slightly around the C(*n*4)—C(*n*7) bonds by *ca* 2–3° out of coplanarity with the aromatic rings.

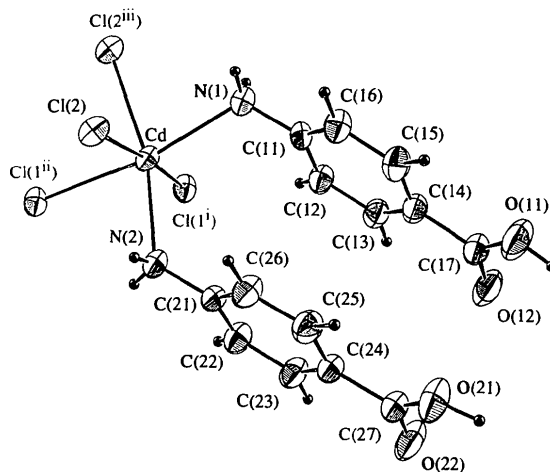


Fig. 1. An ORTEP (Johnson, 1965) drawing of the title compound showing the metal coordination. Displacement ellipsoids for non-H atoms are shown at the 50% probability level.

The coordination of the N atoms is distorted tetrahedral, with a relatively large C(*n*1)—N(*n*) distance of 1.42 Å (*cf.* 1.38 Å in *p*-aminobenzoic acid where this bond is already associated with a non-planar coordination at the amino N atom). The angles subtended at the N atom are H(1N*n*)—N(*n*)—H(2N*n*) 108(4) and 113(4), H(1N*n*)—N(*n*)—Cd 106(3) and 93(3), C(*n*1)—N(*n*)—H(1N*n*) 111(3) and 110(3), C(*n*1)—N(*n*)—Cd

120.4 (2) and 126.6 (2), C(*n*1)—N(*n*)—H(2*Nn*) 111 (3) and 111 (3), and H(2*Nn*)—N(*n*)—Cd 100 (3) and 102 (3)°.

The Cd atoms form an infinite zigzag chain along the *a* axis, with a Cd···Cd···Cd angle of 115.40(1)° and alternate Cd···Cd distances of 3.8293(4) and 3.6969(4) Å. Each Cd atom is located in a distorted octahedron formed from four Cl atoms [two Cl(1) at 2.5673(7) and 2.7287(8) Å and two Cl(2) at 2.6000(8) and 2.6126(8) Å] and two adjacent N atoms [2.357(3) and 2.344(3) Å] belonging to two independent organic residues. The octahedra are edge shared through pairs of Cl atoms, Cl(1)/Cl(1) and Cl(2)/Cl(2) (Fig. 2), as in the octahedral *cis* chain structure of monoclinic MoOCl₃ (Drew & Tomkins, 1970). This type of linkage differs from that observed in Cd(NH₃)₂Cl₂ [National Bureau of Standards (US), 1972] in which very regular octahedra are connected by opposite Cl—Cl edges, building an octahedral *trans* chain structure. The Cd atom is shifted from the centre of the octahedron toward the N(1) and N(2) atoms. Fig. 2 shows how the *p*-aminobenzoic acid residues help to stabilize the chains of CdCl₄N₂ octahedra through N—H···Cl hydrogen bonding (see Table 3).

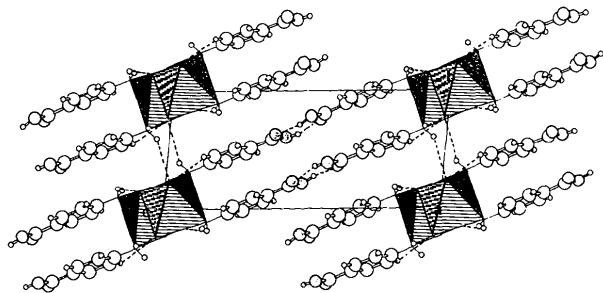


Fig. 2. View along the the *a* axis of the (C₇H₇NO₂)₂CdCl₂ adduct, with hydrogen bonds shown as dashed lines. The organic-inorganic layers parallel to the (011) plane are assembled through N—H···Cl bonds. Atoms are represented by spheres of arbitrary size.

