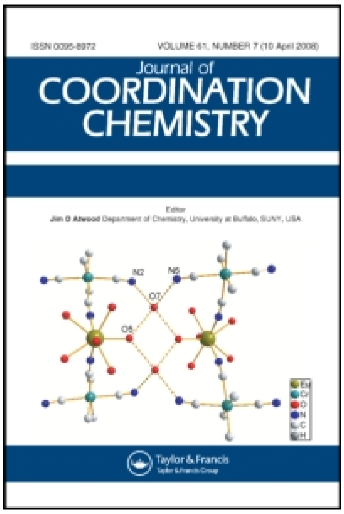

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Synthesis, structural and spectroscopic characterization of a new cadmium(II) complex containing imidazole (Im) as ligand, $[Cd(Im)_6](ClO_4)_2$

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Synthesis, structural and spectroscopic characterization of a new cadmium(II) complex containing imidazole (Im) as ligand, $[Cd(Im)_6](ClO_4)_2$

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Reaction between the 1,1′-carbonyldiimidazole ligand and mixtures of cadmium(II) acetate with sodium perchlorate provided the unusual crystalline material $[Cd(Im)_6](ClO_4)_2$, (Im = imidazole). This new Cd^{II} complex, has been characterized by elemental analysis, IR-, ^{1}H NMR-, ^{13}C NMR and ^{113}Cd NMR spectroscopy. The coordination number in this complex is six, CdN_6 and coordination environment around the Cd(II) may be described as distorted octahedral with a D_{2h} point group. There are both edge-to-face π–π stacking and C–H(Im)$\cdots\pi$ interactions between aromatic "Im" rings belonging to adjacent chains in this network.

Keywords: Cadmium(II) complexes; Crystal structure; Imidazole; π–π stacking

1. Introduction

The chemistry of cadmium constitutes an area of increasing interest, especially in relation to its bioinorganic chemistry and toxicology [1–4]. Imidazole groups play a central role in metal bonding in biological systems [5, 6]. Different Cd(II) complexes of imidazole (Im) such as $Cd(ImH)_2(NCS)(SCN)]_n$, $[Cd(pfan)(NCS)(SCN)]_n$ [5], $[Cd(tsac)_2(im)_2]$, $(Him)[Cd(tsac)_3(H_2O)]$ [6], $Cd(Sal)(Im)_2$, $Cd(Sal)(Im)_4 \cdot H_2O$, $Cd(Sal)(4\text{-}MIm)_4$, $Cd(Im)_2(Im)$ and $Cd(Salox)(4\text{-}Im)_2$ [7], have recently been reported.

Attempts to isolate a cadmium(II) complex of 1,1′-carbonyldiimidazole were not successful and a new imidazole complex was isolated. The 1,1′-carbonyldiimidazole decomposed into imidazole ligand (scheme 1), as recently reported for a Cu^{II} ion [8].

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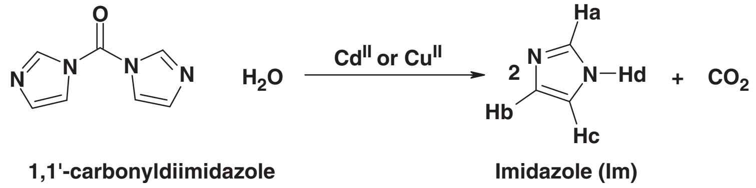

Scheme 1 Hydrolyses of 1,1′-carbonyldiimidazole.

Further investigation is needed, however, this ligand may hydrolyze by the following reaction (scheme 1).

In this article, we report the synthesis and structure of a new Cd^{II} complex of imidazole (Im) $[Cd(Im)_6](ClO_4)_2$ produced by reaction of Cd(II) with 1,1′-carbonyldiimidazole. Cd(II) complexes with six coordinated "Im" ligands are unusual.

