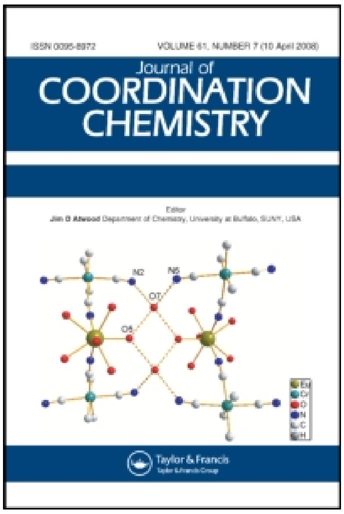

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Synthesis and crystal structure of an iminodiacetatocadmium(ii) complex containing benzimidazole

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Synthesis and crystal structure of an iminodiacetatocadmium(II) complex containing benzimidazole

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The crystal structure of the complex *tris*(benzimidazole)iminodiacetato(2-)cadmium(II) dihydrate, $(BZIM)_3(IDA)Cd \cdot 2H_2O$, was determined by single-crystal X-ray methods. The Cd(II) ion assumes distorted octahedral coordination geometry formed by three benzimidazole molecules and an iminodiacetate dianion. The dianion chelates Cd(II) as a terdentate in the *facial* configuration. Weak intermolecular C–H$\cdots\pi$ interactions exist between neighboring benzimidazole rings. The thermal decomposition of the title complex has been studied. IR assignments based on the molecular structure have been made.

Keywords: Cadmium(II); Iminodiacetate; Benzimidazole; Crystal structure; C–H$\cdots\pi$ interaction

1. Introduction

It has been realized that intermolecular interactions such as hydrogen bonding and C–H$\cdots\pi$ interactions [1,2] form the basis of the functional properties of most molecular assembles, and a detailed understanding of non-covalent chemistry is fundamental to interpreting and predicting relationships between chemical structure and function. As a part of the investigation of non-covalent chemistry, a Cd(II) complex incorporating benzimidazole and the iminodiacetate dianion has been prepared. We present here the crystal structure of the complex *tris*(benzimidazole)iminodiacetato(2-) cadmium(II) dihydrate, $(BZIM)_3(IDA)Cd \cdot 2H_2O$, which shows weak intermolecular interactions in the crystal lattice.

2. Experimental

2.1. *Synthesis*

All reagents were commercially available and of analytical grade. Iminodiacetic acid (H_2IDA, 1 m mol), benzimidazole (BZIM, 2 m mol), Na_2CO_3 (1 m mol) and

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Table 1. Crystal data and structure refinement details for the complex.

Empirical formula	$C_{25}H_{27}N_7O_6Cd$
M	633.94
Crystal size (mm)	0.32 × 0.22 × 0.04
Temperature (K)	293
Wavelength (Å)	0.71069
Crystal system	monoclinic
Space group	$P\,2_1/c$
Unit cell dimensions (Å, °)	a = 13.5939(4) b = 10.5062(2) c = 19.6696(5) β = 104.304(1)
Volume (Å^3)	2722.13(12)
Z	4
Density (calculated) (g cm^{-3})	1.547
Absorption coefficient (mm^{-1})	0.855
$F(000)$	1288
θ range for data collection (°)	1.55–27.45
Reflections collected	24716
Independent reflections	6180
Parameters	352
Goodness-of-fit on F^2	1.075
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0375$, $wR_2 = 0.0881$
R indices (all data)	$R_1 = 0.0695$, $wR_2 = 0.1003$
Largest diff. peak and hole (e Å^{-3})	0.42 and −0.40

$CdCl_2 \cdot 2.5H_2O$ (1 m mol) were dissolved in 15 cm^3 of water. The solution was refluxed for 4 h until a small amount of precipitate appeared. The solution was filtered and the filtrate kept at 353 K. Colorless, single crystals were obtained after one day.