The layer formed by pairs of hydrogen-bonded *p*-aminobenzoic acid residues alternating with CdCl₄N₂ octahedra is about 3.3 Å thick and runs parallel to the (011) plane. The interlayer cohesion is mainly effected by N(1)—H(2N1)···Cl(1) hydrogen bonds.

Experimental

Crystals of the title compound were prepared by dissolving *p*-aminobenzoic acid (0.015 *M*) in 5 ml of aqueous solution containing cadmium chloride (0.01 *M*). The mixture was kept at room temperature for one day, then filtered and evaporated. Elongated colourless prisms (average size 0.5 × 0.6 × 0.8 mm) were obtained. The chemical formula was determined from the crystal structure analysis.

Crystal data

[CdCl₂(C₇H₇NO₂)₂]
M_r = 457.58
 Triclinic
 $\bar{P}1$
a = 6.362 (3) Å
b = 7.512 (3) Å
c = 17.258 (8) Å
 α = 94.55 (4)°
 β = 96.81 (5)°
 γ = 104.59 (4)°
V = 787 (1) Å³
Z = 2
D_x = 1.930 Mg m⁻³
D_m not measured

Data collection

Enraf-Nonius CAD-4
 diffractometer
 θ scans
 Absorption correction:
 none
 5771 measured reflections
 5615 independent reflections
 3317 observed reflections
 $[I > 3\sigma(I)]$

Refinement

Refinement on *F*
R = 0.025
wR = 0.027
S = 0.810
 3317 reflections
 264 parameters
 All H-atom parameters
 refined
 Unit weights applied

Ag K α radiation
 λ = 0.5608 Å
 Cell parameters from 25
 reflections
 θ = 9.97–11.80°
 μ = 0.912 mm⁻¹
T = 295 K
 Short rectangular prism
 0.63 × 0.44 × 0.40 mm
 Colourless

R_{int} = 0.010
 θ_{\max} = 25°
 h = -9 → 9
 k = -11 → 11
 l = 0 → 26
 2 standard reflections
 frequency: 120 min
 intensity decay: none

$(\Delta/\sigma)_{\max}$ = 0.20
 $\Delta\rho_{\max}$ = 0.635 e Å⁻³
 $\Delta\rho_{\min}$ = -0.533 e Å⁻³
 Extinction correction: none
 Atomic scattering factors
 from *International Tables*
 for *X-ray Crystallography*
 (1974, Vol. IV, Table
 2.3.1)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

	$B_{\text{eq}} = (4/3)\sum_i \sum_j \beta_{ij} a_i \cdot a_j$			B_{eq}
	<i>x</i>	<i>y</i>	<i>z</i>	
Cd	-0.24386 (4)	-0.05535 (3)	0.05114 (1)	2.212 (3)
Cl(1)	0.3510 (1)	0.7652 (1)	0.01429 (4)	2.55 (1)
Cl(2)	0.1549 (1)	0.1542 (1)	0.08724 (4)	2.60 (1)
O(11)	0.1878 (5)	0.6061 (4)	0.5798 (1)	4.39 (6)
O(12)	0.5414 (4)	0.6287 (4)	0.6170 (1)	4.21 (6)
O(21)	0.6781 (5)	-0.2158 (4)	0.4944 (2)	4.52 (6)
O(22)	0.3261 (5)	-0.2367 (4)	0.4592 (2)	4.63 (6)
N(1)	0.1479 (4)	0.3260 (3)	0.9158 (1)	2.46 (5)
N(2)	0.6985 (5)	0.1061 (4)	0.1652 (2)	2.80 (5)
C(11)	0.1936 (5)	0.3967 (4)	0.8437 (2)	2.32 (5)
C(12)	0.4088 (5)	0.4503 (4)	0.8304 (2)	2.64 (6)
C(13)	0.4543 (5)	0.5126 (4)	0.7600 (2)	2.86 (6)
C(14)	0.2900 (5)	0.5229 (4)	0.7029 (2)	2.69 (6)
C(15)	0.0749 (6)	0.4716 (5)	0.7168 (2)	3.04 (6)
C(16)	0.0267 (5)	0.4090 (4)	0.7875 (2)	2.80 (6)
C(17)	0.3493 (6)	0.5906 (4)	0.6284 (2)	3.11 (6)
C(21)	0.6585 (5)	0.0336 (4)	0.2371 (2)	2.52 (5)
C(22)	0.8282 (6)	0.0150 (5)	0.2903 (2)	3.19 (7)
C(23)	0.7867 (6)	-0.0575 (5)	0.3593 (2)	3.28 (7)
C(24)	0.5734 (5)	-0.1110 (4)	0.3755 (2)	2.74 (6)
C(25)	0.4055 (5)	-0.0895 (5)	0.3223 (2)	3.01 (6)
C(26)	0.4471 (5)	-0.0199 (5)	0.2529 (2)	3.01 (6)
C(27)	0.5174 (6)	-0.1926 (5)	0.4472 (2)	3.22 (7)

