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Structure of *trans*-Diiodotetrakis(pyridine)cadmium(II)–Pyridine (1/2), $[\text{CdI}_2(\text{C}_5\text{H}_5\text{N})_4]_2 \cdot 2\text{C}_5\text{H}_5\text{N}$

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Abstract. $M_r = 840.8$, orthorhombic, *Ccca*, $a = 11.620$ (2), $b = 15.847$ (2), $c = 17.245$ (4) Å, $V = 3175$ (1) Å³, $Z = 4$, $D_m = 1.7$ (1) (1,2-dichloroethane/1,2-dibromoethane), $D_x = 1.759$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 11.88$ mm⁻¹, $F(000) = 1624$, $T = 298$ K, final $R = 0.058$ for 1589 unique observed reflections. Cd is octahedrally coordinated with the N atoms of four pyridine molecules and two I⁻ ions in *trans* positions at average distances of 2.411 (7) and 2.9693 (7) Å, respectively. The crystal structure consists of layers perpendicular to *c*, built up of *trans*-CdI₂(py)₄ units linked together by van der Waals interactions between the ligating pyridine(py) molecules. The guest pyridine molecules are enclathrated in the cavities formed between the layers.

Introduction. A series of complexes of the type MP_4X_2 (where *M* is a divalent transition metal, *P* a pyridine derivative and *X* a halide or thiocyanate ion) form clathrate compounds with various guest molecules (Schaeffer, Dorsey, Skinner & Christian, 1957).

There has been no report on cadmium–pyridine complexes except for the early work of Paulus (1969) on Cd(py)₂Cl₂ which possesses a pseudooctahedral polymeric structure with bridging halide ligands. The crystal structure of the new clathrate compound, diiodotetrakis(pyridine)cadmium(II), which contains enclathrated pyridine guest molecules, has been determined.

Experimental. Cadmium iodide was dissolved in a pyridine–ethanol (1:1) mixture at 360 K. The colorless plate-like crystals immediately precipitated after cooling at room temperature. The crystal specimen for X-ray work was sealed in a Lindemann-glass capillary along with a small amount of mother liquid, since the crystals tend to lose pyridine easily. The large experimental error in density measurements is due to deterioration of the crystal in solution. Approximate dimensions of crystal 0.67 × 0.45 × 0.40 mm. Rigaku AFC-5 automated four-circle diffractometer, graphite monochromator. Cell parameters refined by least-squares method on the basis of 20 2θ values, Mo *K*α radiation (35° < 2θ < 40°). Intensity measurement performed to $2\theta = 70^\circ$ (+*h*, +*k*, +*l* set), ω – 2θ scan technique, scan speed 2° min⁻¹(θ). Mean ratio of structure factors of five standard reflections $0.95 < \sum(|F_o|/|F_o|_{\text{initial}})/5 \leq 1.00$. 2824 reflections measured, 1235 unobserved, 1589 unique [$|F_o| > 3\sigma(|F_o|)$]. Corrections for Lp and absorption (min. and max. transmission factors 0.118 and 0.307). Patterson map revealed the positions of I atoms; remaining non-H atoms found by successive Fourier syntheses and refined by block-diagonal least squares with anisotropic thermal parameters using the UNICSIII computation program system (Sakurai & Kobayashi, 1979); six H atoms of coordinated pyridine molecules were found from difference density maps and refined isotropically; $\sum w||F_o| - |F_c||^2$ minimized, $w^{-1} = \sigma^2(|F_o|) + (0.015|F_o|)^2$; final $R = 0.058$, wR

= 0.077, $S = 3.48$ for 1589 observed reflections. In final cycle $(\Delta/\sigma)_{\max} = 0.5$ for the y coordinate of C(7). No peaks higher than $0.45 \text{ e } \text{\AA}^{-3}$ in the final difference density map. Complex neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974).

