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Synthesis and Crystal Structure of Tetra[pyridine]diperchlorato-K^2 O-Cadmium(II)

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The crystal structure of $[Cd(C_5H_5N)_4(ClO_4)_2]$ has been determined by single crystal X-ray diffraction method. The crystal belongs to orthorhombic system, space group $P2_12_12_1$ with unit cell constants a = 10.368(2), b = 14.403(3), c = 16.647(3) Å, V = 2485.9(8) $Å^3$, Z = 4, D_c = 1.677 g/cm^3, μ = 1.145 mm^{-1}, F(000) = 1256, R and wR are 0.0447 and 0.1304 respectively for 4867 unique reflections with 4450 observed reflections ($I > 2\sigma(I)$). The central Cd(II) atom is coordinated by four N atoms from four pyridine ligands and two O atoms from two perchlorate counter-ions. The coordination geometry is slightly distorted octahedral, with the four N atoms occupying the equatorial positions, while two O atoms being in the axial positons. The packing is stabilized by C—H···O intermolecular interactions.

Key Words: Synthesis, Crystal structure, Cd(II) complex.

INTRODUCTION

In recent years, self-assembly has been the most efficient approach towards novel organic/inorganic composite materials. During the search of molecule-based materials with interesting properties such as catalysis, clathration etc., much attention has been focussed on the synthesis of one-, two- and three-dimensional extended solids involving cadmium[1], as its d^{10} configuration permits a wide variety of geometries and coordination numbers[2–6]. A variety of coordination complexes have been prepared from isonicotinic or nicotinic as it is a multidentate ligand[7]. Here we study the hydrothermal synthesis about isonicotinic and cadmium perchlorate. To our surprise, the carboxyl was removed under the

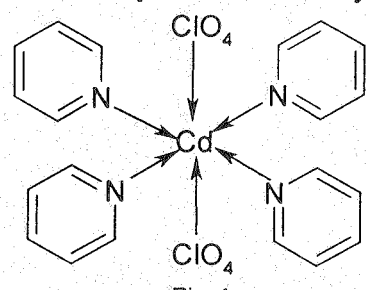

Fig. 1

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hydrothermal conditions, resulted unexpectively a novel crystal $[Cd(C_5H_5N)_4(ClO_4)_2]$ (Fig. 1).

EXPERIMENTAL

All chemicals were of analytical reagent grade and used directly without further purification. The crystal was prepared by hydrothermal reaction. To a warm solution of $Cd(ClO_4)_2 \cdot 6H_2O$ (0.056 g, 0.5 mmol) and isonicotinic (0.0246 g, 2.0 mmol) in 20 mL water, was added ethanol (5 mL). The mixture was heated for 2 h with stirring and sealed in a 30 mL teflon-lined autoclave and heated at 180°C for 72 h. Colourless single crystals suitable for X-ray crystallographic analysis were obtained by slow evaporation of the solvent at room temperature.

Crystal data and structure determination

A colourless single crystal with approximate dimension of $0.11 \times 0.28 \times 0.40$ mm was mounted on a glass fibre in a random orientation. The data were collected by Bruker Smart 1000 CCD diffractometer with graphite monochromated MoK_α radiation ($\lambda = 0.71073$ Å) using ω scan mode in the range of $1.9 \le \theta \le 26.1°$ at temperature 293(2) K. A total of 13968 reflections were collected with 4867 unique ones ($R_{int} = 0.016$), of which 4450 reflections with $I > 2\sigma(I)$ were considered to be observed and used in the succeeding refinements. Intensity data were corrected for Lp factors and empirical absorption. The structure was solved by direct methods and expanded by using Fourier differential techniques with SHELXL-97[8]. All non-hydrogen atoms were located with successive difference Fourier syntheses. The structure was refined by full-matrix least-squares method on F^2 with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added according to the theoretical models. Full matrix least-squares refinement gave the final R = 0.0447 and wR = 0.1304, $W = 1/[\sigma^2(F_0)^2 + (0.0824P)^2 + 1.5791P]$ where $P = (F_0^2 + 2F_c^2)/3$.

RESULTS AND DISCUSSION

X-ray crystal structure of the title compound

The final atomic parameters and equivalent isotropic thermal parameters for the non-hydrogen atoms are given in Table-1. Selected bond lengths and bond angles are illustrated in Table-2. The hydrogen bonding geometries are shown in Table-3. Fig. 1 shows the molecular structure of the compound.

