

Synthesis, spectral, and thermal properties, and crystal structure of cobalt (III) complex derived from Imazameth

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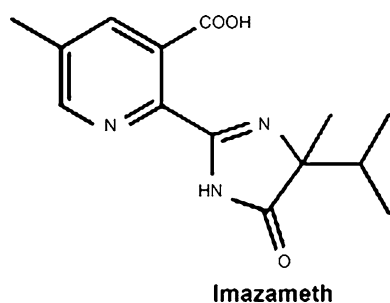
Abstract A novel metal–organic coordination compound [Co(Imazameth)₃]·0.5DMF·4H₂O (where Imazameth = (±)-2-(4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl)-5-methyl-3-pyridinecarboxylic acid; DMF = *N,N*-dimethylformamide) has been prepared and characterized by spectral method (IR), elemental analysis, thermal gravimetric analysis (TGA), fluorescence properties, and single crystal X-ray diffraction techniques. It crystallizes in the trigonal system, space group *R*-3 and the asymmetric unit contains four water molecules. The four lattice water molecules and their symmetric equivalent form a slight distorted cubical water cluster through hydrogen bonds. The O...O bonds of the water cluster are in the range of (2.80(7)–2.99(2) Å), and O...O...O angles are in the range of (82.54°–101.38°). In the cubical water clusters, the six O(5) atoms of each cube are connected to six O(1) atoms of the six molecules (O(1)...O(5) = 2.77(1) Å) by hydrogen bonding, respectively. The Co atom is six-coordinated by six N atoms in distorted octahedron coordination geometry. Intramolecular N–H...O and intermolecular O–H...O hydrogen bonds result in the formation of a supermolecular crystal, in which they seem to be effective in the stabilization of the structure. The complex displays strong fluorescence property and good thermal stability.

Keywords Imazameth · Crystal structure · Thermal gravimetric analysis · Fluorescence properties · Water octamer

Introduction

Much effort has been devoted to the synthesis [1, 2], crystal structure [3, 4], and catalysis [5, 6] of the compounds containing imidazolidinone during the last few years. One of them is (±)-2-(4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl)-5-methyl-3-pyridinecarboxylic acid (Imazameth), which provides with efficient metal-chelating ability (Scheme 1). The Imazameth contains a pyridine carboxylic acid and an imidazole ring, which are well-known versatile ligands. The pyridine carboxylic acid and its anion have been extensively used in the design of coordination compounds, due to a variety of its bonding ability and exhibiting strong hydrogen bonds [7–10]. Imidazole ring, which is one of the polydentate amine ligands, generally coordinates to metal ions using the N atoms as donors. To the best of our knowledge, researches have been done into the transition-metal complexes, which are synthesized by the ligands with the similar structure to Imazameth and their respective properties such as asymmetric catalysis, second harmonic generation, piezoelectric and ferroelectric in the past few years. These transition-metal complexes are [Cu(Himz)₂]_n [11], [Cu(Himz)₂(H₂O)] [11], [Cu(Imz)(H₂O)]_n [11], [Cu₃(Himz)₄(H₂O)₄]²⁺ [11], [Cu(ImzOMe)₂(H₂O)] [11], [Co(Imz)₃]·3H₂O [3], [Mn(Imz)₂] [3], [Co(Imz)₂]·4H₂O [3], [Ni(Imz)₂]·4H₂O [3] (H₂Imz = (±)-2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-nicotinic acid), [Cu₂Cl₂L₂] [6] (L = (±)-2-(1-methyl-4-methyl-4,5-dihydro-1H-imidazol-5-one-2-yl)-pyridine), [Cd(Ima)₂]_n [4] (Ima = 5-ethyl-2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-nicotinic acid), among which, [Co(Imz)₃]·3H₂O, has the similar structure to the complex mentioned in the title. Not only the crystal system and space group are identical, but also the distorted octahedron which is formed by the cobalt atom and six N atoms in coordination has the same structure. As far as we know, the coordination

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Scheme 1 Imazameth

chemistry of Imazameth to metal ions remains largely unexplored though it is a chiral compound, which can be used as a powerful building block to construct metal–organic frameworks (MOF).