2.2. *Physical measurements*

Elemental analyses were carried out using a Carlo-Erba 1160 instrument. *Anal.* Calc. for $C_{25}H_{27}N_7O_6Cd$ (%): C, 47.37; N, 15.47; H, 4.29; Found: C, 48.01; N, 15.51; H, 4.44. Infrared spectra were recorded using KBr pellets in the range 4000–400 cm^{-1} using a Nicolet 5DX FTIR spectrophotometer. Thermogravimetric (TG) and differential scanning calorimetric (DSC) analyses of the complex were carried out with a Netzsch STA 409 PG/PC analyser. Some 4.0 mg of the complex was used for TG, and highly sintered Al_2O_3 was the reference material for DSC measurements. TG and DSC curves were recorded up to 900°C at 5° min^{-1} in static air.

2.3. *Crystal structure determination*

X-ray diffraction intensities of a single crystal of the complex were collected with the Rigaku RAXIS-RAPID diffractometer at room temperature. The crystal structure was solved by direct methods followed by Fourier syntheses using Sir92 [3]. Structure refinement was performed by full-matrix least-squares procedures using SHELX-97 on F^2 [4]. Crystal data and refinement details are summarized in table 1. Final fractional atomic coordinates and equivalent isotropic thermal parameters for the non-H atoms are listed in table 2. Crystallographic data (excluding structure factors) for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 241580.

Table 2. Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$\text{Å}^2 \times 10^3$]. *U*(eq) is defined as one third of the trace of the orthogonalized *Uij* tensor.

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*eq
Cd	2496(1)	2530(1)	2267(1)	34(1)
O(1)	2106(2)	3133(3)	3293(1)	51(1)
O(2)	941(2)	3919(3)	3777(1)	63(1)
O(3)	2607(2)	4792(2)	2020(1)	45(1)
O(4)	1792(2)	6245(2)	1296(1)	67(1)
O(1W)	19(2)	6207(3)	4028(1)	66(1)
O(2W)	530(3)	7989(4)	431(2)	110(1)
N(3)	846(2)	3374(3)	1934(1)	39(1)
N(11)	2168(2)	393(2)	2437(1)	43(1)
N(13)	2165(3)	−1665(3)	2173(2)	54(1)
N(21)	4173(2)	2317(2)	2813(1)	39(1)
N(23)	5721(2)	1505(3)	3168(1)	46(1)
N(31)	2694(2)	2320(2)	1136(1)	40(1)
N(33)	2357(2)	2018(3)	−9(1)	46(1)
C(1)	1263(3)	3587(3)	3256(2)	40(1)
C(2)	510(3)	3743(5)	2554(2)	70(1)
C(4)	859(2)	4419(3)	1443(2)	44(1)
C(5)	1834(3)	5200(3)	1611(2)	42(1)
C(12)	2151(3)	−466(3)	1944(2)	52(1)
C(14)	2184(3)	−2557(4)	3365(2)	69(1)
C(15)	2165(4)	−2157(5)	4021(3)	85(2)
C(16)	2150(4)	−876(5)	4194(2)	76(1)
C(17)	2158(3)	65(4)	3706(2)	54(1)
C(18)	2179(2)	−321(3)	3038(2)	41(1)
C(19)	2181(3)	−1620(3)	2872(2)	47(1)
C(22)	4783(3)	1390(3)	2745(2)	44(1)
C(24)	6463(3)	3155(4)	4089(2)	54(1)
C(25)	6187(3)	4276(4)	4358(2)	60(1)
C(26)	5227(3)	4835(3)	4114(2)	55(1)
C(27)	4497(3)	4263(3)	3589(2)	44(1)
C(28)	4761(2)	3123(3)	3315(2)	35(1)
C(29)	5729(2)	2605(3)	3549(2)	41(1)
C(32)	2043(3)	1883(3)	578(2)	44(1)
C(34)	3983(3)	2911(3)	−217(2)	49(1)
C(35)	4882(3)	3443(3)	144(2)	55(1)
C(36)	5094(3)	3663(3)	864(2)	53(1)
C(37)	4416(3)	3340(3)	1248(2)	43(1)
C(38)	3505(2)	2777(3)	896(2)	35(1)
C(39)	3298(3)	2586(3)	171(2)	39(1)

Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk).

