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Crystal Structure and Thermal Chemical Properties of Tetraaquabis(N′-acetoxyl-benzimidazole-N-acetoxyl-κO)-Cobalt(II) dihydrate

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The crystal structure of tetraaquabis(N′-acetoxyl-benzimidazole-N-acetoxyl-κO)-cobalt(II) dihydrate has been determined by single crystal X-ray diffraction method. the molecules are linked by N1—H1A·····O3 intermolecular interactions into zig-zag chains. The packing is stabilized by dipole-dipole and van der Waals forces.

Key Words: **Synthesis, Crystal structure, Thermal chemical properties.**

INTRODUCTION

The benzimidazole derivatives and their metal complexes are of considerable interest because of the specific topological framework, interesting properties and the unique application in its supramolecule framework. As an interesting heterocyclic compound, the derivatives of benzimidazole and their coordination complexes are widely used for medicaments[1–3] due to their biological activities[4].

In the light of the general importance of metallotetrapyrrole cofactors, the study of the tetrapyrroles and their related metal complexes has remained an active area of research despite extensive investigation[5–8]. The macrocycle "bisbenzimidazole" ligand has the same ring size as a porphyrin of phthalocyanine, suggesting that it might exhibit similar metal-chelating behaviour.

Because of the ease of substitution at the N-3 benzimidazole, the preparation of derivatized forms is relatively straightforward. We tried to use monosubstituted benzimidazole to obtain polymer. What a surprise, we got the disubstituted zwitterions complex! In this paper, we summarize the synthesis and characterization of the tetraaquabis(N′-acetoxyl-benzimidazole-N-acetoxyl-κO)-cobalt(II) dihydrate.

EXPERIMENTAL

Preparation of the title complex

To a solution of benzimidazole (8.9 g, 0.075 mol) in 20% NaOH (30 mL) at ambient temperature, was added chloroacetic acid (14.2 g, 0.15 mol). The mixture was refluxed for 4 h with stirring in a boiling water bath, during which NaOH solution was added dropwise to keep pH 8–10. After being cooled to room

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temperature, the reaction mixture was brought to pH 2–3 with addition of concentrated HCl. The suspension was separated by evaporation *in vacuo*. The resulting precipitate was recrystallized from water to give a white solid. Yield: 68%.

To a solution of $Co(CH_3COO)_2 \cdot 4H_2O$ (24.9 mg, 0.1 mmol) in 40 mL H_2O, was added the above white solid (17.6 mg, 0.1 mmol), and the mixture was refluxed for 2 h. Pink single crystals suitable for X-ray crystallographic analysis were obtained over three weeks by slow evaporation at room termperature.

Crystal data and structure determination

A colourless single crystal with approximate dimension of $0.10 \times 0.18 \times 0.28$ mm was mounted on a glass fibre in a random orientation. The data were collected by Bruker Smart 1000 CCD diffactometer with graphite monochromated MoK_α radiation ($\lambda = 0.71073$ Å) using ω scan mode in the range of $2.2 \leq \theta \leq 26.1°$ at temperature 293(2) K. A total of 3617 reflections were collected with 2464 unique ones ($R_{int} = 0.010$), of which 2288 reflections with $I > 2\sigma(I)$ were considered to be observed and used in the succeeding refinements. Intensity data were corrected for Lp factors and empirical absorption. The structure was solved by direct methods and expanded by using Fourier differential techniques with SHELXL-97[9]. All non-hydrogen atoms were located with successive difference Fourier syntheses. The structure was refined by full-matrix least-squares method on F^2 with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were located in a difference Fourier map except while the free water H atoms were added according to the theoretical models. Full matrix least-squares refinement gave the final $R = 0.0500$ and $wR = 0.1596$, $W = 1/[\sigma^2(F0)^2 + (0.1000\,P)^2 + 0.0000\,P]$ where $P = (F_0^2 + 2F_c^2)/3$.

RESULTS AND DISCUSSION

X-ray crystal structure of the title compound

Crystal data and structure refinement for the title compound are shown in Table-1. Selected bond lengths and bond angles are illustrated in Table-2. Fig. 1 shows the molecular structure of the compound. Packing diagram of the title compound in a unit cell is shown in Fig. 2.

