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Synthesis and Structure of Hexakis(Imidazole)Cobalt(II) Dichloride Monohydrate

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The crystal and molecular structures of $[Co(Im)_6]Cl_2 \cdot 2H_2O$ (Im = imidazole) have been determined by X-ray crystallography. It crystallizes in the triclinic system, space group P-1, with cell dimensions of a = 8.792(2), b = 9.067(2), c = 10.562(2) Å, $\alpha = 75.13(3)°$, $\beta = 83.12(3)°$, $\gamma = 61.78(3)°$, and Z = 1. The crystal structure of the title compound is composed of three parts, *viz.*, the hexakis(imidazole)cobalt(II) cation, the chlorine anions and aqua molecule. The cobalt(II) ions have an octahedral geometry with the CoN_6 chromophore. The water molecule plays important roles in the structure acting as a bridge between the cation and anion moieties. The whole molecules are linked into two-dimensional framework perpendicular to the *b*-axis.

Key Words: Cobalt(II) complexes, Imidazole, X-ray crystal structure.

INTRODUCTION

Imidazole is of considerable interest as a ligand in that its presence in many biological systems provides a potential binding site for metal ions[1, 2]. Imidazole itself is usually an unidentate ligand and forms complexes with metal ions through its nitrogen atom. It has been reported that a large number of imidazole derivatives possess diverse pharmacological effects, including antiinflammatory, antimicrobial, antimalarial and antitumour activities[3, 4]. The presence of imidazole in the histidyl residue of proteins provides a potential binding site for metal ions[5].

Zinc is a relatively abundant element in biological organisms and plays an essential role in a large number of enzymatic reactions. Zinc(II), being a d^{10} ion, provides few spectroscopic signatures for the monitoring of structure and can be substituted with cobalt(II) ion since the resulting cobalt(II) enzymes give characteristic visible absorption spectra and often show about as much catalytic activity as the native zinc enzymes[6, 7].

This is a general characteristic since the coordination chemistry of cobalt(II) is very similar to that of zinc(II) and two metal ions also show virtually identical ionic radii. Cobalt(II) complexes with carboxylate and imidazole ligands have

been studied as models for metalloproteins since they both contain functionalities in the side chain[8]. In this paper, we reported the synthesis and crystal structure of the title compound.

EXPERIMENTAL

All chemicals were of analytical reagent grade and used directly without further purification. To a warm solution of imidazole (0.4 g, 6 mmol) in H_2O (40 mL), 0.3 g of $CoCl_2 \cdot 6H_2O$ (1 mmol) was added with stirring and the mixture was refluxed for 60 min. The pink solution was filtered and the filtrate was left to stand undisturbed. Upon slow evaporation at room temperature, an amaranthine crystalline solid appeared several weeks later and was separated by filtration.

A summary of the key crystallographic information is given in Table-1.

TABLE-1
CRYSTAL DATA AND STRUCTURE REFINEMENT
FOR THE TITLE COMPOUND

Formula	$C_{18}H_{28}Cl_2CoN_{12}O_2$
Formula weight	645.25
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions (Å, deg)	a = 8.792(2), α = 75.13(3)
	b = 9.067(2), β = 83.12(3)
	c = 10.562(2), γ = 61.78(3)
Volume ($Å^3$)	717.1(2)
Z, calculated desity (g/cm^3)	1, 1.494
F (000)	331.0
Crystal size (mm^3)	0.22 × 0.18 × 0.16
θ Range for data collection (°)	1.99–24.97
Limiting indices	$-17 \le h \le 0, -10 \le k \le 9, -12 \le l \le 12$
Reflections collected/unique	2707/2236
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2525/0/178
Goodness-of-fit on F^2	1.087
Final R indices [$I > 2\sigma(I)$]	R = 0.0559, wR = 0.1731
R indices (all data)	R = 0.0588, wR = 0.1769
μ (mm^{-1})	1.01
$w = 1/[\sigma^2(F_0^2) + (0.1031P)^2 + 1.2979P]$	$P = (F_0^2 + 2(F_c^2))/3$

The selected crystal of $[Co(Im)_6]Cl_2 \cdot 2H_2O$ was mounted on a Nonius CAD4 diffractometer. Reflection data and reflections for the unit cell determination were measured at 20°C using MoK_α radiation ($\lambda = 0.71073$ Å) with a graphite monochromator. The technique used was ω-scan with θ range 1.99–24.97° for the complex. Absorption correction was made with psi-scans[9]. The structure was solved by direct method and refined by full-matrix least-squares method on F^2_{obs} by using the SHELXTL[10] software package. All non-H atoms were anisotropically refined. The hydrogen atoms were geometrically fixed and allowed to ride on the parent atoms to which they are attached. The final conventional $R = 0.0559$, $wR = 0.1731$ for 2366 reflections with $I > 2\sigma(I)$; $w = 1/[\sigma^2(F_0^2) + (0.1031P)^2 + 1.2979P]$, where $P = (F_2^0 + 2(F_c^2))/3$. The molecular graphics were created by using SHELXTL. Atomic scattering factors and anomalous dispersion correction were taken from International Table for X-Ray Crystallography[11]. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre[12].