In the title unsymmetric mononuclear Cd(II) compound, the central Cd(II) atom is coordinated by four N atoms from four pyridine ligands and two O atoms from two perchlorate counter-ions. The coordination geometry is slightly distorted octahedral, with the four N atoms occupying the equatorial positions, while two O atoms being in the axial positons. The Cd—N bond lengths are in the ranges of 2.289(5)–2.347(4) Å, which are longer than those values in the related complex [2.310–2.346 Å][9], maybe due to the two perchlorate ligands. The packing is stabilized by C—H···O intermolecular interactions. Packing diagram of the title compound in a unit cell is shown in Fig. 2.

TABLE 1

ATOMIC COORDINATES ($\times 10^4$) AND THERMAL PARAMETERS ($Å^2$)

Atom	x	y	z	U(eq)
Cd1	0.73158 (3)	0.26335 (2)	0.75052(2)	0.0611 (1)
Cl1	0.03550 (19)	0.84293 (13)	0.89174 (10)	0.0879 (6)
Cl2	0.51894 (14)	0.17684 (11)	0.90305 (8)	0.0693 (4)
O1	0.0344 (9)	0.8765 (5)	0.9662 (3)	0.155 (4)
O2	–0.0161 (7)	0.9109 (4)	0.8324 (3)	0.119 (3)
O3	0.1516 (7)	0.8181 (7)	0.8631 (4)	0.147 (4)
O4	–0.0386 (8)	0.7585 (6)	0.8868 (6)	0.163 (4)
O5	0.4538 (11)	0.1318 (8)	0.8413 (6)	0.213 (6)
O6	0.5721 (15)	0.1286 (8)	0.9598 (5)	0.257 (7)
O7	0.4382 (8)	0.2454 (8)	0.9299 (6)	0.206 (5)
O8	0.6093 (11)	0.2155 (9)	0.8611 (7)	0.251 (7)
N1	0.7521 (4)	0.4089 (3)	0.8126 (3)	0.0620 (14)
N2	0.5509 (5)	0.3157 (3)	0.6824 (3)	0.0657 (16)
N3	0.9091 (5)	0.2155 (3)	0.8210 (3)	0.0667 (14)
N4	0.7234 (4)	0.1209 (3)	0.6839 (3)	0.0663 (14)
C1	0.7356 (6)	0.4874 (4)	0.7723 (4)	0.0713 (19)
C2	0.7490 (8)	0.5741 (4)	0.8086 (5)	0.087 (3)
C3	0.7766 (7)	0.5784 (5)	0.8872 (5)	0.090(3)
C4	0.7935 (7)	0.4981 (5)	0.9288 (4)	0.086 (3)
C5	0.7809 (6)	0.4149 (4)	0.8903 (3)	0.0690 (17)
C6	0.5436 (8)	0.3148 (6)	0.6004 (4)	0.090 (2)
C7	0.4373 (10)	0.3454 (8)	0.5616 (4)	0.118 (4)
C8	0.3386 (7)	0.3846 (6)	0.6034 (4)	0.094 (3)
C9	0.3437 (7)	0.3825 (6)	0.6839 (4)	0.093 (3)
C10	0.4509 (6)	0.3489 (5)	0.7222 (3)	0.077 (2)
C11	1.0191 (6)	0.2629 (4)	0.8195 (3)	0.0697 (17)
C12	1.1300 (7)	0.2380 (5)	0.8583 (4)	0.083 (2)
C13	1.1284 (8)	0.1584 (5)	0.9039 (4)	0.087 (2)
C14	1.0118 (9)	0.1072 (5)	0.9071 (4)	0.094 (3)
C15	0.9086 (9)	0.1381 (5)	0.8662 (4)	0.089 (3)
C16	0.6092 (6)	0.0841 (5)	0.6606 (4)	0.076 (2)
C17	0.6008 (7)	0.0066 (5)	0.6124 (4)	0.078 (2)
C18	0.7111 (7)	–0.0362 (5)	0.5873 (4)	0.076 (2)
C19	0.8257 (7)	–0.0004 (4)	0.6113 (4)	0.081 (2)
C20	0.8294 (6)	0.0771 (4)	0.6584 (4)	0.074 (2)