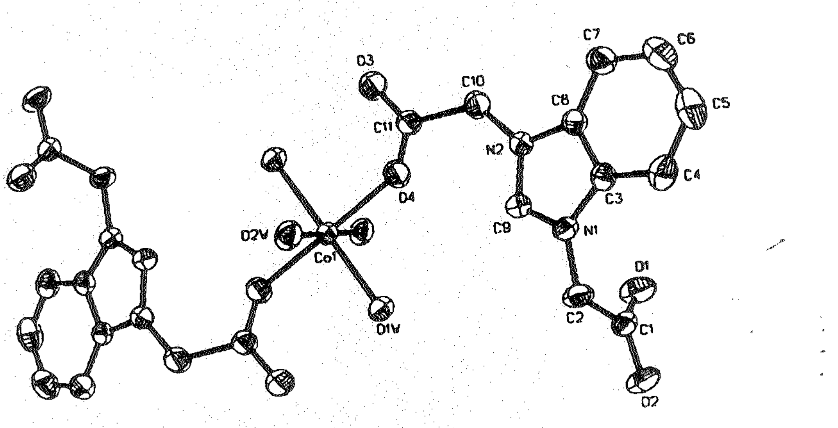

Fig. 1. Molecular structure of the title compound with the atomic numbering scheme, all the H atoms were omitted for clarity

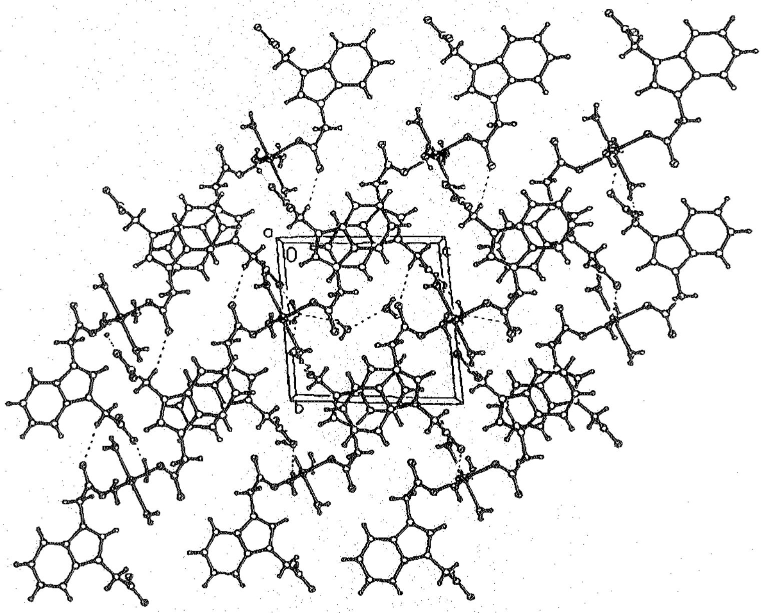

Fig. 2. A view of the crystal packing for the title compound showing the zig-zag chains

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

Crystal data:

$C_{22}H_{26}CoN_4O_{12}\cdot 2(H_2O)$
MW = 633.43
Pink column
$0.10 \times 0.18 \times 0.28$ mm
Triclinic
P-1
a = 7.4306(11) Å α = 81.449(2)°
b = 9.4379(14) Å β = 76.030(2)°
c = 9.6537(14) Å γ = 77.766(2)°

V = 638.66(16) $Å^3$
Z = 1
D_m = not measured
D_x = 1.647 Mg m^{-3}
T = 293(2) K
μ = 0.754 mm^{-1}
MoK_α radiation
λ = 0.71073 Å
Crystallization solvent: Water

Data collection:

Bruker SMART 1000 CCD area-detector diffractometer
ω-scans
3617 measured reflections
2464 independent reflections
2288 reflections with I > 2 s(I)
Abs. Corr.: T_{min} = 0.82, T_{max} = 0.93
R_{int} = 0.010

θ_{max} = 26.1
h = −5 9
k = −10 11
l = −11 11

Intensity decay: none

Refinement:

Refinement on F_2
$R[F^2 > 2s(F^2)] = 0.0500$
$R[F^2$, all data] = 0.0529
$wR(F^2) = 0.1551$
239 parameters

H atoms refined mixtedly
$(D/s)_{max}$ = 0.002
Dr_{max} = 0.58 e $Å^{-3}$
Dr_{min} = 0.79 e $Å^{-3}$

