Synthesis, structure and Hirshfeld surface analysis of the first coordination compound of 2-aminobenzoxazole - a case of the complex with cadmium

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Abstract: The article give information about synthesis, structure and Hirshfeld surface analysis of the first coordination compound of 2-aminobenzoxazole - a case of the complex with cadmium.

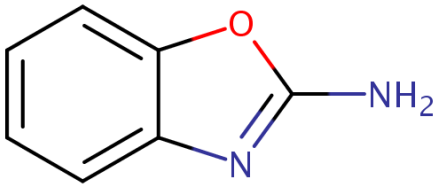
Keywords: synthesis, structure, 2-aminobenzoxazole

A first coordination compound of 2-aminobenzoxazole [Cd(2-aminobenzoxazole)$_2$(CH_3COO)$_2$] has been synthesized on the example of the cadmium complex from ethanol solutions of Cd(CH_3(COO)$_2$ and 2-aminobenzoxazole. In monoclinic crystals with space group $C2_1/c$ cadmium ions coordinate two neutral 2-aminobenzoxazole molecules by monodentate fashion through nitrogen atom of the oxazole ring while two acetic acid molecules in the carboxylate form are coordinated through oxygen atoms by bidentate mode. The coordination polyhedron of the central ion is substantially distorted octahedron. There are two sufficiently strong intramolecular H-bonds in the complex molecule. Two intermolecular H-bonds associate complex molecules into columns running in directions [1 -1 0] and [1 1 0]. The Hirshfeld surface analysis attests that 45.7% of the intermolecular interactions are from H···H contacts, 24.7% are from O···H/H···O contacts and 18.8% are from C···H/H···C contacts while other interactions are from N···H/H···N, O··· O and etc. ones.

1. Chemical context

Benzoxazole is an aromatic organic compound with a benzene-fused oxazole ring structure, and an odor similar to pyridine (Katritzky et al., 2000; Clayden e al., 2001). Although benzoxazole itself is of a little practical value, many derivatives of benzoxazoles are commercially important. They play an important role in medicinal chemistry and chemical biology (Potashman et al., 2007; Lachtova et al., 2018) and are described as potential therapeutic agents including various enzyme inhibitors

(Chikhale et al., 2018). Aminobenzoxazoles, in particular derivatives of 2-aminobenzoxazole, have anticancer and antibacterial properties (Khajondetchairit et al., 2017; Ouyang et al., 2012).



2-aminobenzoxazole

An analysis of Cambridge Structural Database (CSD, Version 5.43, update of November 2021; Groom et al., 2016) attested that there is no X-ray structure of 2-aminobenzoxazole and its metal complexes in database. Theoretically, in metal complexes 2-aminobenzoxazole may be coordinated through nitrogen or oxygen atoms of the oxazole ring and nitrogen atom of the amino group. In order to define which way of these possibilities will be realized we have obtained coordination complex of 2-aminobenzoxazole with cadmium and report here its molecular and crystal structure as well Hirshfeld surface analysis.

2. Structural commentary

The structure of the obtained complex with formula $[Cd^{2+}$(2-aminobenzoxazole)$_2(CH_3COO^-)_2]$ is shown in Figure 1. Metal complex is obtained using $Cd(CH_3COO)_2$ salt for the synthesis. Cd(II)-ion coordinates two 2-aminobenzoxazole molecules through nitrogen atom of the oxazole ring by monodentate fashion. In order to compensate a positive charge of the central atom two acetic acid molecules in the carboxylate form are coordinated by bidentate mode through oxygen atoms. Bond lengths of the Cd-ion are in the interval 2.269(2)-2.400(3) Å while bond angles are vary from 53.34(9) until 139.71(9)º. Such large difference in bond distances and angles lead to essential distortion of the polyhedron in the form of octahedron.

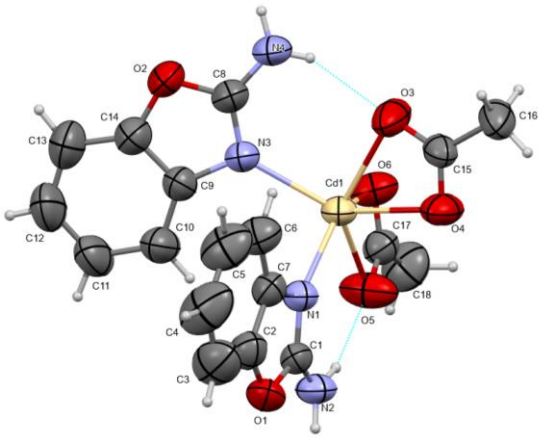


Figure 1. The molecular structure of the complex with atom numbering scheme. Intramolecular H-bonds are indicated by dashed lines. Thermal ellipsoids of atoms are plotted at 50% level of probability.