Water clusters can play an important role in the stabilization of supramolecular systems both in solution and in the solid state, and there is clearly a need for a better understanding of how such water aggregations are influenced by the overall structure of their surroundings [12–17]. In the past several decades, considerable attention has been focused on theoretical [18, 19] and experimental [20–25] studies of small water clusters to understand the structures and characteristics of liquid water and ice [26–28]. MOF structures with suitable organic ligands can provide void spaces where discrete water clusters can exist. Metal ions in such structures can also act as glues in holding the water clusters. Interactions between the water aggregates and the surroundings often play a key role in stabilizing the unusual water clusters in the crystal lattice. Small water clusters $(\text{H}_2\text{O})_n$ ($n = 4\text{--}6$) are crucial building units for extended water morphologies including tapes [29] and layers [30] whose physical properties are closely associated with those of bulk water.

The reaction of Imazameth with $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ was carried out under hydrothermal conditions to obtain $[\text{Co}(\text{Imazameth})_3] \cdot 0.5\text{DMF} \cdot 4\text{H}_2\text{O}$. In this work, we report its synthesis, crystal structure, spectral analysis (IR), elemental analysis, thermo gravimetric analysis (TGA), and fluorescence properties. The title complex is the first MOF derived from Imazameth, with a slight distorted cubical water cluster.

Experimental

Materials and instrumentation

The ligand, Imazameth, was synthesized from 2-amino-2,3-dimethylbutyronitrile, 5-methylpyridine-2,3-dicarboxylic acid and other chemicals and solvents. All other chemicals

were reagent grade and used without further purification. Elemental analysis for C, H, and N was carried out on a Perkin–Elmer 2400 II elemental analyzer. The FT-IR spectrum was obtained on a PE Spectrum One FT-IR Spectrometer Fourier transform infrared spectroscopy in the $4000\text{--}400\text{ cm}^{-1}$ regions, using KBr pellets. Perkin–Elmer Diamond TG/DTA thermal analyzer was used to record simultaneous TG and DTG curves in the static air atmosphere at a heating rate of 10 K min^{-1} in the temperature range $25\text{--}1000\text{ }^\circ\text{C}$ using platinum crucibles. Fluorescence spectra were recorded on Perkin Elmer instruments LS55 Luminescence Spectrometer.

Synthesis of the complex

$[\text{Co}(\text{Imazameth})_3] \cdot 0.5\text{DMF} \cdot 4\text{H}_2\text{O}$

A solution of Imazameth (0.41 g, 1.5 mmol) in 15 mL DMF was added dropwise with stirring at room temperature to a solution of $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (0.13 g, 0.5 mmol) in 8 mL water. The mixture was stirred at room temperature until it was homogeneous, and then sealed in a 25 mL Teflon-lined stainless reactor, kept under autogenous pressure at $150\text{ }^\circ\text{C}$ for 12 h, and then slowly cooled to room temperature at a rate of $5\text{ }^\circ\text{C per hour}$. After 9 days, red block crystals suitable for X-ray diffraction were separated and washed with water, which were stable in air and insoluble in water and common organic solvents. (Yield: 67% based on Co.) Calcd. for $\text{C}_{43.5}\text{H}_{59.5}\text{N}_{9.5}\text{O}_{13.5}\text{Co}$: C 52.75, H 6.06, N 13.43%. Found: C 52.79, H 6.04, N 13.45%.

