



NOTE

Hydrothermal Synthesis and Crystal Structure of Binuclear Complex $[\text{Cd}(\text{5-ClHsal})_2(2,2'\text{-bipy})_2]$

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A novel cadmium complex $[\text{Cd}(\text{5-ClHsal})_2(2,2'\text{-bipy})(\text{H}_2\text{O})_2]$ (5-ClHsal = 5-chlorosalicylate anion, 2,2'-bipy = 2,2'-bipyridine) was synthesized by hydrothermal reaction and characterized by elemental analysis and X-ray single crystal diffraction. The crystal is monoclinic, space group $P2_1/c$ with $a = 9.138(3) \text{ \AA}$, $b = 17.174(6) \text{ \AA}$, $c = 16.174(5) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 106.06(1)^\circ$, $\gamma = 90^\circ$, $M_r = 1259.41$, $V = 2439(1) \text{ \AA}^3$, $D_c = 1.715 \text{ g/cm}^3$, $F(000) = 1256$ and $Z = 2$. The structure analysis shows that the complex exhibits a binuclear structure. The adjacent binuclear molecules are connected together by the hydrogen bonds to 1D supramolecular chain structure. The crystal structure is stabilized by hydrogen bonds and π - π stacking interactions.

Key Words: Hydrothermal synthesis, Crystal structure, Cd(II) complex, Binuclear.

Salicylic acid possesses two functional groups, -COOH and -OH and can be partly (Hsal^-) or fully (sal^{2-}) deprotonated. The ability of salicylic acid to act as an oxygen donor and to form complexes with different metal atoms is well known. Recently, much attention has been paid to the metal salicylate owing to their intriguing structural features and biological applications¹⁻⁶. Polynuclear d^{10} metal [Cu(I), Ag(I), Au(I), Zn(II) or Cd(II)] complexes have been found to exhibit appealing structural and photoluminescent properties⁷⁻⁹. A series of d^{10} metal organic frameworks have been described recently¹⁰⁻¹³. Additionally, 2,2'-bipyridine (2,2'-bipy) often acts as a chelating ligand due to its high affinity to metal ions. Herein, we report hydrothermal synthesis and crystal structure of a novel cadmium complex with 5-chlorosalicylate ligand^{14,15} and 2,2'-bipy.

All chemicals were of AR grade and used as received from commercial sources. Elemental analyses were conducted on a Perkin-Elmer 2400 CHN elemental analyzer.

Synthesis of $[\text{Cd}(\text{5-ClHsal})_2(2,2'\text{-bipy})_2]$: A mixture of $\text{Cd}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.1 mmol), 2,2'-bipy (0.1 mmol), 5-chlorosalicylic acid (0.2 mmol) and distilled water (10 mL) was put into a Teflon-lined autoclave (20 mL) and then heated at 413 K for 72 h. Colourless block-like crystals of the title complex formed. Yield 25 % (based on Cd). Anal. calcd. (%) for $\text{C}_{48}\text{H}_{36}\text{N}_4\text{O}_{14}\text{Cl}_4\text{Cd}_2$: C, 45.77; H, 2.88; N, 4.45. Found (%): C, 45.74; H, 2.90; N, 4.49.

X-ray crystallography: A colourless block-like single crystal with dimension of 0.28 mm \times 0.26 mm \times 0.23 mm for

the present complex was used for X-ray diffraction analysis. Data collection was carried out at 293 K on a Rigaku RAXIS-RAPID Weissengberg IP diffractometer with graphite monochromated MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$). A total of 22450 reflections were obtained and 5308 unique ($R_{\text{int}} = 0.0325$) were collected in the range of $3.19 < \theta < 27.00^\circ$ by ω scan mode, of which 4480 reflections with $I > 2\sigma(I)$ were used in the succeeding refinement. The final $R = 0.0276$, $wR = 0.0641$ ($w = 1/[\sigma^2(\text{Fo}^2) + (0.0329\text{P})^2 + 0.5736\text{P}]$, where $\text{P} = (\text{Fo}^2 + 2\text{Fc}^2)/3$). The highest and lowest residual peaks in the final difference Fourier map are 0.394 and $-0.542 \text{ e} \cdot \text{\AA}^{-3}$, respectively. All calculations were performed by the SHELXTL 97 program¹⁶. CCDC: 809574.

The molecular structure of the present cadmium(II) complex is shown in Fig. 1. The selected bond distances and angles of the complex are given in Table-1.