There are two sufficiently strong intramolecular H-bonds in the complex molecule: amino groups N2-H_2 and N4-H_2 form H-bonds with nearest oxygen atoms O5 and O3 of the coordinated acetic acid molecules with lengths of 2.760 (4) and 2.794(4) Å, respectively (Table 1). These H-bonds enclose 6-membered rings with graph-set notations of S1,1(6) (Etter, 1990).

3. Supramolecular features and Hirshfeld surface analysis

There are 2 proton donor H-bonding groups N2-H_2 and N4-H_2 in the complex molecule. Both of these groups realize their H-bonding capabilities by forming intramolecular (first 2 H-bonds in the Table 1) and 2 intermolecular H-bonds (remaining 2 bonds in the Table 1). These intermolecular H-bonds between nitrogen atoms of the amino groups and oxygen atoms of the carboxylate groups of the acetic acid molecules associate complex molecules into columns running in directions [1 -1 0] and [1 1 0] (Fig. 2).

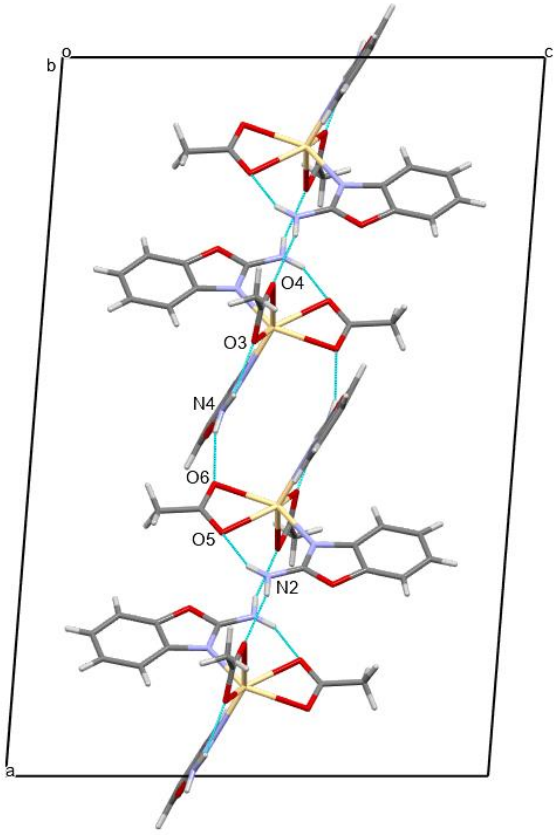


Figure 2. Formation of the columns in the crystal structure of the complex.

Table 1.

Hydrogen bond geometry (Å, º)

D-H···A	D-H	H····A	D····A	>D-H···A	symmetry
N2-H2A···O5	0.87(3)	1.95(3)	2.760(4)	156(3)	
N4-H4A···O3	0.78(4)	2.07(4)	2.794(4)	153(4)	
N2-H2B···O4	0.81(3)	2.06(3)	2.814(4)	156(3)	3/2-x,1/2-y,1-z
N4-H4B···O6	0.83(4)	2.00(4)	2.806(4)	164(3)	1-x,1-y,1-z

The Hirshfeld surfaces were calculated and two dimensional (2D) fingerprint plots generated using CrystalExplorer (Version 17.5; Turner et al., 2017). Fig. 3 shows the 3D Hirshfeld surface of the complex with d_{norm} (normalized contact distance) plotted over the range from -0.6027 to 1.5939 a.u. The interactions given in Table 1 play a key role in the molecular packing of the complex. The overall 2D fingerprint plot and those delineated into H···H, O···H/H···O, C···H/H···C, N···H/H···N, and O···O interactions are shown in Fig. 4. The percentage contributions to the Hirshfeld surfaces from the various interatomic contacts are as follows: H···H 45.7%, O···H/H···O 24.7%, C···H/H···C 18.8%, N···H/H···N 4.3% and O···O 2.5%. Other minor contributions to the Hirshfeld surface are from C···C 2.4 % and O···C/C···O 1.6% contacts.

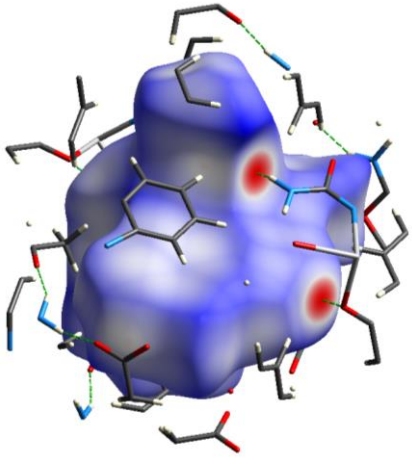


Figure 3. View of the 3D Hirshfeld surface of the complex plotted over d_{norm} in the range from -0.6027 to 1.5939 a.u.