X-ray data collection and structure refinement

Crystallographic data were collected on a Bruker SMART CCD diffractometer with graphite monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$) at $T = 298\text{ K}$. Absorption corrections were applied by using the multi-scan program [31]. The structure was solved by direct methods and successive Fourier difference syntheses (SHELXS-97), and anisotropic thermal parameters for all nonhydrogen atoms were refined by full-matrix least-squares procedure against F^2 (SHELXL-97) [32, 33]. Hydrogen atoms were located by geometric calculations. H atoms for H_2O molecules were located in different synthesis and refined isotropically [$\text{O}\text{--}\text{H} = 0.849\text{--}0.851\text{ \AA}$, $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}$ (carrier atoms of H_2O)]. The remaining H atoms were positioned geometrically, with $\text{N}\text{--}\text{H} = 0.86\text{ \AA}$ (for NH), $\text{C}\text{--}\text{H} = 0.98\text{ \AA}$ (for CH), $\text{C}\text{--}\text{H} = 0.96\text{ \AA}$ (for CH_3), and $\text{C}\text{--}\text{H} = 0.93\text{ \AA}$ for aldehyde group H and aromatic H atoms, respectively. In addition, they were constrained to ride on their parent atoms with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}$ (carrier atoms of CH, NH) and $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}$ (carrier atoms of CH_3).

Results and discussion

FT-IR spectrum

The most significant frequencies in the IR spectrum of complex $[\text{Co}(\text{Imazameth})_3] \cdot 0.5\text{DMF} \cdot 4\text{H}_2\text{O}$ are given in Table 1. The strong and broad absorption bands at about $3460\text{--}3210\text{ cm}^{-1}$ and 1627 cm^{-1} are attributed to the symmetric O–H stretching modes and O–H bending modes of crystal water molecules in the crystal, respectively. Single crystal X-ray data support the presence of water in the complex. The shift to lower frequencies of these stretching modes and the shift to higher frequencies of the accompanying O–H bending modes may be attributed to hydrogen bonding. Other peculiar feature is observed, which exhibits a band at 1349 cm^{-1} . An intense absorption of similar wavenumber was observed previously for a Cu(II) complex of the methyl ester of Imazapyr coordinating through the deprotonated lactam group [11]. Owing to the similar structure features, the title complex and $[\text{Co}(\text{Imz})_3] \cdot 3\text{H}_2\text{O}$ complex exhibit the similar wavenumber values for the carboxylate stretches. The COO groups of the former complex are $\nu_{\text{as}}(\text{O}=\text{C}-\text{O})$ 1628 cm^{-1} , $\nu_{\text{s}}(\text{O}=\text{C}-\text{O})$ 1391 cm^{-1} , $\Delta\nu = 237\text{ cm}^{-1}$ and the latter are 1628 cm^{-1} , 1401 cm^{-1} , $\Delta\nu = 227\text{ cm}^{-1}$, respectively. These values are very close to those of the sodium salt of ligand which exhibits bands at 1653 and 1396 cm^{-1} for $\nu_{\text{as}}(\text{O}=\text{C}-\text{O})$ and $\nu_{\text{s}}(\text{O}=\text{C}-\text{O})$, respectively, with a $\Delta\nu$ value of 257 cm^{-1} . In the complex, the carboxylate groups are involved in the hydrogen bonding contact, $\text{O} \cdots \text{H}-\text{N}$ and $\text{O} \cdots \text{C}=\text{O}$, via the same O atom. While the $\nu_{\text{as}}(\text{O}=\text{C}-\text{O})$ and $\nu_{\text{s}}(\text{O}=\text{C}-\text{O})$ of $[\text{Mn}(\text{Imz})_2]$ complex are 1628 cm^{-1} and 1391 cm^{-1} , $\Delta\nu = 143\text{ cm}^{-1}$, respectively, because the O atoms of COO groups are engaged in the metal coordination in the Mn(II) complex, except for the $\text{O} \cdots \text{H}-\text{N}$ hydrogen bonding. As regards the $\nu(\text{C}=\text{N})$ modes, these are distinguished at 1695 cm^{-1} in Imazameth and at 1626 cm^{-1} in the Co(III) complex, which is consistent with the $[\text{Mn}(\text{Imz})_2]$ complex, 1627 cm^{-1} . In comparison, the $[\text{Co}(\text{Imz})_3] \cdot 3\text{H}_2\text{O}$ derivative exhibits a high wavenumber

value (1661 cm^{-1}) consistent with the decreased length of the C=N bond (1.29 \AA).