3. Results and discussion

3.1. *Crystal structure*

The asymmetric unit consists of a mononuclear Cd(II) complex and two crystalline water molecules, as shown in figure 1. Selected bond distances and angles are listed in table 3. The Cd(II) atom is octahedrally coordinated by one IDA dianion and three BZIM molecules. Two nitrogen atoms (N11 and N31) of BZIM molecules and two oxygen atoms (O1 and O3) of the IDA dianion form a plane with the Cd(II)

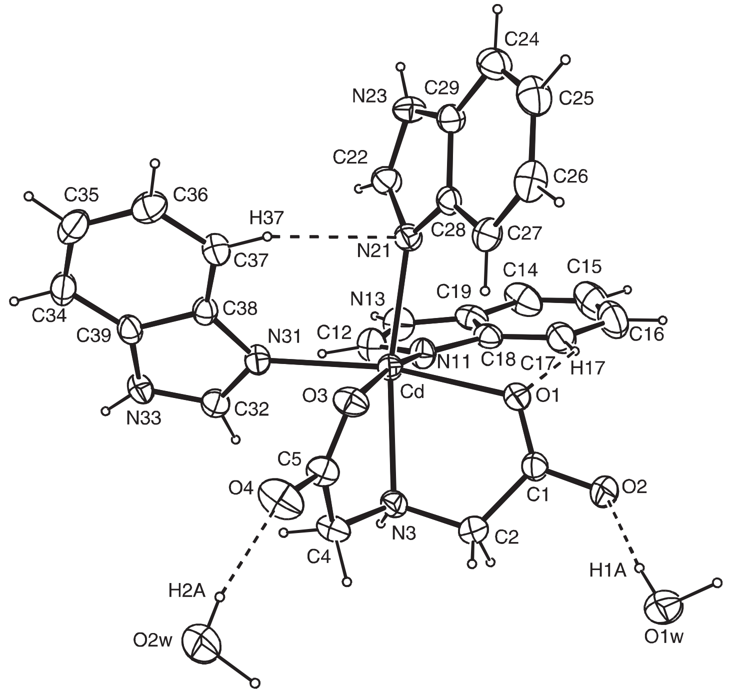

Figure 1. The molecular structure of the complex drawn with 30% probability thermal displacement ellipsoids showing the atom numbering scheme. Dashed lines indicate hydrogen bonding.

Table 3. Selected bond lengths [Å] and angles [°] for the complex.

Cd–O(1)	2.299(2)	Cd–O(3)	2.437(2)
Cd–N(3)	2.350(3)	Cd–N(11)	2.330(3)
Cd–N(21)	2.278(3)	Cd–N(31)	2.316(3)
C(1)–O(1)	1.227(4)	C(1)–O(2)	1.259(4)
C(5)–O(3)	1.231(4)	C(5)–O(4)	1.255(4)
N(3)–Cd–O(1)	74.28(8)	N(21)–Cd–O(1)	91.93(9)
N(3)–Cd–O(3)	71.23(8)	N(21)–Cd–O(3)	94.95(8)
N(3)–Cd–N(11)	101.53(10)	N(21)–Cd–N(11)	92.43(9)
N(3)–Cd–N(31)	95.60(9)	N(21)–Cd–N(31)	95.97(10)
N(3)–Cd–N(21)	160.66(9)		

atom. The Cd(II) atom is displaced from the equatorial plane by 0.1541(13) Å towards the N21 atom in an axial direction, implying a weaker interaction in the opposite direction to the Cd–N21 bond. Both N3–Cd–N21 [160.66(9)°] and N3–Cd–N11 [101.53(10)°] angles indicate poor overlap between atomic orbitals of Cd and N3 atoms, and the longer Cd–N3 bond [2.350(3) Å] confirms the weaker coordination of the N3 atom to Cd(II).