Table 1. Positional parameters ($\times 10^4$; for $I \times 10^5$) and equivalent isotropic thermal parameters (Hamilton, 1959)

$$B_{\text{eq}} = \frac{1}{3} \sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$$

| | x | y | z | $B_{\text{eq}}(\text{\AA}^2)$ |
|------|-----------|----------|----------|-------------------------------|
| I | 25553 (5) | 0 | 0 | 4.0 |
| Cd | 0 | 0 | 0 | 3.1 |
| N(1) | 0 | 1494 (4) | 0 | 3.3 |
| N(2) | 0 | 0 | 1423 (5) | 3.9 |
| N(3) | 2500 | 2500 | 2951 (6) | 7.0 |
| C(1) | 776 (5) | 1923 (3) | -411 (4) | 3.0 |
| C(2) | 794 (5) | 2795 (3) | -429 (4) | 3.3 |
| C(3) | 0 | 3242 (5) | 0 | 4.0 |
| C(4) | 841 (7) | 402 (4) | 1834 (4) | 4.6 |
| C(5) | 849 (8) | 412 (5) | 2636 (5) | 5.7 |
| C(6) | 0 | 0 | 3039 (7) | 6.5 |
| C(7) | 3325 (9) | 2075 (8) | 2574 (5) | 7.5 |
| C(8) | 3325 (8) | 2048 (7) | 1774 (6) | 7.6 |
| C(9) | 2500 | 2500 | 1375 (7) | 7.0 |

Table 2. Bond lengths (\AA) and bond angles ($^\circ$)

| | | | |
|--------------------------------|------------|--------------------------------|------------|
| Cd—I | 2.9693 (7) | Cd—N(2) | 2.454 (9) |
| Cd—N(1) | 2.368 (6) | N(2)—C(4) | 1.365 (9) |
| N(1)—C(1) | 1.333 (7) | C(1)—C(2) | 1.382 (7) |
| N(3)—C(7) | 1.340 (12) | C(4)—C(5) | 1.383 (11) |
| C(2)—C(3) | 1.379 (7) | C(7)—C(8) | 1.380 (13) |
| C(5)—C(6) | 1.372 (11) | | |
| C(8)—C(9) | 1.380 (12) | | |
| Cd—N(1)—C(1) | 120.7 (3) | Cd—N(2)—C(4) | 121.3 (4) |
| C(1)—N(1)—C(1 ⁱⁱ) | 118.7 (6) | C(4)—N(2)—C(4 ⁱⁱⁱ) | 117.5 (7) |
| C(7)—N(3)—C(7 ⁱⁱⁱ) | 121.9 (10) | N(1)—C(1)—C(2) | 122.2 (5) |
| C(1)—C(2)—C(3) | 119.4 (6) | C(2)—C(3)—C(2 ⁱ) | 118.1 (7) |
| N(2)—C(4)—C(5) | 121.9 (7) | C(4)—C(5)—C(6) | 119.8 (8) |
| C(5)—C(6)—C(5 ⁱⁱⁱ) | 119.1 (10) | N(3)—C(7)—C(8) | 120.1 (10) |
| C(7)—C(8)—C(9) | 118.9 (10) | C(8)—C(9)—C(8 ⁱⁱⁱ) | 120.2 (11) |

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

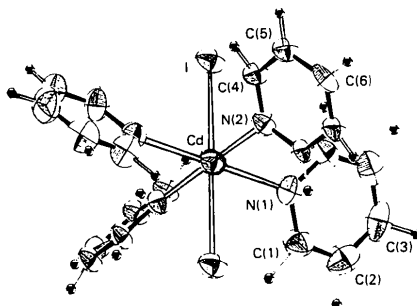


Fig. 1. ORTEP drawing (Johnson, 1965) of *trans*-CdI₂(py)₄. Thermal ellipsoids are at the 50% probability level.

Discussion. Atomic parameters are given in Table 1.* Interatomic distances and bond angles in the complex and the pyridine molecules are listed in Table 2. The structure of the complex Cd(py)₄I₂ is shown in Fig. 1 together with the numbering scheme. The complex possesses approximate 422 but strict 222 symmetry and exhibits pseudooctahedral coordination geometry. The I—I vector, 'pseudotetragonal' molecular axis, is parallel with **c**. Therefore, the complex adopts 'propeller-shaped' conformations of the pyridine rings.

Bond distances and angles within the two crystallographically independent pyridine moieties are equal within experimental error. The C(1)—C(2) bond distance, 1.382 (7) \AA , is comparable with the C(2)—C(3) distance 1.379 (7) \AA ; however, the N(1)—C(1)—C(2) angle, 122.2 (5)°, is significantly greater than the other angles, 118.7 (6), 119.4 (6) and 118.1 (7)°.

The dihedral angles between the least-squares CdN₄ coordination plane and the least-squares planes of the pyridine ligands are 32 (1) and 38 (1)°. There exist weak hydrogen-bonding interactions between I and H atoms HC(1), 3.17 (8) \AA , and HC(4), 3.17 (5) \AA , of the ligating pyridine molecules, which are less than 3.35 \AA , the sum of the van der Waals radii (Pauling, 1960). These I—HC(1) or HC(4) hydrogen-bonding interactions and intramolecular repulsion between adjacent coordinated pyridine molecules are important in determining the dihedral angle.

