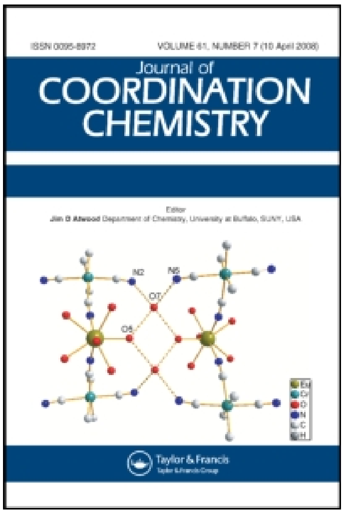

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Synthesis, X-ray structure and spectroscopic investigation of an eight-coordinate cadmium(II) complex

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Reaction of 4-methylimidazole-5-carbaldehyde (L) with cadmium(II) nitrate ($M:L=1:2$; EtOH) yields a novel eight-coordinate mononuclear complex, $[CdL_2(NO_3)_2]$. X-ray structural analysis indicates that the Cd(II) ion possesses what can be described as a double coordination sphere. The inner coordination sphere is pseudo-tetrahedral and consists of four atoms, N(1), N(11), O(21) and O(42), with bond lengths ranging from 2.252(2) to 2.371(2) Å. The second or outer coordination sphere is composed of four oxygen donors, O(7), O(17), O(22) and O(41), with Cd–O distances of 2.543(2) to 2.756(2) Å. The atoms of the external coordination sphere form pyramids with the pseudo-tetrahedral faces of the inner coordination sphere. IR and Raman spectra confirm the stabilization of the Nπ–H isomer of the ligand.

Keywords: Eight-coordination; Cadmium(II); Imidazole derivatives; Bidentate ligands; Crystal structure; IR, Raman spectra

1. Introduction

The ligand 4-methylimidazole-5-carbaldehyde (4-Me-5-CHOIm, L) is a molecule of considerable interest as a potential bidentate N,O donor that can exist in two tautomeric forms (scheme 1), an Nτ–H tautomer (**1**) and an Nπ–H tautomer (**2**). Tautomeric equilibrium in the imidazole ring can lead to different modes of coordination of 4-Me-5-CHOIm to metal ions. It is possible to predict that tautomer **1** can coordinate as a monodentate through nitrogen or oxygen donors or as a bridging bidentate. Tautomer **2** allows the formation of five-membered N,O chelate rings with metal ions. It is well known that imidazole–metal ion derivatives as model compounds of metallobiopolymers generally use the simple imidazole heterocycle to mimic local metal coordination sites [1–4]. It would be of interest to obtain a Cd(II) complex with the above-mentioned ligand to establish the coordination mode of 4-Me-5-CHOIm. Additionally, cadmium is a toxic d^{10} metal ion that can readily replace native metal

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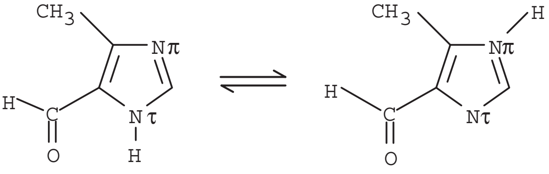

Scheme 1. Tautomeric forms of 4-Me-5-CHOIm.

ions in many proteins [5–9]. Therefore, in this work special attention has been paid to characterization of the Cd(II) ion chromophore in the complex using single-crystal X-ray diffraction, IR and Raman spectroscopic methods.

2. Experimental

2.1. *General procedures*

Cadmium nitrate tetrahydrate and 4-Me-5-CHOIm were purchased from Aldrich and used as received. Elemental analyses were run on a Perkin Elmer 240 CHN instrument. Infrared spectra (4000–400 cm^{-1}), in KBr, and FIR spectra (400–30 cm^{-1}), with samples applied as suspensions of the complex in Nujol onto a polyethylene window, were recorded on a Perkin Elmer 180 spectrophotometer. Raman spectra were recorded at room temperature with a Bio-Rad spectrophotometer having a resolution of 4 cm^{-1}. The incident radiation ($\lambda = 1064$ nm) was supplied by a Spectra-Physics neodymium YAG laser.

2.2. *[CdL$_2$(NO$_3$)$_2$]*

The ligand 4-Me-5-CHOIm (2.0 mmol) dissolved in 20 cm^3 of analytically pure EtOH was stirred with 1.0 mmol of $Cd(NO_3)_2 \cdot 4H_2O$ dissolved in 20 cm^3 of the same solvent. The molar ratio M : L was 1 : 2. The solution was set aside to crystallize at −2°C (at low temperature). After 2 weeks, fine, colorless crystals suitable for X-ray investigation were obtained. The product was filtered off, washed with 30 cm^3 of 2-propanol and dried under vacuum. Yield: 58%. Anal. Calcd. for $C_{10}H_{12}N_6O_8Cd$(%): C, 26.3; H, 2.6; N, 18.4. Found: C, 26.8; H, 2.8; N, 18.3.