TABLE-2
SELECTED BOND DISTANCES (nm) AND ANGLES (°) OF THE TITLE COMPOUND

Co1-O1W	2.102(2)	C7-C8	1.387(4)	N2-C10	1.468(3)
Co1-O2W	2.116(2)	C10-C11	1.528(5)	C1-C2	1.518(5)
Co1-O4	2.072(2)	N1-C9	1.329(3)	C3-C4	1.390(4)
O1-C1	1.249(4)	N1-C2	1.455(4)	C3-C8	1.392(4)
O2-C1	1.250(4)	N1-C3	1.390(3)	C4-C5	1.381(5)
O3-C11	1.238(3)	N2-C9	1.329(3)	C5-C8	1.387(5)
O4-C$_{11}$	1.253(4)	N2-C8	1.401(3)	C6-C7	1.383(5)
O1W -Co1-O2W	86.95(10)	O1W-Co1-O4a	90.01(9)	O2W-Co1-O4a	88.74(10)
O1W-Co1-O4	89.99(9)	O2W-Co1-O4	91.26(10)	O1Wa-Co1-O4	90.01(9)
O1W-Co1-O1Wa	180.00	O1Wa-Co1-O2W	93.05(10)	O2Wa-C01-O4	88.74(10)
O1W-Co1-O2Wa	93.05(10)	O2W-Co1-O2Wa	180.00	O4-Co1-O4a	180.00

The asymmetric unit of (I) contanis one half of the monomer complex and one free water molecule, the other half being related by an inversion centre. The Co(II) atom, which is located on a crystallographic inversion centre, is six-membered by two O atoms from two benzimidazole ligands and four O atoms from four water molecules. The existence of any steric hindrance due to chelation effects results in distorted octahedral cation environment, with angles differing from an ideal value of 90° by less than 3.4%, and with 180° angles being imposed by symmetry. Coordination distances are normal and similar to the average calculated for the related ligands in other hexacoordinated Co complexes[10]. The benzimidazole ligands each is zwitterion, in which the positive and negative charges are localized on the imidazole ring and acetoxyl group, respectively. The bond lengths in the imidazole ring show an intermediate character[11], implying the π-conjugation in the ring. This is also confirmed by the geometric parameters and the unambiguous location and refinement of all H atoms in the structure. The N1-C9 and N2-C9 bond lengths are both 1.329(3) Å, which is different from other benzimidazole derivatives[12, 13]. The imidazole groups depart from planarity by less than 0.0169 Å; the benzimidazole moieties are each coplanar, with the dihedral angle being 1.72(16)° between the benzene ring and its fused imidazole ring.

The H9····O4 distance is smaller than the sum of their van der Waals radii, implying an intramolecular hydrogen bond, which forms a six-membered ring. The two coordination water molecules play an important role in the crystal structure, acting as hydrogen-bond donors. Molecules of (I) are linked into three-dimensional framework by these O—H····O and C—H····O intermolecular hydrogen-bonds. The packing is further stabilized by π-π interactions, involving the centroids of the benzene and imidazole rings: Cg1····Cg2 at 3.651 Å (Cg1 and Cg$_2$ denote the centroids of rings N1/N2/N3/C8/C9 and C3-C8, respectively). The shortest distance between two Co atoms is 7.431(1) Å.

Thermal Chemical Properties

Thermal analysis curves of the title compound are shown in Fig. 3. Thermogravimetric (TG) analysis and differential thermogravimetric (DTG) analysis show that the thermal decomposition of the title compound includes two transitions. There are

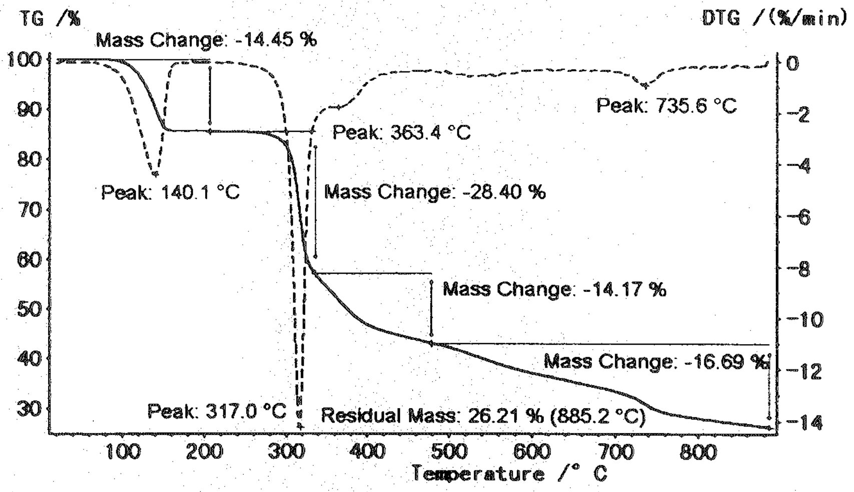

Fig. 3. Thermal analysis curves of the title compound

two peaks corresponding to exothermal processes—that is, a weak peak at 140.1 °C correcponding to removal of water and a strong peak at 396.6 °C implying the decomposition of the title compound.

ACKNOWLEDGEMENTS

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