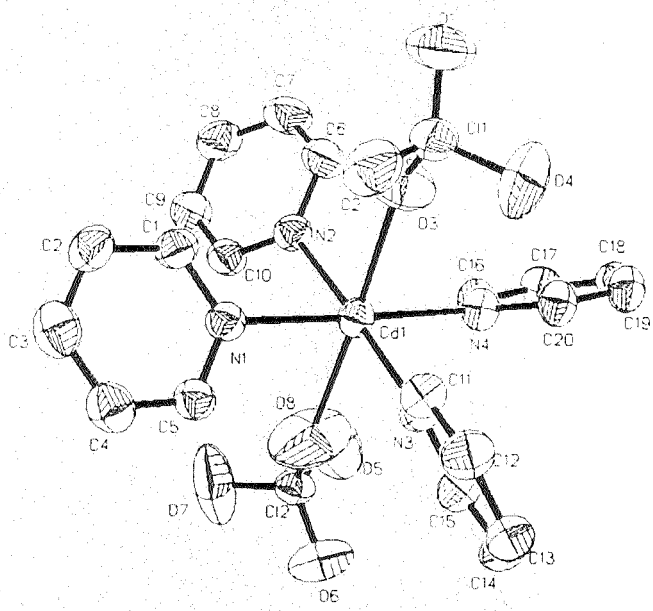

Fig. 1. Molecular structure of the title compound with the atomic numbering scheme

TABLE-2
SELECTED BOND LENGTHS (Å) AND ANGLES (°)

Bond	Distance	Bond	Distance
Cd1-O8	2.339(12)	Cd1-N3	2.289(5)
Cd1-N1	2.347(4)	Cd1-N4	2.334(5)
Cd1-N2	2.316(5)	Cd1-O3	2.380(7)
O8-Cd1-N1	88.0(3)	Cd1-O8-C12	160.7(8)
O8-Cd1-N2	92.5(3)	Cd1-N1-C1	121.8(4)
O8-Cd1-N3	86.8(3)	Cd1-N1-C5	120.4(4)
O8-Cd1-N4	95.5(3)	C1-N1-C5	117.7(5)
N1-Cd1-N2	89.89(15)	Cd1-N2-C6	122.0(5)
N1-Cd1-N3	88.30(16)	Cd1-N2-C10	120.5(4)
N1-Cd1-N4	176.21(15)	C6-N2-C10	117.5(6)

TABLE-3
THE HYDROGEN BOND LENGTHS (Å) AND BOND ANGLE (°) FOR THE TITLE COMPOUND

D—H···A	D—H	H···A	D···A	D—H···A
C_3—H_3A···$O4^{i}$	0.9295	2.5894	3.225(11)	126.02
C11—H11A···$O2^{ii}$	0.9300	2.4379	3.307(8)	155.64

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

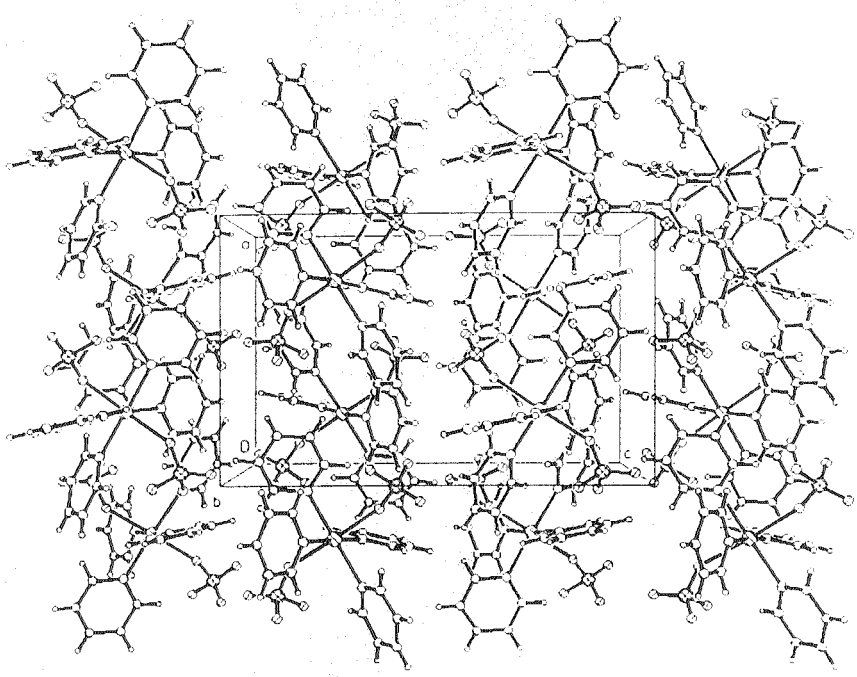

Fig. 2 A view of the crystal packing for the title compound

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