The two symmetrically independent Cd—N distances, 2.368 (6) and 2.454 (9) \AA , differ significantly. The Cd—I distance, 2.9693 (7) \AA , is similar to those in CdI₂. These structural features of the complex are very

* Lists of structure factors, anisotropic thermal parameters for non-H atoms and H-atom coordinates of the pyridine ligands have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39685 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

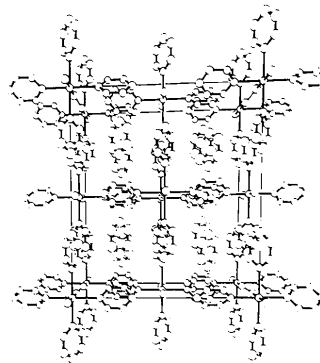


Fig. 2. Packing of the molecules in the unit cell. The origin is at the lower left corner with the positive b axis horizontal and to the right, the positive c axis vertical, and the positive a axis in the direction toward the viewer.

similar to the early results for tetrakis(pyridine)metal(II) (Ni, Fe, Co) chloride complexes (Long & Clarke, 1978).

The crystal structure is shown in Fig. 2. The structure consists of the host *trans*-diiodotetrakis(pyridine) complexes and the guest pyridine molecules. The host complexes form layers with I—Cd—I bonds parallel to *a*, held together by van der Waals forces between the coordinated pyridine molecules. The guest pyridine molecules are enclathrated in the cavities formed between the host layers. The cavity is surrounded by the ligating pyridine molecules and I atoms. It has a twofold axis of symmetry, and 2:1 is the maximum value for the guest/host molar ratio. The low measured density indicates partial occupancy of the guest pyridine sites, since clathrates are potentially non-stoichiometric. This is consistent with the large thermal parameters of the guest pyridine atoms N(3), C(7), C(8), C(9) in comparison with the complexed pyridine molecules of the host structure. The individual molecules of Cd(py)₄I₂ are remarkably well isolated from each other. No significant shortening of the intermolecular distances compared to the sum of the

van der Waals radii is observed. Only two are less than 3.6 Å: between N(3) of a guest pyridine molecule and C(1) [3.581 (10) Å] and C(2) [3.456 (10) Å] of a coordinated pyridine ligand.

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Structure of Tetrakis[μ -(β -alanine)-*O,O'*]-diaquadicopper(II) Tetranitrate Tetrahydrate, [Cu₂(H₂O)₂(C₃H₇NO₂)₄](NO₃)₄·4H₂O

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Abstract. $M_r = 839.6$, triclinic, $P\bar{1}$, $a = 12.499$ (1), $b = 8.717$ (1), $c = 8.070$ (1) Å, $\alpha = 77.74$ (2), $\beta = 82.44$ (1), $\gamma = 71.48$ (1)°, $V = 812.8$ Å³, $D_x = 1.715$, D_m (floatation) = 1.758 Mg m⁻³, $Z = 1$, $F(000) = 434$, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 1.35$ mm⁻¹, room temperature, $R = 0.048$ for 2225 observed reflexions. Four alanine groups form centrosymmetric dimers with two Cu atoms; they are nearly mutually perpendicular and are in *cis* configuration. The Cu—Cu separation is 2.639 (1) Å. The four carboxyl O atoms and an axial water O coordinate with Cu to form a square pyramid. The Cu—O(alanyl) bonds are in the range 1.961 (4)–1.981 (4) Å and Cu—O(water) is 2.124 (3) Å.

Introduction. Alanine residues have been the subject of intensive study because of the variety of conformations in which alanine is found to be bonded in certain peptides, appearing, for instance, repetitively in the form of an Ala-Pro sequence over the light chain of rabbit skeletal muscle myosin (Kamwaya, Oster, Bradaczek, Ponnuswamy, Parthasarathy, Naraj & Balaram, 1982) and because of some interesting physical properties of complexes of metallic salts with amino acids (Griffith, 1943; Blakeslee & Hoard, 1956; Tomita, 1961; Jose, Pant & Biswas, 1964; Jose & Pant, 1965; Rao & Viswamitra, 1972; Herak, Prelesnik, Manojlović-Muir & Muir, 1974). In particular, it has been observed that certain derivatives of β -alanine with Cu(NO₃)₂·3H₂O form a bacteriocidal composition

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