RESULTS AND DISCUSSION

The asymmetric unit of the title compound is composed of three parts, *viz.*, hexakis(imidazole)cobalt(II) cation, chlorine anions and aqua molecule. The cation moiety is formed by one half of the hexakis(imidazole)cobalt(II) molecule; the other half is related by inversion symmetry through the Co atom located at the inversion centre. Fig. 1 shows a perspective view of the monomeric unit with the atomic numbering scheme of the title compound. Fig. 2 shows a perspective view of the crystal packing in the unit cell for the complex. Selected bond lengths and angles are presented in Table-2. Non-hydrogen atomic coordinates and equivalent isotropic displacement parameters are shown in Table-3.

The Co atom is in an octahedral environment formed by the tertiary N atoms of the imidazole moieties. The bond lengths involved in this octahedral geometry, ranging from 2.137(3) to 2.152(3) Å, are shorter than those of the complex hexakis (1H-imidazole-N^3)cobalt(II) tetrahydrate[13]. All the imidazole rings are each planar and are coplanar with respect to their symmetry counterparts. Meanwhile, the three pairs of symmetry counterparts are almost perpendicular to each other, with the dihedral angles ranging from 85.4(2) to 89.1(2)°.

In complex, the Cl anions are linked to the cation *via* C—H···Cl and NHCl interaction as acceptors (Fig. 1). The water molecule is linked to Cl anion and acts as hydrogen bond donor *via* O(1W)–H(2W1)···Cl(1) and O(1W)—H(1W1)···Cl(2) hydrogen bonds. Meanwhile, the water, acting as a hydrogen-bond acceptor, is linked to the cation, *via* C(4)–H(4B)···O(1W) hydrogen bond (Fig. 2 and Table-4).

Therefore, the water molecule plays important roles in the structure, acting as a bridge between the cation and anion moieties. The whole molecules are linked into two-dimensional framework perpendicular to the b-axis.

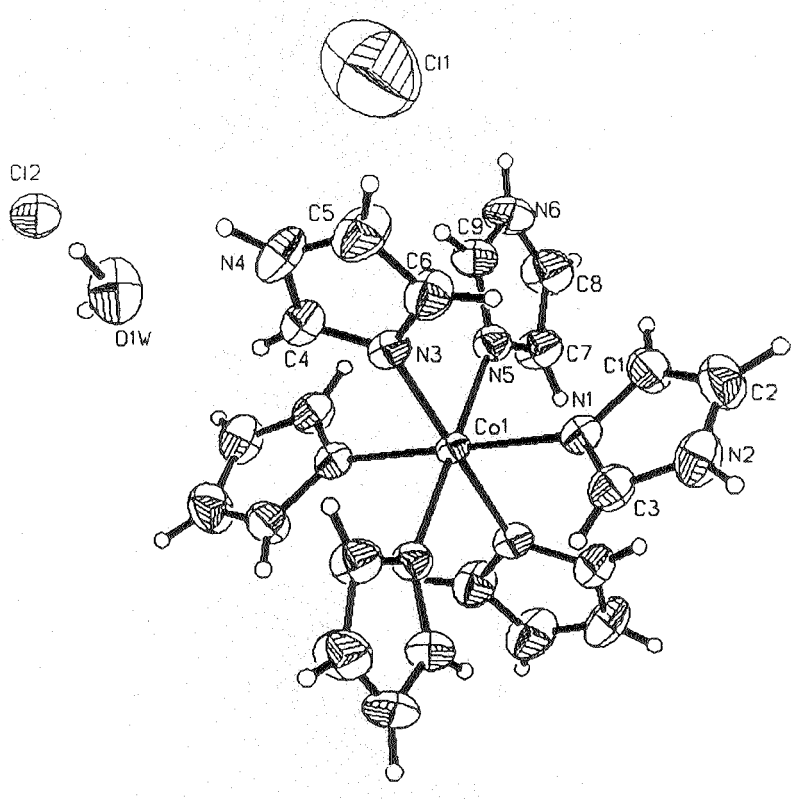

Fig. 1. The molecular structure of $[Co(Im)_6]Cl_2 \cdot 2H_2O$ with the atomic numbering scheme