Thermal analysis

The thermal decomposition behaviors of the complex were followed up to $1000\text{ }^\circ\text{C}$ in static air atmosphere. The TG–DTG curves of the complex $[\text{Co}(\text{Imazameth})_3] \cdot 0.5\text{DMF} \cdot 4\text{H}_2\text{O}$ are shown in Fig. 1, which exhibits three decomposition stages. The TGA indicate that the complex loses 7.93% of total weight in the $28\text{--}83\text{ }^\circ\text{C}$ temperature range ($\text{DTG}_{\text{max}} = 69\text{ }^\circ\text{C}$), corresponding to the removal of the four lattice water molecules per formula unit. A good agreement between the experimental and calculated values was observed for the weight loss (calcd. 7.28%). The anhydrous complex is stable in air up to $196\text{ }^\circ\text{C}$. When the temperature holds on rising, the products lose 49.87% of the total weight in the $196\text{--}332\text{ }^\circ\text{C}$ temperature range, which is related to the loss of DMF and endothermic decomposition of the imidazole ring of the Imazameth ligand (calcd. 48.24%; $\text{DTG}_{\text{max}} = 233, 296, 327\text{ }^\circ\text{C}$). In this stage, the Imazameth ligands decompose gradually. The third stage with 35.54% mass loss starts at $333\text{ }^\circ\text{C}$, finishes at $915\text{ }^\circ\text{C}$. The mass loss percentage is near the loss of the nicotinic acid of the ligand from the complex (calcd. 36.90%). The residual percentage weight (observed 7.85%) at the end of the decomposition of the complex is consistent with the formation of CoO (expected 7.58%), which was identified by IR spectroscopy.

Fluorescence properties

The fluorescence spectra of complex $[\text{Co}(\text{Imazameth})_3] \cdot 0.5\text{DMF} \cdot 4\text{H}_2\text{O}$ and free ligand in the solid state at room temperature are presented in Fig. 2. The free ligand Imazameth shows intense emission bands at 377 and

Table 1 IR spectral data of $[\text{Co}(\text{Imazameth})_3] \cdot 0.5\text{DMF} \cdot 4\text{H}_2\text{O}$ (cm^{-1})

Assignments	$[\text{Co}(\text{Imazameth})_3] \cdot 0.5\text{DMF} \cdot 4\text{H}_2\text{O}$
$\nu(\text{OH})_{\text{water}}$	$3460\text{--}3210\text{ b m}$
$\nu(\text{CH}_3)$	$2973\text{--}2878\text{ m}$
$\nu(\text{CH})_{\text{pyridine ring}}$	3069 w
$\nu(\text{C}=\text{O})$	1730 vs
$\nu(\text{C}=\text{N})$	1626 vs
$\nu_{\text{s}}(\text{O}=\text{C}-\text{O})$	1391 s
$\nu_{\text{as}}(\text{O}=\text{C}-\text{O})$	1628 s
Co–N	$583\text{--}448\text{ w}$

w weak, m medium, s strong, vs very strong, b broad

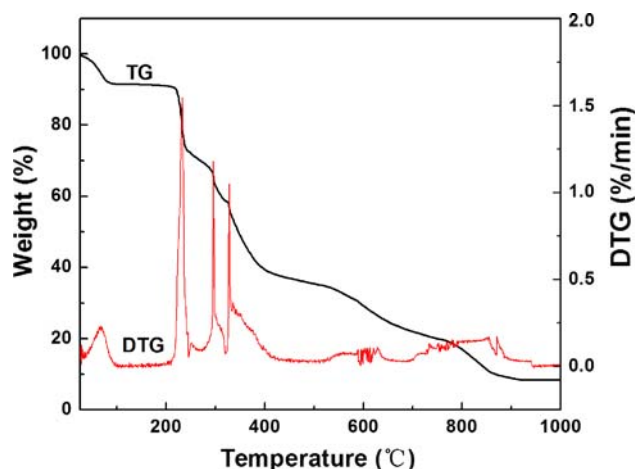


Fig. 1 The TG–DTG curves of $[\text{Co}^{\text{III}}(\text{Imazameth})_3] \cdot 0.5\text{DMF} \cdot 4\text{H}_2\text{O}$