2.3. *X-ray crystal structure analysis*

Diffraction intensity data for a single crystal of the Cd(II) complex were collected at room temperature on a Nonius Kappa CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). A total of 7164 [$R_{\text{int}} = 0.0139$] independent reflections was collected by $\varphi + \omega$ scans (θ range 1.45–30.01°), of which 4492 [$I > 2\sigma(I)$] were unique. Corrections for Lorentz polarization and absorption effects [10] were applied. The structure was solved by direct methods using the program package SIR-92 [11] and refined using full-matrix least-squares procedures on F^2 using SHELXL-97 [12]. Anisotropic displacement parameters for all nonhydrogen atoms

Table 1. Crystal data and structure refinement details for $[CdL_2(NO_3)_2]$.

Empirical formula	$C_{10}H_{12}N_6O_8Cd$
Molecular weight	456.66
Temperature	293(2) K
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	$a = 7.2537(1)$ Å $b = 7.6542(1)$ Å $c = 14.2534(2)$ Å $\alpha = 82.635(1)^\circ$ $\beta = 83.905(1)^\circ$ $\gamma = 86.025(1)^\circ$
Volume	779.155(18) $Å^3$
Z	1
Density (calculated)	1.946 $g\,cm^{-3}$
Absorption coefficient	1.458 mm^{-1}
$F(000)$	452
Crystal size	$0.57 \times 0.32 \times 0.27$ mm
Index ranges	$-10 \leq h \leq 9$, $-10 \leq k \leq 10$, $-20 \leq l \leq 19$
Refinement method	Full-matrix least-squares on F^2
Data $[I > 2\sigma(I)]$/restraints/parameters	4492 / 0 /251
Goodness-of-fit on F^2	1.151
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0277$, $wR_2 = 0.0751$
R indices (all data)	$R_1 = 0.0303$, $wR_2 = 0.0767$
Largest difference peak and hole	0.659 and $-0.622\,e\,Å^{-3}$

and isotropic temperature factors for hydrogen atoms were introduced. Further details of the structure analysis are given in table 1 and in the Supplementary material.

3. Result and discussion

3.1. *Description of the structure*

The molecular structure of $[CdL_2(NO_3)_2]$ is shown in figure 1. Four ligands (two molecules of 4-Me-5-CHOIm and two nitrate anions) are bound directly to the metal ion as bidentates to give a CdN_2O_6 chromophore in which eight donor atoms participate. Structural data indicate that Cd(II) has what can be described as a double coordination sphere. The inner coordination sphere is pseudo-tetrahedral and consists of the four atoms N(1), N(11), O(21) and O(42), with bond lengths ranging from 2.252(2) to 2.371(2) Å. Cd–N(τ) bond distances are relatively short [2.252(2) and 2.262(2) Å]. The second or external coordination sphere is composed of the four oxygen donors O(7), O(17), O(22) and O(41) with Cd–O distances of 2.543(2) to 2.756(2) Å. The atoms of the external coordination sphere form pyramids with the pseudo-tetrahedral faces of the inner coordination sphere. Selected bond distances and angles are given in table 2.

Observed Cd–O bond distances are in good agreement with values reported previously for eight-coordinate cadmium(II) complexes [13–17]. Inspection of bond lengths and valence angles for the ligand molecules reveals that double bonds exist between C4 and C5 (C14–C15) and N1 and C2 (N11–C12), rather than between C2 and N3. Complex molecules are held together by hydrogen bonds of the N–H···O type (table 3).

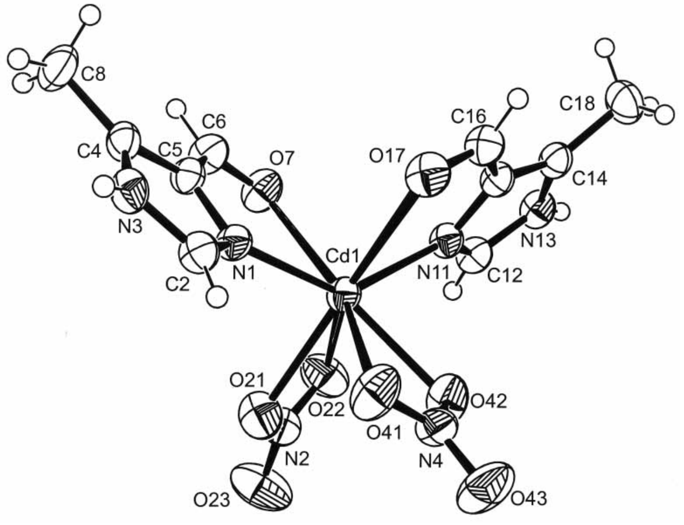

Figure 1. The molecular structure of $[CdL_2(NO_3)_2]$ and atom labeling scheme with thermal ellipsoids drawn at the 50% probability level.