Table 2. Selected geometric parameters (Å, °)

C(11)—N(1)	1.423 (4)	C(27)—O(22)	1.225 (5)
C(14)—C(17)	1.474 (4)	Cd—Cl(1 ⁱ)	2.5673 (7)
C(17)—O(11)	1.282 (4)	Cd—Cl(1 ⁱⁱ)	2.7287 (8)
C(17)—O(12)	1.226 (5)	Cd—Cl(2)	2.6000 (7)
C(21)—N(2)	1.419 (4)	Cd—Cl(2 ⁱⁱⁱ)	2.6126 (8)
C(24)—C(27)	1.466 (5)	Cd—N(1 ^{iv})	2.357 (3)
C(27)—O(21)	1.286 (5)	Cd—N(2 ^v)	2.344 (3)
N(1)—C(11)—C(12)	118.8 (3)	Cl(1 ⁱ)—Cd—Cl(2)	174.71 (3)
N(1)—C(11)—C(16)	121.0 (3)	Cl(1 ⁱ)—Cd—Cl(2 ⁱⁱⁱ)	91.79 (2)
C(13)—C(14)—C(17)	118.7 (3)	Cl(1 ⁱ)—Cd—N(1 ^{iv})	91.23 (6)
C(15)—C(14)—C(17)	121.9 (3)	Cl(1 ⁱ)—Cd—N(2 ^v)	94.12 (7)
O(11)—C(17)—O(12)	124.9 (3)	Cl(1 ⁱⁱ)—Cd—Cl(2)	87.58 (2)
O(11)—C(17)—C(14)	114.9 (3)	Cl(1 ⁱⁱ)—Cd—Cl(2 ⁱⁱⁱ)	86.11 (3)
O(12)—C(17)—C(14)	120.1 (3)	Cl(1 ⁱⁱ)—Cd—N(1 ^{iv})	169.65 (6)
N(2)—C(21)—C(22)	121.0 (3)	Cl(1 ⁱⁱ)—Cd—N(2 ^v)	81.37 (7)
N(2)—C(21)—C(26)	119.2 (3)	Cl(2)—Cd—Cl(2 ⁱⁱⁱ)	89.66 (2)
C(23)—C(24)—C(27)	122.6 (3)	Cl(2)—Cd—N(1 ^{iv})	93.99 (6)
C(25)—C(24)—C(27)	118.1 (3)	Cl(2)—Cd—N(2 ^v)	83.36 (6)
O(21)—C(27)—O(22)	123.4 (3)	Cl(2 ⁱⁱⁱ)—Cd—N(1 ^{iv})	83.67 (7)
O(21)—C(27)—C(24)	116.3 (3)	Cl(2 ⁱⁱⁱ)—Cd—N(2 ^v)	165.89 (7)
O(22)—C(27)—C(24)	120.5 (3)	N(1 ^{iv})—Cd—N(2 ^v)	108.96 (9)
Cl(1 ⁱ)—Cd—Cl(1 ⁱⁱ)	87.44 (2)		

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

Table 3. Hydrogen-bonding geometry (Å, °)