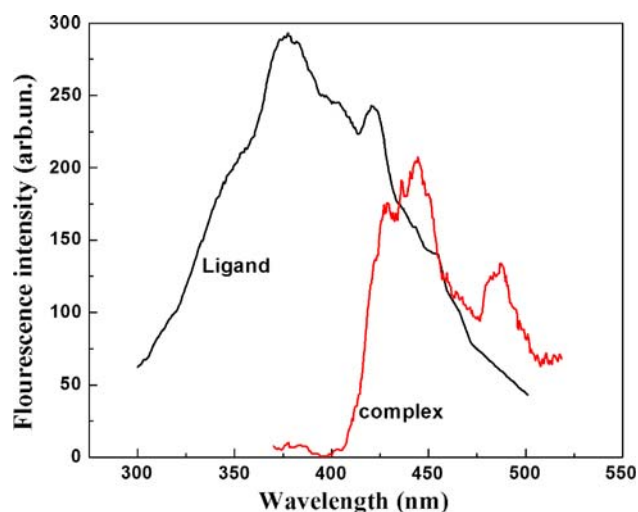


Fig. 2 Fluorescence emission spectra of complex and free ligand in the solid-state at room temperature

420 nm when excited with light of 230 nm, which might be assigned to intraligand $\pi-\pi^*$ and $n-\pi^*$ charge transfer. These intensities are reduced many-fold in the complex $[\text{Co}(\text{Imazameth})_3] \cdot 0.5\text{DMF} \cdot 4\text{H}_2\text{O}$ and red-shifted to 444 and 487 nm, respectively, which is ca. 67 nm red-shifted compared to the free ligand, could be assigned to the emission of ligand to metal charge transfer according to the previous literatures [34, 35]. Quenching of fluorescence of ligands by transition metal ions upon complexation is a rather common phenomenon and can be explained by processes such as magnetic perturbation, redox activity, electronic energy transfer, donation of lone pairs of electrons, etc. [36, 37]. The emission bands of the free ligand show reduction of intensities on complexation, and the phenomenon can be attributed to $n-\pi^*$ transition rather than $\pi-\pi^*$ transition [38]. Because the pairs of electrons on the free ligand are donated to the metal centers in the complex, the $n-\pi^*$ emission intensities are reduced in the complex $[\text{Co}(\text{Imazameth})_3] \cdot 0.5\text{DMF} \cdot 4\text{H}_2\text{O}$.

Description of crystal structure

A perspective view of the molecular structure of the complex along with the atom-numbering scheme is depicted in Fig. 3. The experimental data are listed in Table 2, and selected bond lengths and angles and hydrogen-bond geometry are given in Tables 3 and 4, respectively.

The structure reveals discrete complex molecules in which the metal ion lies on a threefold axis so that the asymmetric unit comprises one-third of the formula unit. The cobalt center is surrounded by three Imazameth (-1) ligands and it is six-coordinated by six N atoms in distorted octahedron coordination geometry. Each ligand is bound to the metal through two nitrogen atoms, N(1) and N(3),