The terdentate IDA dianion chelates the Cd(II) atom with the *facial* configuration. Of the two five-membered chelate rings, one is planar with a maximum deviation of 0.019(2) Å [N(3)] and the other assumes an envelope conformation, with Cd lying in the flap position and out of the mean plane formed by the other four atoms by 1.002(6) Å. A similar chelating mode of IDA has been observed in the Co analogue [5] and in other IDA complexes [6].

Table 4. Hydrogen bonding parameters [Å, °] for the complex.*

D–H···A	D–H	H···A	D···A	D–H–A
O(1W)–H(1A)···O(2)	0.91	1.91	2.810(4)	170
O(1W)–H(1B)···O(2W)^{i}	1.00	1.84	2.805(4)	160
O(2W)–H(2A)···O(4)	0.86	1.94	2.784(5)	168
O(2W)–H(2B)···O(2)^{ii}	1.03	1.98	2.985(5)	163
N(3)–H(3)···O(1W)^{iii}	0.91	2.16	3.008(4)	154
N(13)–H(13)···O(4)^{iv}	0.86	1.92	2.761(4)	165
N(23)–H(23)···O(3)^{v}	0.86	2.15	2.993(4)	165
N(33)–H(33)···O(1)^{vi}	0.86	2.55	3.276(3)	142
N(33)–H(33)···O(2)^{vi}	0.86	2.02	2.846(4)	161
C(17)–H(17)···O(1)	0.93	2.54	3.321(5)	141
C(32)–H(32)···O(1W)^{iii}	0.93	2.30	3.168(5)	156
C(37)–H(37)···N(21)	0.93	2.63	3.353(4)	135

*Symmetry codes are: $^{i} = x, -y+3/2, z+1/2$; $^{ii} = -x, y+1/2, -z+1/2$; $^{iii} = -x, y-1/2, -z+1/2$; $^{iv} = x, y-1, z$; $^{v} = -x+1, y-1/2, -z+1/2$; $^{vi} = x, -y+1/2, z-1/2$.

Extensive hydrogen bonding interactions exist in the crystal (table 4). The imino-N atoms of BZIM are intermolecularly hydrogen bonded to carboxyl-O atoms of IDA to form a hydrogen bonded supra-molecular structure. The crystalline water molecules are also involved in the supra-molecular structure through hydrogen bonding with uncoordinated carboxyl-O atoms, the imino-N atom of IDA and each other. BZIM molecules coordinated to the same Cd(II) atom display different spatial orientations. An intermolecular C–H···π interaction exists between neighboring BZIM rings, as verified by separations ranging from 2.81 to 2.82 Å between H atoms and the centroids of benzene rings (C_g); C–H···C_g angles range from 139 to 146°. The C–H···π interaction seems to play an important role in determining the crystal packing [7–9].

3.2. *Thermal analysis*

TG and DSC curves show that the title complex is more stable than the Co analogue [5]. A 4.6% weight loss in the first decomposition beginning at 70°C with an endothermic peak corresponds to the loss of crystalline water. The second decomposition step begins at 190 and finishes at 360°C with a sharp endothermic peak. This decomposition is identified with the loss of IDA (calc. 20.7%, found 21.5%). Decomposition in the final step is exothermic and finishes at 620°C. The final residue (found 45.1%) is stable up to 900°C.

3.3. *IR spectra*

Infrared spectra of the complex were assigned based on the crystal structure. Absorptions at 619 and 425 $\mathrm{cm^{-1}}$ are ascribed to Cd–O and Cd–N stretching, respectively. It agrees with the crystal structure of the title complex. For the carboxyl group, ν_{as}(coo) and ν_{s}(coo) were observed at 1600 and 1400 $\mathrm{cm^{-1}}$, respectively. The $\Delta\nu$ value of 200 $\mathrm{cm^{-1}}$ is in accord with monodentate coordination of the carboxyl group [10].

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