D—H...A	D—H	H...A	D...A	D—H...A
O(11)—H(O11)...O(22 ⁱ)	0.83 (6)	1.79 (5)	2.608 (4)	169 (6)
O(21)—H(O21)...O(12 ⁱⁱ)	0.92 (6)	1.72 (6)	2.630 (4)	169 (6)
N(1)—H(N1)...Cl(1 ⁱⁱⁱ)	0.87 (4)	2.63 (4)	3.456 (3)	158 (3)
N(1)—H(2N1)...Cl(1 ^{iv})	0.82 (3)	2.74 (4)	3.448 (2)	145 (4)
N(2)—H(1N2)...Cl(2 ^v)	0.80 (4)	2.75 (4)	3.293 (3)	126 (4)
N(2)—H(2N2)...Cl(2)	0.85 (4)	2.88 (4)	3.674 (3)	156 (3)
C(12)—H(C12)...Cl(1 ^{vi})	0.89 (4)	2.85 (4)	3.619 (3)	145 (3)

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

Data collection: *CAD-4 Operations Manual* (Enraf–Nonius, 1977a). Cell refinement: *CAD-4 Operations Manual*. Data reduction: *SDP* (Enraf–Nonius, 1977b). Program(s) used to solve structure: *MULTAN77* (Main, Lessinger, Woolfson, Germain & Declercq, 1977). Program(s) used to refine structure: *SDP*. Molecular graphics: *MOLVIEW* (Cense, 1989) and *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *SDP*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and least-squares-planes data have been deposited with the IUCr (Reference: MU1252). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Cense, J. M. (1989). *Tetrahedron Comput. Methodol.* **2**, 65–71.
 Desiraju, G. R. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 2311–2327.
 Drew, M. G. B. & Tomkins, I. B. (1970). *J. Chem. Soc. London A*, pp. 22–25.
 Enraf–Nonius (1977a). *CAD-4 Operations Manual*. Enraf–Nonius, Delft, The Netherlands.
 Enraf–Nonius (1977b). *Structure Determination Package*. Version RSX11M. Enraf–Nonius, Delft, The Netherlands.
 Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
 Lai, T. F. & Marsh, R. E. (1967). *Acta Cryst.* **22**, 885–893.

Main, P., Lessinger, L., Woolfson, M. M., Germain, G. & Declercq, J. P. (1977). *MULTAN77. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Universities of York, England, and Louvain, Belgium.
 National Bureau of Standards (US) (1972). *Monogr.* **25**, Section 10, p. 14.

Acta Cryst. (1996). **C52**, 2185–2188

Caesium 2-(2-Hydroxy-5,5-dimethyl-1,3-dioxo-2-cyclohexyl)-5,5-dimethyl-1,3-cyclohexanedionato(1-) Monohydrate

JOHN C. BARNES

Chemistry Department, University of Dundee, Dundee DD1 4HN, Scotland. E-mail: j.c.barnes@dundee.ac.uk

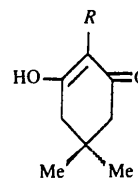
(Received 26 April 1996; accepted 4 June 1996)

Abstract

One of the 5,5-dimethyl-1,3-cyclohexanedione residues of the title compound, $\text{Cs}^+ \cdot \text{C}_{16}\text{H}_{21}\text{O}_5 \cdot \text{H}_2\text{O}$, appears as the anion whereas the other is in the keto form; in the parent molecule the enol predominates. The Cs atom is seven coordinate, with Cs—O distances between 3.008 (3) and 3.396 (4) Å.

Comment

There has been interest recently in the roles of cyclic β -diketones in above-molecular host–guest structures and as potential ligands to metal ions (Braga & Grepioni, 1996). The structures of cyclohexane-1,3-dione (CHD) (Etter, Urbanczyck-Lipkowska, Jahn & Frey, 1986), 4,4-dimethyl-CHD (Barnes, 1996b) and 5,5-dimethyl-CHD [(1a), dimedone; Singh & Calvo, 1975] show that the CHD derivatives exist in the enol form in the crystal as well as in solution. Hydrogen-bonded inclusion compounds (CHD)₆-benzene (Etter *et al.*, 1986) and 2,5,5-dimethyl-CHD monohydrate [(1b); Barnes, 1996b] have been reported, and Braga, Grepioni, Bryne & Wolf



- (1a) $R = \text{H}$
 (1b) $R = \text{CH}_3$
 (1c) $R = \text{SO}_3^-$