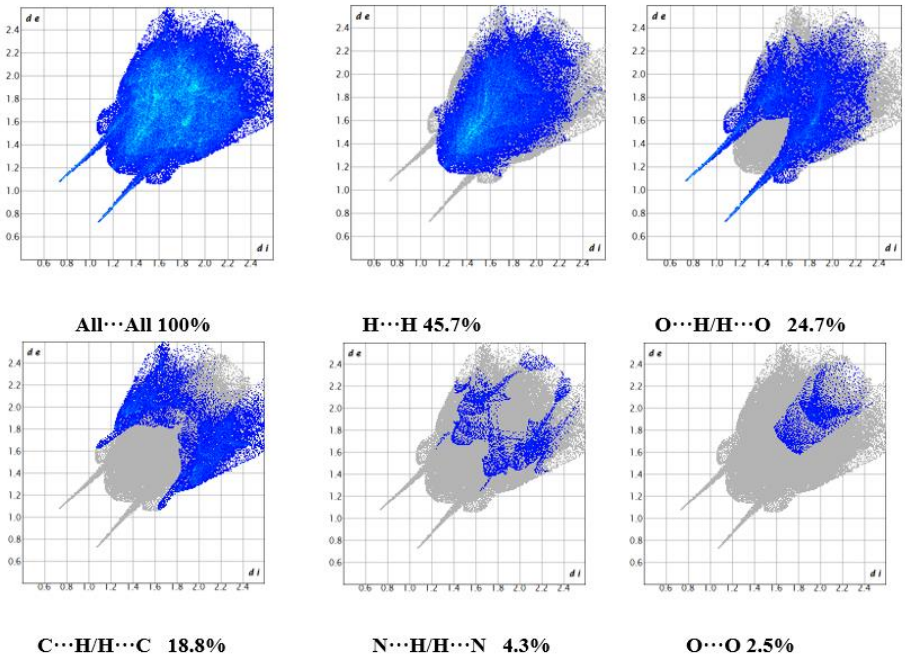


Figure 4. The full 2D fingerprint plots for the complex showing all interactions and delineated into separate interactions. The d_i and d_e values are the closest internal and external distances (Å) from given points on the Hirshfeld surface contacts.

4. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.43, update of November 2021; Groom et al., 2016) for the free 2-aminobenzoxazole and its metal complexes indicated no hits in the database.

5. Synthesis and crystallization

$Cd(CH_3COO)\cdot 2H_2O$ (0.266 g, 1 mmol) and 2-aminobenzoxazole (0.268 g, 2 mmol) were dissolved separately in ethanol (5 mL), mixed together and stirred for 1.5 h. The obtained colorless solution was filtered and left for crystallization. Single crystals of the complex suitable for X-ray analysis were obtained by slow evaporation of the solution over a period of 10 days.

6. Refinement

Hydrogen atoms of the acetic acid methyl groups were placed in calculated positions and refined in the riding-model approximation with $U_{iso}(H) = 1.5U_{eq}(C)$, C-H = 0.96. Remaining hydrogen atoms were located experimentally and refined freely. Crystal data, data collection and structure refinement details are summarized in Table 2.

Table 2.

Experimental details

Crystal data	
Chemical formula	$C_{18}H_{18}CdN_4O_6$
M_r	498.76
Crystal system, space group	Monoclinic, C2/c
Temperature (K)	293
a, b, c (A°)	25.0497(3) 9.8428(1) 16.7577(2)
α, β, γ (°)	90 94.534(1) 90
V(Å^3)	4118.84(8)
Z	8
Radiation type	CuK_α
μ (mm–^{1})	8.866
Data collection	
Diffractometer	XtaLAB Synergy-i
Absorption correction	Multi-scan (CrysAlis PRO; Agilent, 2014)
Tmin, Tmax	3.5, 71.2
No. of measured, independent and observed [I > 2_(I)] reflections	11316, 3971, 3434
Rint	0.030
Refinement	
R[F2 > 2_(F2)], wR(F2), S	0.029, 0.08, 1.05
No. of parameters	313
Min. and max. resd. dens.,[e/Å^3]	-0.59, 0.26

Computer programs: CrysAlis PRO (Agilent, 2014), OLEX2 (Dolomanov et al., 2009) and SHELXL2014 (Sheldrick, 2015).

Acknowledgements

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