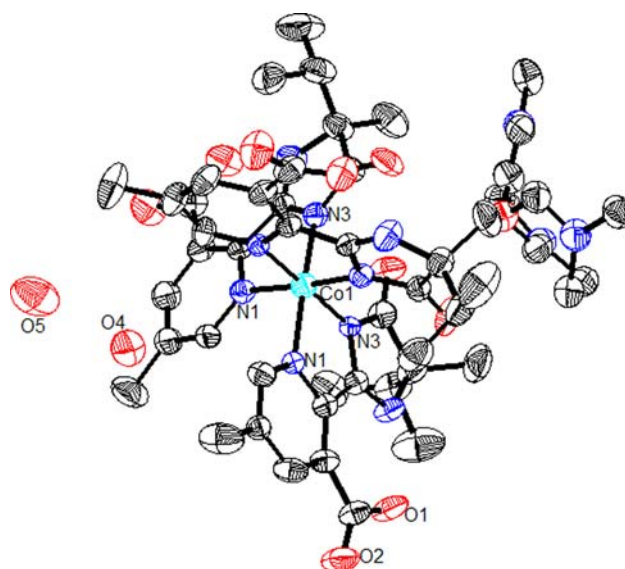


Fig. 3 The coordination environments of Co atoms of complex. All the hydrogen atoms are omitted for clarity

Table 2 Experimental data for complex $[\text{Co}^{\text{III}}(\text{Imazameth})_3] \cdot 0.5\text{DMF} \cdot 4\text{H}_2\text{O}$

Empirical formula	$\text{C}_{43.5}\text{H}_{59.5}\text{CoN}_{9.5}\text{O}_{13.5}$
Color/shape	Red/block
Formula weight	990.44
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system, space group	Trigonal, $R\bar{3}$
Unit cell dimensions	
a (Å)	17.8171(16)
b (Å)	17.8171(16)
c (Å)	28.390(3)
γ (°)	120
Volume (Å ³)	7805.0(12)
Z	3
D_{calc} (g cm ⁻³)	1.264
Absorption coefficient (mm ⁻¹)	0.398
$F(000)$	3132
Crystal size	0.41 × 0.39 × 0.28
θ range for data collection (°)	1.95–25.0
Reflections collected	12849
Unique reflections	3059 [$R(\text{int}) = 0.0415$]
Completeness to $\theta = 25.00$	99.6%
Absorption correction	Semi-empirical
Max. and min. transmission	0.8968 and 0.8540
Data/restraints/parameters	3059/0/235
Goodness-of-fit on F^2	1.112
R indices [$I > 2\sigma(I)$]	$R_1 = 0.0681$, $wR_2 = 0.1855$
R indices (all data)	$R_1 = 0.1085$, $wR_2 = 0.2410$
Largest diff. features (e Å ⁻³)	0.606 and -1.159

Table 3 The selected bond lengths (Å) and angles (°)

Co1–N3	1.893(4)	N3–C8	1.338(6)
Co1–N3 ^a	1.893(4)	N3–C9	1.374(6)
Co1–N3 ^b	1.893(4)	O1–C1	1.252(7)
Co1–N1	1.969(4)	O2–C1	1.224(7)
Co1–N1 ^a	1.969(4)	O3–C9	1.213(6)
Co1–N1 ^b	1.969(4)	C2–C8 ^a	1.470(6)
N1–C6	1.323(6)	C8–C2 ^b	1.470(6)
N1–C2	1.370(6)		
N3 ^b –Co1–N1 ^b	176.59(15)	N1 ^b –Co1–N1 ^a	96.41(14)
N3 ^a –Co1–N3 ^b	94.44(15)	N3–Co1–N1 ^b	82.32(15)
N3 ^a –Co1–N3	94.44(15)	N1–Co1–N1 ^b	96.41(14)
N3 ^b –Co1–N3	94.44(15)	N3 ^a –Co1–N1 ^a	176.59(15)
N3 ^a –Co1–N1	82.32(14)	N3 ^b –Co1–N1 ^a	82.32(15)
N3 ^b –Co1–N1	86.88(15)	N3–Co1–N1 ^a	86.88(15)
N3–Co1–N1	176.59(15)	N1–Co1–N1 ^a	96.41(14)
N3 ^a –Co1–N1 ^b	86.88(15)		