2. Experimental

2.1. *Physical measurements*

IR spectra were recorded as nujol mulls using Perkin-Elmer 597 and Nicolet 510P spectrophotometers. Microanalyses were carried out using a Heraeus CHN-O- Rapid analyzer. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. The ^{1}H, ^{13}C NMR and ^{113}Cd solution NMR spectra were recorded on a Bruker DRX-500 AVANCE spectrometer at 500, 125 and 104.6 MHz, respectively. The cadmium chemical shift is reported (ppm) downfield from $(Cd(ClO_4)_2 \cdot xH_2O)$ as an external standard.

2.2. *Preparation of $[Cd(HIm)_6](ClO_4)_2$*

The $[Cd(Im)_6](ClO_4)_2$ complex was prepared by dissolving cadmium(II) acetate (0.230 g, 1 mmol) and sodium perchlorate (0.246 g, 2 mmol) in distilled water (10 mL) and adding an ethanolic solution of 1,1′-carbonyldiimidazole (0.324 g, 2 mmol). The resulting solution was stirred for 1 h at room temperature, and then allowed to stand for 10 days at room temperature (ca 25°C). Yellow crystals of the desired product precipitated, were filtered off, washed with acetone and ether and air dried (m.p. 210°C). A single crystal suitable for X-ray analysis was obtained by slow evaporation of acetonitrile solution of the product at room temperature. (Found C: 30.50; H: 3.30; N: 24.10, calculated for $C_{18}H_{24}CdCl_2N_{12}O_8$ are C: 30.00; H: 3.33; N: 23.34%). -IR (KBr) selected bonds: $\nu = 619$(m), 653(m), 752(m), 930(w), 1059(vs), 1087(vs), 1105(vs), 1141(vs), 1252(w), 1476(w), 1523(w), 3070(w), 3190(s) cm^{-1}. ^{1}H NMR ([D$_6$]-DMSO): $\delta = 7.40$(s, 2H), 7.70(s, 1H) and 12.5(b, 1H) ppm. ^{13}C-{^{1}H} NMR ([D$_6$]-DMSO): $\delta = 102.70$ and 179.25 ppm. ^{113}Cd NMR (DMSO): $\delta = 25.93$ ppm.

2.3. *X-Ray crystal-structure*

Crystallographic measurements of a single crystal of dimensions $0.42 \times 0.29 \times 0.28$ mm^3 were made at 298(2) K on a *Bruker APEX area-detector* diffractometer. The intensity data were collected within the range $2.12^\circ \leq \theta \leq 25.29^\circ$ using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Accurate unit-cell parameters and an orientation matrix for data collection were obtained from least-squares refinement. The intensities of 7240 unique reflections were collected, from which 2572 with $I > 2\sigma(I)$ were used in the refinement. The structure was solved by direct methods and refined by full-matrix least-squares techniques on F^2. The positions of the H-atoms were idealized and included in the calculations of the structure factors as fixed contributions. Each H-atom was assigned an isotropic thermal parameter. The structure was solved by direct methods and refined by full-matrix least-squares techniques on F^2 (SHELX97) [9].

Crystal data and structure refinement are given in table 1. Selected bond lengths and angles are given in table 2.

3. Results and discussion

3.1. *Synthesis*

Reaction between the 1,1′-carbonyldiimidazole ligand and mixtures of cadmium(II) acetate and sodium perchlorate provided the crystalline material $[Cd(Im)_6](ClO_4)_2$. The IR spectrum of this complex show $\nu(ClO_4^-$, (asymmetric stretching mode)) at ca 1087(vs), 1105(vs), 1141(vs) cm^{-1} and absorption bands resulting from the skeletal

Table 1. Crystal data and structure refinement $[Cd(Im)_6](ClO_4)_2$.