Table 2. Selected bond lengths [Å] and angles [°] for the complex.

Cd(1)–N(1)	2.2521(16)	N(1)–Cd(l)–O(22)	125.10(7)
Cd(1)–N(11)	2.2616(17)	O(42)–Cd(1)–O(21)	81.63(8)
Cd(1)–O(42)	2.3402(19)	N(l)–Cd(l)–O(7)	70.27(6)
Cd(1)–O(21)	2.371(2)	N(11)–Cd(1)–O(7)	81.32(6)
Cd(1)–O(7)	2.5426(19)	N(11)–Cd(1)–O(22)	80.75(7)
Cd(1)–O(41)	2.756(2)	O(42)–Cd(1)–O(22)	84.36(7)
Cd(1)–O(22)	2.603(2)	O(21)–Cd(l)–O(22)	50.94(7)
Cd(1)–O(17)	2.6121(19)	O(7)–Cd(1)–O(22)	81.60(7)
		N(1)–Cd(l)–O(17)	79.38(6)
N(1)–Cd(1)–N(11)	136.13(6)	N(11)–Cd(1)–O(17)	69.30(6)
N(1)–Cd(1)–O(42)	129.18(6)	O(42)–Cd(1)–O(17)	92.31(7)
N(11)–Cd(l)–O(42)	83.13(6)	O(21)–Cd(1)–O(17)	157.82(6)
N(1)–Cd(1)–O(21)	87.93(6)	O(7)–Cd(l)–O(17)	93.13(6)
N(11)–Cd(1)–O(21)	130.36(6)	O(22)–Cd(1)–O(17)	150.05(6)
O(42)–Cd(l)–O(7)	160.50(6)	O(21)–Cd(l)–O(7)	99.67(7)

Table 3. Hydrogen bond details [Å, °].*

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	< (DHA)
N(3)–H(3)···0(17)[a]	0.67(4)	2.30(4)	2.913(2)	154(4)
N(13)–H(13)···0(42)[b]	0.84(3)	2.10(3)	2.832(2)	145(3)

*Symmetry transformations used to generate equivalent atoms are: [a] $-x, -y, -z+2$; [b] $-x, -y+1, -z+1$.

3.2. *IR and Raman spectra*

IR spectra of $[CdL_2(NO_3)_2]$ exhibit a medium intensity, broad band at 3226 cm^{-1}. This band can be assigned to ν(N–H) and the broadness is indicative of hydrogen bonding, in accord with the crystal structure. The strong IR band at *ca* 1664 cm^{-1} in free

4-Me-5-CHOIm, attributed to ν(C=O) of the aldehyde group [18], is shifted by *ca* 40 cm^{-1} to lower frequency upon coordination and splits into two bands at 1652 and 1620 cm^{-1}. This can be attributed, according to the X-ray data, to the existence of two different types of aldehyde groups in the solid state. Only one of them interacts through hydrogen bond with a hydrogen atom (N–H) of a neighboring molecule. According to Lever [19], the $\mathrm{NO_3}^-$ ion in the Cd(II) complex would be coordinated as a bidentate because the separation of two $(\nu_1 + \nu_4)$ bands in the 1800–1700 cm^{-1} region is *ca* 30 cm^{-1}. This is borne out by the structure analysis. The Raman spectrum of the ligand shows a strong peak at 1664 cm^{-1}, attributed to the ν(C=O) group, which is shifted upon coordination to 1634 cm^{-1} ($\Delta = 29\,\mathrm{cm}^{-1}$). In the range 450–150 cm^{-1} the spectrum of the complex shows peaks for the metal–ligand stretching modes; those at 375 and 121 cm^{-1} can be assigned to ν(Cd–O) and ν(Cd–N), respectively. FIR spectra exhibit peaks at 353 and 338 cm^{-1} that can be assigned to ν(Cd–O) and a broad band at 119 cm^{-1} due to Cd–N stretching, consistent with results for other Cd(II) complexes of N-substituted imidazoles [20].

It is noteworthy that the molecular structure, supported by IR and Raman data, reveals stabilization of isomer **2** of the ligand as the only form able to participate in the formation of a five-membered N(τ),O chelate ring with the Cd(II) ion.

Supplementary material

Crystallographic data (excluding structure factors) for the structure reported here have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 233612. 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).

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