Symmetry transformations used to generate equivalent atoms

^a $-x + y, -x + 1, z$; ^b $-y + 1, x - y + 1, z$ **Table 4** Hydrogen-bond geometry (Å, °)

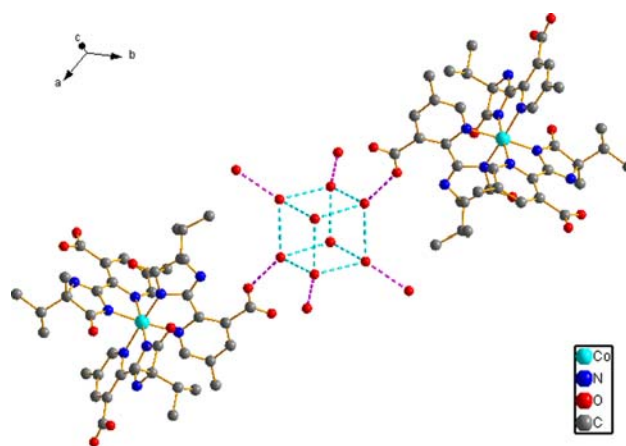
D–H...A	D–H	H...A	D...A	D–H...A
N2–H2...O1 ^a	0.860	1.728	2.490	146.44
O4–H4C...O5 ^b	0.850	1.959	2.80	174.77
O5–H5C...O1 ^c	0.851	1.939	2.770	165.32
O5–H5D...O5 ^d	0.850	2.159	2.992	166.25
O5–H5B...O5 ^e	0.849	2.356	2.992	132.93

Symmetry codes: ^a $-y + 1, x - y + 1, z$; ^b $x - 2/3, y + 2/3, z + 2/3$; ^c $-x + 1, -y + 1, -z + 1$; ^d $x - y, x - 1, -z$; ^e $y + 1, -x + y + 1, -z$

thereby forming an almost planar five-membered chelated ring, which is evident from the sum of the interior angles, 539.7°, nearly to 540°. The COO groups do not take part in metal binding: C–O distances close to each other (1.224(7) and 1.252(7) Å) are therefore measured. The O–C–O angle within the carboxylic group has a normal value of ~123°. In comparison, distances of 1.217 and 1.292 Å and an angle of 121.0° have been measured in the free acid [39]. In conclusion, the cobalt ion is hexa-coordinated with a nearly octahedral geometry and a *fac* configuration. In each complex molecule, the three rings of each ligand almost are nearly co-planar (a dihedral angle of the imidazolinone and pyridine rings is 0.94°), and the three Imazameth ligands are perpendicular to one another, which is due to the steric hindrance. The involvement of the lactam N(3) in the place of the imidazole-type N(2) atom in metal coordination is surprising, unless deprotonated, the amide nitrogen atoms is not an effective donor. A comparison of the bond lengths in the chelated ring reveals that the pyridine N(1)–Co bond,

which is over the long-range side of Co(III)–N bond distance (1.88–1.97 Å) [40–42], is significantly longer than the imidazole N(3)–Co bond. Most probably, this is a consequence of the different basicity of the N(1) and N(3) donors. As usual in such systems, the N–Co–N angle of the chelated ring (82.3°) is significantly contracted relative to that for the regular octahedron geometry. In conclusion, the coordination octahedron is distorted, as would be expected for a tris-chelated complex.