Empirical formula	$C_{18}H_{24}CdCl_2N_{12}O_8$
Formula weight	719.79
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P21/n$
Unit cell dimensions (Å, °)	$a = 11.8368(10)$ $b = 7.2451(6)$ $c = 16.5020(14)$ $\beta = 90.1140(10)$
Volume (Å^3)	1415.2(2)
Z	2
Density (calculated) (Mg m^{-3})	1.689
Absorption coefficient (mm^{-1})	1.025
$F(000)$	724
Crystal size (mm^3)	0.42 × 0.29 × 0.28
Theta range for data collection (°)	2.12 to 25.29
Index ranges	$-14 \leq h \leq 14$ $-8 \leq k \leq 8$ $-19 \leq l \leq 14$
Reflections collected	7240
Independent reflections	2572 [R(int) = 0.0158]
Completeness to $\theta = 25.29^\circ$	99.7%
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Max. and min. transmission	0.7623 and 0.6727
Data/restraints/parameters	2572/0/187
Goodness-of-fit on F^2	1.087
Final R [$I > 2\sigma(I)$]	$R_1 = 0.0394$, $wR_2 = 0.1013$
R indices (all data)	$R_1 = 0.0415$, $wR_2 = 0.1026$
Largest diff. Peak, hole (e Å^{-3})	0.409 and −0.537

Table 2. Bond lengths (Å) and bond angles (°) for $[Cd(Im)_6](ClO_4)_2$.

Cd(1)–N(1)^{iii}	2.346(3)	N(1)^{iii}–Cd(1)–N(1)	180.0
Cd(1)–N(1)	2.346(3)	N(1)^{iii}–Cd(1)–N(5)^{iii}	91.10(11)
Cd(1)–N(5)^{iii}	2.363(3)	N(1)–Cd(1)–N(5)^{iii}	88.90(11)
Cd(1)–N(5)	2.363(3)	N(1)^{iii}–Cd(1)–N(5)	88.90(11)
Cd(1)–N(3)	2.376(3)	N(1)–Cd(1)–N(5)	91.10(11)
Cd(1)–N(3)^{iii}	2.376(3)	N(5)^{iii}–Cd(1)–N(5)	180.00(8)
		N(1)^{iii}–Cd(1)–N(3)	87.59(11)
		N(1)–Cd(1)–N(3)	92.41(11)
		N(5)^{iii}–Cd(1)–N(3)	87.73(11)
		N(5)–Cd(1)–N(3)	92.27(11)
		N(1)^{iii}–Cd(1)–N(3)^{iii}	92.41(11)
		N(1)–Cd(1)–N(3)^{iii}	87.59(11)
		N(5)^{iii}–Cd(1)–N(3)^{iii}	92.27(11)
		N(5)–Cd(1)–N(3)^{iii}	87.73(11)
		N(3)–Cd(1)–N(3)^{iii}	180.0

Symmetry transformations used to generate equivalent atoms: iii: $-x+1$, $-y+2$, $-z$.

vibrations of aromatic rings in the 1400–1523 cm^{-1} range. The four normal modes of vibrations of a free ClO_4^- are expected to occur at 930, 459, 1102 (asymmetric stretching mode) and 625 cm^{-1}, respectively [10]. The asymmetric stretching mode in this complex splits (1087, 1105, 1141 cm^{-1}) in the IR spectrum indicating that the tetrahedral symmetry is lowered. The hydrogen bonding pattern reveals that the anions are bidendate through two of their oxygen atoms, lowering the symmetry to the ClO_2 group. This is confirmed by the crystal structure of this complex. In $[Cd(Im)_6](ClO_4)_2$, the Cl–O bond distances are Cl1–O3 = 1.387(4), Cl1–O2 = 1.395(4), Cl1–O1 = 1.397(5) and Cl1–O4 = 1.402(6) Å; the O–Cl–O bond angles are O3–Cl1–O2 = 112.0(3), O3–Cl1–O1 = 112.1(3), O2–Cl1–O1 = 113.1(3), O3–Cl1–O4 = 107.9(4), O2–Cl1–O4 = 109.1(4) and O1–Cl1–O4 = 102.1(4)°, confirming C_{2v} symmetry. These assignments are in close agreement with reported perchlorate compounds [11–13].