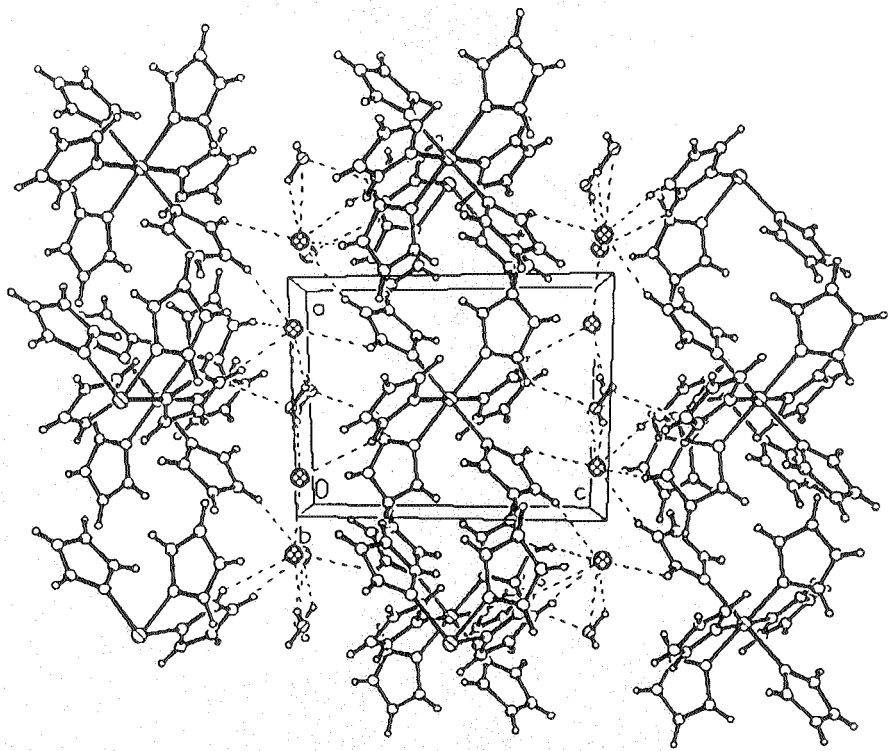

Fig. 2 A view of the crystal packing down the *b*-axis for $[Co(Im)_6]Cl_2 \cdot 2H_2O$

TABLE-2
BOND LENGTHS (Å) AND ANGLES (°) FOR THE TITLE COMPOUND

Co-N(5)	2.137(3)	N(4)-C(5)	1.344(7)
Co-N(1)	2.149(3)	N(5)-C(7)	1.377(6)
Co-N(3)	2.152(3)	N(6)-C(9)	1.334(6)
N(1)-C(3)	1.309(5)	N(6)-C(8)	1.334(7)
N(1)-C(1)	1.365(5)	C(1)-C(2)	1.340(6)
N(2)-C(3)	1.333(6)	C(7)-C(8)	1.339(7)
N(2)-C(2)	1.349(7)	N(3)-C(6)	1.366(6)
N(3)-C(4)	1.303(5)		
N(5)-Co-N(5A)	180.00(11)	N(3)-Co-N(3)	180.00(1)
N(5)-Co-N(1)	90.27(13)	C(3)-N(1)-Co	125.6(3)
N(5)-Co-N(1A)	89.73(13)	C(1)-N(1)-Co	129.6(3)
N(1)-Co-N(1A)	180.0	C(6)-N(3)-Co	128.4(3)
N(5)-Co-N(3)	90.11(13)	C(4)-N(3)-Co	126.4(3)
N(5)-Co-N(3A)	89.89(13)	C(9)-N(5)-Co	127.1(2)
N(1)-Co-N(3)	90.52(13)	C(7)-N(5)-Co	128.9(3)
N(1)-Co-N(3A)	89.48(13)		

TABLE-3
ATOMIC COORDINATES AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS ($Å^2$)

ATOM	x	y	z	Ueq
Co(1)	0.5000	0.5000	0.5000	0.0257
Cl(1)	0.1662	0.9573	0.0119	0.2320
Cl(2)	0.1973	0.2936	0.0045	0.0438
O(1)	0.5379	0.3290	0.0263	0.0773
N(1)	0.3059	0.6450	0.6251	0.0340
N(2)	0.1152	0.7039	0.7818	0.0520
N(3)	0.2998	0.5353	0.3790	0.0351
N(4)	0.1722	0.5219	0.2213	0.0557
N(5)	0.4968	0.7321	0.3837	0.0354
N(6)	0.4268	0.9690	0.2320	0.0535
C(1)	0.2167	0.8187	0.6126	0.0454
C(2)	0.0992	0.8561	0.7082	0.0581
C(3)	0.2401	0.5809	0.7290	0.0422
C(4)	0.3216	0.4724	0.2764	0.0435
C(5)	0.0459	0.6242	0.2906	0.0641
C(6)	0.1254	0.6311	0.3889	0.0497
(7)	0.5886	0.8135	0.4008	0.0482
C(8)	0.5464	0.9575	0.3068	0.0611
C(9)	0.3996	0.8323	0.2798	0.0432

TABLE-4
HYDROGEN BOND DISTANCES (nm) AND ANGLE (°)
OF THE TITLE COMPOUND

D	H	A	Symm	D—H	H···A	D···A	D—H···A
N(2)	H(2A)	Cl(2)	–x, 1 – y, 1 – z	0.8597	2.5114	3.336	160.91
N(4)	H(4A)	Cl(2)	—	0.8597	2.5744	3.385	157.49
N(6)	H(6A)	Cl(2)	x,1 + y, z	0.8600	2.3779	3.229	170.16
O(1W)	H(1W1)	Cl(2)	—	1.0300	2.3200	3.199	142.00
O(1W)	H(2W1)	Cl(1)	1 – x, 1 – y, –z	0.5600	2.2100	2.751	162.00
C(4)	H(4B)	O(1W)	—	0.9297	2.5257	3.241	134.00
C(9)	H(9A)	Cl(1)	—	0.9298	2.6641	3.324	128.53

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