The asymmetric unit also contains four uncoordinated water molecules. The four water molecules complete the complex structure of [Co(Imazameth)₃·0.5DMF·4H₂O]. One of them, O(5), is H-bonded to the O(1) atom of COO group, which therefore acts as a double acceptor [O(5)···O(1) = 2.77(1) Å]. A striking feature of the structure is that four lattice water molecules and their symmetric equivalent form a slight distorted cubical water cluster through hydrogen bonds (Fig. 4). So far, a variety of tetramer [43], pentamer [44], hexamer [45], octamer [46], and decamer [47] water clusters have been isolated in different solid crystalline hosts. As reported previously, the cubic form is the most stable. The structure and stabilization energies of the conformers are studied [48]. The O···O bonds of the water cluster are in the range of [2.80(7)–2.99(2) Å], and the average O···O distance in the water cluster is 2.89(5) Å at 298 K. While the average O···O distance in the water cluster is 2.725(2) Å at 100 K in [Ce(dipic)₂(H₂O)₃·4H₂O] complex [48]. The O···O···O angles are in the range of [82.54–101.38°], which proves that the water cluster is a slightly distorted cube. Six complex molecules link the six O atoms of every water cluster through hydrogen bonds, which is shaped like a snowflake when seen along the *c*-axis (Fig. 5). Under the interaction of the hydrogen bonds among molecules, the three O(1) atoms of every complex molecule are connected to three cubical water clusters, respectively, and every water cluster links six complex molecules,

**Fig. 4** Perspective views of supramolecular (H₂O)₈ morphology in Co complex. All the hydrogen atoms are omitted for clarity

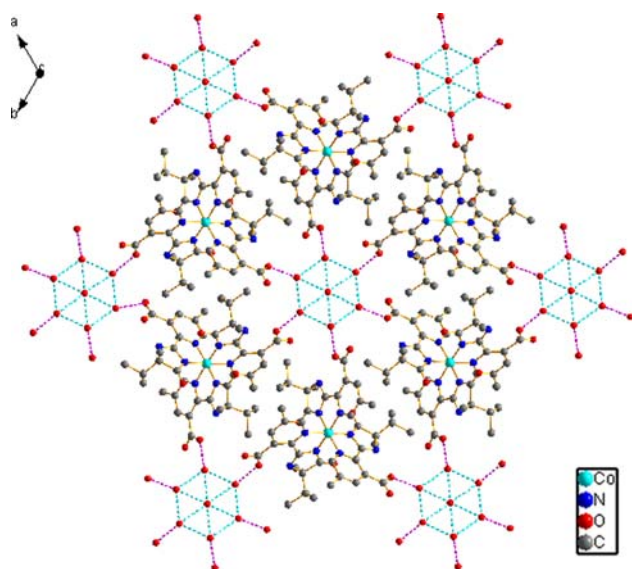


Fig. 5 Perspective view of six molecules connected to the cubic water cluster, “snowflake”, along the crystallographic *c*-axis. All the hydrogen atoms are omitted for clarity

therefore a 2D acentric MOF is formed. The intra- and inter-molecular hydrogen bonds effectively stabilize the structure, helping to form a supramolecular structure.

Conclusion

In this work, we report the synthesis and characterization of complex $[\text{Co}(\text{Imazameth})_3] \cdot 0.5\text{DMF} \cdot 4\text{H}_2\text{O}$ by spectral method (IR), elemental analysis, thermal analysis (TG, DTG), fluorescence properties, and single-crystal X-ray diffraction techniques. It crystallizes in the trigonal system, space group *R*-3. The cobalt ion is hexa-coordinated with a nearly octahedral geometry and a *fac* configuration. The asymmetric unit contains four hydrogen-bonded water molecules. The unusual crystal water molecules and their symmetric equivalent form a light distorted cubic water cluster through hydrogen bonds. It is natural to expect the formation of hydrates when metal complexes containing hydrogen-bond donors or acceptors are crystallized from water, but the formation of cluster of water molecules in such complexes is not of widespread occurrence. It is only in the recent time that the structures have been analyzed from this angle. Modern graphics software has doubtless aided this type of analysis, and there may be water cluster hidden according to the early literature [49]. Six Co(III) molecules are connected to a water cluster by hydrogen bonding, and three COO groups of every complex molecule are connected to three cubic water clusters, which result in a supramolecular structure under the interactions of inter-molecular hydrogen bonds. The complex displays strong fluorescence property, and to the best of our knowledge, this is the first

Imazameth MOF with fluorescence property and thermal gravimetric analysis.

Supplementary material

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic data Centre as the supplementary publication No. CCDC 740780. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

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