The relatively weak band at 3070 cm^{-1} is assigned to the ν(CH) mode of Im aromatic rings. The broad absorption band for ν(HN) is at ca 3190 cm^{-1}. The broad band is perhaps attributable to $\nu(N\text{–}H\cdots X)$, indicating the presence of hydrogen bonds in this complex, which is confirmed by the crystal structure. The ^{1}H NMR spectrum of the DMSO solution displays two distinct absorption bands at 7.04(s, 2H) and 7.70(s, 1H) ppm that have been assigned to the aromatic protons {(Hc, Hb) and Ha (scheme 1), respectively} and one other broad absorption band at 12.5(b, 1H) ppm that has been assigned to amino protons, Hd (scheme 1). The ^{13}C NMR spectrum displays two distinct absorption bands at 102.70 and 179.25 ppm assigned to the aromatic carbons. Comparison of the ^{113}Cd NMR spectrum of a DMSO solution of this complex and other reported Cd(II) complexes with similar ligands demonstrated that the Cd(II)–Im complex is stable in solution [14]. The IR-, ^{1}H NMR-, ^{13}C NMR and ^{113}Cd NMR spectroscopy data do not show presence of 1,1′-carbonyldiimidazole ligand in the complex. The structure of $[Cd(Im)_6](ClO_4)_2$ complex was confirmed by X-ray crystallography.

3.2. *Crystal structure of $[Cd(Im)_6](ClO_4)_2$*

An ORTEP drawing of the $[Cd(Im)_6](ClO_4)_2$ complex is shown in figure 1, while selected bond distances and angles are listed in table 2. Single X-ray crystal analysis

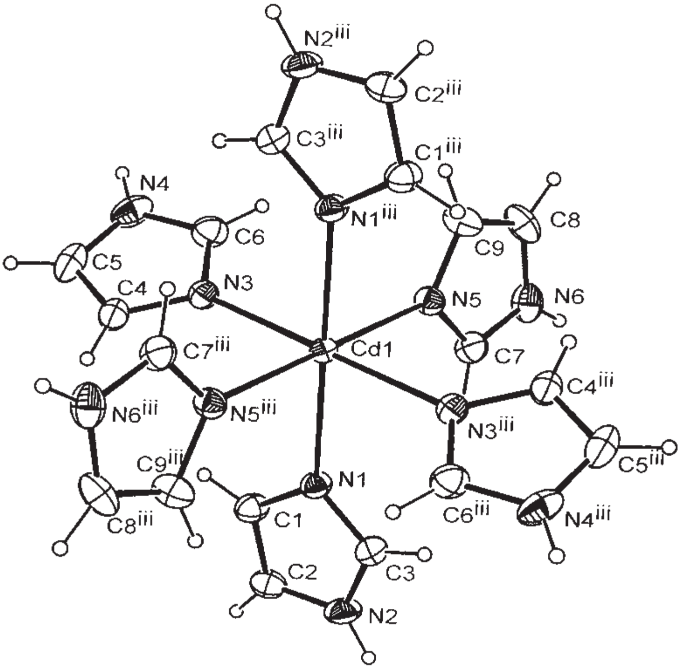

Figure 1 ORTEP diagram of the $[Cd(Im)_6](ClO_4)_2$ complex.