As shown in Fig. 1, the title complex consists of two Cd(II) atoms, four 5-chlorosalicylate anion ligands, two phen ligands and two coordinated water molecules, forming a binuclear structure. Cd(1) is seven-coordinated by two nitrogen atoms from 2,2'-bipy, four oxygen atoms from three 5-chlorosalicylate anion (5-ClHsal) ligands and one oxygen atom from a coordinated water. Therefore, the cadmium atom exhibits a N_2O_5 environment, approximately described as a distorted capped octahedron. The four atoms (O4, O7, N1, N2) consist the basal plane, two atoms (O1, O4A) are in the apical positions. The O2 atom caps the triangular face formed by O1, O4 and N2. The Cd-N bond lengths [2.349(2) \AA , 2.314(2)

TABLE-1
SELECTED BOND LENGTHS (Å) AND ANGLES (°) OF [Cd(5-ClHsal)₂(2,2'-bipy)(H₂O)]₂

Cd(1)-O(7)	2.296 (2)	Cd(1)-O(4)	2.315 (2)	Cd(1)-O(2)	2.417 (2)
Cd(1)-O(1)	2.528 (2)	Cd(1)-O(4) A	2.545 (2)	Cd(1)-N(1)	2.349 (2)
Cd(1)-N(2)	2.314 (2)	—	—	—	—
O(7)-Cd(1)-N(2)	158.10(6)	O(7)-Cd(1)-O(4)	87.01(6)	N(2)-Cd(1)-O(4)	104.45(6)
O(7)-Cd(1)-N(1)	92.90(7)	N(2)-Cd(1)-N(1)	71.12(7)	O(4)-Cd(1)-N(1)	164.77(6)
O(7)-Cd(1)-O(2)	120.96(7)	N(2)-Cd(1)-O(2)	80.33(7)	O(4)-Cd(1)-O(2)	76.36(6)
N(1)-Cd(1)-O(2)	116.22(7)	O(7)-Cd(1)-O(1)	83.69(7)	N(2)-Cd(1)-O(1)	108.72(6)
O(4)-Cd(1)-O(1)	110.61(6)	N(1)-Cd(1)-O(1)	84.48(6)	O(2)-Cd(1)-O(1)	52.70(6)
O(7)-Cd(1)-O(4)A	86.43(6)	N(2)-Cd(1)-O(4)A	78.92(6)	O(4)-Cd(1)-O(4)A	74.71(5)
N(1)-Cd(1)-O(4)A	90.08(6)	O(2)-Cd(1)-O(4)A	138.57(6)	O(1)-Cd(1)-O(4)A	168.45(5)

Symmetry code: A 1-x, -y, 2-z

Å] and the Cd-O bond lengths [ranging from 2.296(2) Å to 2.545(2) Å] are similar to some reported examples of Cd complexes¹⁷. The two rings in the 2,2'-bipy ligand are a little twisted relative to each other with a dihedral angle of 6.5(1)°. Two coordination modes of the four 5-ClHsal ligands are present in the title complex. Two carboxylate groups act as chelating ligands to coordinate to Cd centers, while the other two carboxylate groups act as monodentate ligands to bond to two Cd centers, the core of the binuclear structure being a Cd₂O₂ parallelogram with Cd...Cd distance of 3.87 (1) Å.

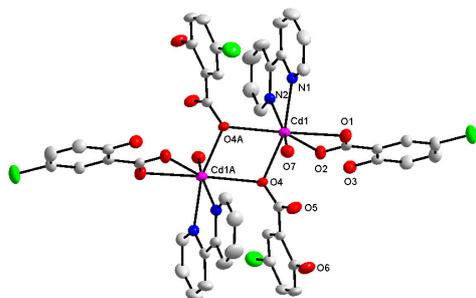


Fig. 1. Binuclear structure of the title complex with 30 % probability ellipsoid. Hydrogen atoms are omitted for clarity. Symmetry code A, 1-x, -y, 2-z

As shown in Fig. 2, the complex has rich intramolecular and intermolecular hydrogen bonds, generated from interactions between the carboxylate groups and hydroxy groups of the salicylate ligands and the coordinated water molecules. Detailed data are given in Table-2. Then adjacent binuclear structure units are connected together by the hydrogen bonds to 1D supramolecular chain along the a axis. In addition, weak π - π stacking interactions present among 2,2'-bipy ligands and 5-chlorosalicylate ligands, with a centroid-centroid distance between neighbouring aromatic rings of 3.70 (2) Å. The crystal structure is stabilized by hydrogen bonds and π - π stacking interactions.

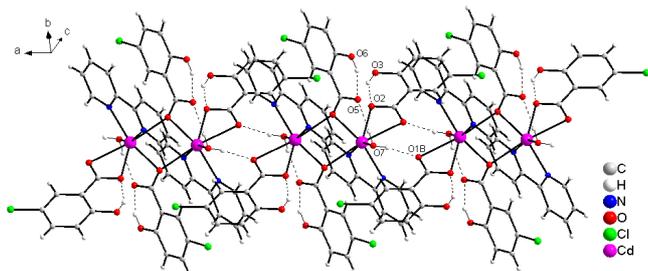


Fig. 2. Extended 1D structure in the title complex. Hydrogen bonds interactions are shown as dashed lines. Symmetry code B, 2-x, -y, 2-z

TABLE-2
HYDROGEN BOND LENGTHS (Å) AND ANGLES (°)
OF THE TITLE COMPLEX

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(6)-H(6A)...O(5)	0.82	1.82	2.548(3)	146.5
O(3)-H(3A)...O(2)	0.82	1.80	2.522(3)	146.1
O(7)-H(7B)...O(5)	0.82(1)	1.87(1)	2.665(3)	164(3)
O(7)-H(7A)...O(1)B	0.82(1)	1.95(1)	2.758(3)	168(3)

Symmetry code: B 2-x, -y, 2-z

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