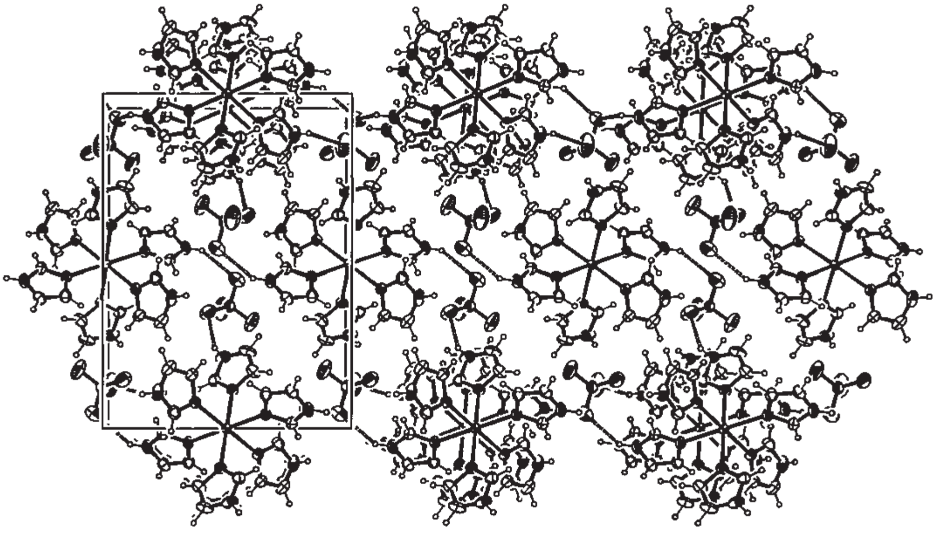

Figure 2 The unit cell and showing the hydrogen bonding in the $[Cd(Im)_6](ClO_4)_2$ complex.

reveals that $[Cd(Im)_6](ClO_4)_2$ crystallizes in the monoclinic space group $P21/n$. The structure of the complex consists of discrete $[Cd(Im)_6]^{2+}$ cations and two ClO_4^- anions. The coordination number of Cd is six with six "Im" ligands giving a CdN_6 chromophore, with a distorted octahedron of D_{2h} symmetry. The N3, $N3^{iii}$, N5, $N5^{iii}$

Table 3. Hydrogen bonds for $[Cd(Im)_6](ClO_4)_2$ [Å and °].

D–H···A	d(D–H)	∠(DHA)	d(H···A)	d(D···A)
N(6)–H(6A)···O(2)^{ii}	0.86	155.2	2.29	3.093(5)
N(4)–H(4A)···O(4)^{iii}	0.86	159.5	2.07	2.888(6)
N(2)–H(2A)···O(1)^{iv}	0.86	140.8	2.36	3.074(6)

Symmetry transformations used to generate equivalent atoms: ii: $x, y, z-1$; iii: $x-1/2, -y+1/2, z-1/2$; iv: $-x+3/2, y+1/2, -z+1/2$.

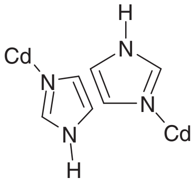

Figure 3 Projection of nearest neighbor pairs in the π–π stacks of heteroaromatic bases in $[Cd(Im)_6](ClO_4)_2$.

atoms of the "Im" ligands define the best equatorial tetragonal plane, while the N1 and N1^{iii} atoms of "Im" occupy the axial positions [N(1)^{iii}–Cd(1)–N(1) = 180.0, N(5)^{iii}–Cd(1)–N(5) = 180, N(3)^{iii}–Cd(1)–N(3) = 180°]. The large distortion of the coordination polyhedron is between the "Im" ligands in the *cis* positions, N(1)^{iii}–Cd(1)–N(3) = 87.59(11)°. The Cd–N distances are Cd(1)–N(1)^{iii} = 2.346(3), Cd(1)–N(1)^{iii} = 2.346(3), Cd(1)–N(5)^{iii} = 2.363(3), Cd(1)–N(5) = 2.363(3), Cd(3)–N(1)^{iii} = 2.376(3) and Cd(5)–N(1) = 2.376(3) Å, that are similar to corresponding values in other cadmium(II) complexes of "Im" [1–2]. Each "Im" ligand is unidentate.

The complex is linked by inter-molecular hydrogen bonding (figure 2 and table 3). The coordinated "Im" molecules are involved in hydrogen bonding as hydrogen-bond acceptors with O atoms from perchlorates as hydrogen-bond donors. Consequently, hydrogen bonds grow the structure into a hybrid two-dimensional network [15–17] (see figure 2).

There are edge-to-face π–π stacking and C–H(Im)···π [18–21] interactions between aromatic "Im" rings belonging to adjacent chains in this network (figures 2 and 3), with distances 3.644 and 2.731 Å, respectively.

Supplementary material

Complete bond lengths and angles, co-ordinates and displacement parameters have been deposited at Cambridge Crystallography Data Centre. Supplementary data are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK on request, quoting the deposition number 268028 for $[Cd(Im)_6](ClO_4)_2$.

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