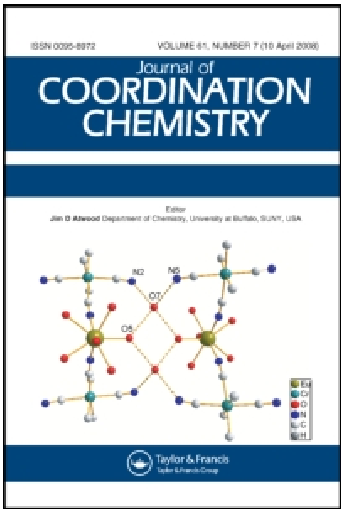

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Hydrothermal synthesis and structure of $[Co(imi)_6] \cdot (NBA)_2 \cdot 2H_2O$ (imi = imidazole, NBA = 4-nitrobenzoic acid)

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Hydrothermal synthesis and structure of $[Co(imi)_6]\cdot(NBA)_2\cdot 2H_2O$ (imi = imidazole, NBA = 4-nitrobenzoic acid)

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A novel cobalt complex $[Co(imi)_6]\cdot(NBA)_2\cdot 2H_2O$ (**1**), (imi = imidazole, NBA = 4-nitrobenzoic acid) has been hydrothermally synthesized and characterized by physical measurements and single-crystal X-ray diffraction techniques. The complex is triclinic, space group $P1$, with $a = 8.0057(16)$, $b = 9.2327(18)$, $c = 13.618(3)$ Å, $\alpha = 95.89(3)$, $\beta = 101.27(3)$, $\gamma = 103.71(3)$, $V = 947.2(3)$ Å^3, $Z = 1$. In **1**, the cobalt(II) ion is octahedral, coordinated by six nitrogen atoms from imidazole rings. An extensive three-dimensional supramolecular structure is formed via O–H···N and O–H···O hydrogen bonds between $[Co(imi)_6]^{2+}$ cations, NBA anions and water molecules, and π–π interactions between NBA molecules.

Keywords: Cobalt; Crystal structure; Hydrothermal synthesis; Supramolecular architecture

1. Introduction

Investigation of novel inorganic–organic hybrid framework assemblies represents one of the most active areas of materials science [1] for various potential applications, such as magnetism [2], electrical conductivity [3], catalysis [4], sorption [5] and so on. Recently, attention has focussed on organic ligands with biological functions. For example, cobalt(II) complexes with imidazole and carboxyl ligands have been studied as models for metalloproteins [6].

The $[Co(imi)_6]^{2+}$ cation (imi = imidazole), reported in 1972 [7], contains six imidazole rings, which in histidine coordinates with transition metal ions in a number of biologically important molecules [6, 8, 9]. Each imidazole in $[Co(imi)_6]^{2+}$ has a non-coordinated nitrogen atom which can coordinate to another metal ion or act in hydrogen bond formations. Thus for its potential to yield novel supramolecular structures, $[Co(imi)_6]^{2+}$ is a good candidate for further study.

Here, we report a new complex, $[Co(imi)_6](NBA)_2\cdot 2H_2O$ (NBA = 4-nitrobenzoic acid). Compared with the complexes composed of $[M(imi)_6]^{2+}$ and simple anion [10–13],

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some of which possess a simple binary structure and ordinary hydrogen bonds, the complex is not only rich in hydrogen-bonds, but also π–π interactions between layers of NBA molecules.

2. Experimental

2.1. *Materials and methods*

All reagents and solvents employed were commercially available and used as received without further purification. X-ray powder diffraction (XRD) data were collected on a Shimadazu XRD-6000 diffractometer with Cu-Kα radiation ($\lambda = 1.5418$ Å). Elemental analyses (C, H, N) were performed on a Perkin-Elmer 2400 CHN system. IR spectra were recorded in the range 400–4000 cm^{-1} on a Nicolet 5PC FT-IR spectrophotometer using KBr pellets.

2.2. *Synthesis*

Orange crystals of the title compound were synthesized hydrothermally by heating a mixture of $CoCl_2 \cdot 6H_2O$ (0.238 g, 0.1 mmol), NBA (0.167 g, 0.1 mmol), and imidazole (0.272 g, 4 mmol) in a 23 cm^3 Teflon-lined stainless steel autoclave under autogenous pressure at 170°C for 3 days. The crystalline product was filtered off, washed with distilled water, and dried at ambient temperatures. Yield: 45%. Anal. Calcd for $C_{32}H_{36}N_{14}O_{10}Co$ (%): C, 45.95; H, 4.34; N, 23.47. Found: C, 44.12; H, 4.09; N, 22.62. IR (cm^{-1}): 3437 (s), 3415 (s), 3049 (s), 2943 (s), 2850 (s), 2615 (m), 1618 (s), 1577 (s), 1385 (s), 1344 (s), 1255 (m), 1170 (w), 1144 (w), 1103 (m), 1070 (s), 1011 (w), 941 (m), 883 (w), 831 (s), 752 (m), 725 (s), 663 (s), 621 (s), 509 (s).

2.3. *X-ray crystallography*

Data collection was performed on a Siemens SMART CCD diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) in the ω-scan mode. Data processing was accomplished with the SAINT processing program. The structure was solved in space group $P1$ by direct methods and refined on F^2 by full-matrix least-squares using SHELXTL97 [14]. No adsorption correction was applied. All non-hydrogen atoms were refined with anisotropic displacement parameters. Crystallographic data are summarized in table 1, and selected bond lengths and angles are listed in table 2; hydrogen bond lengths and angles are listed in table 3.

3. Results and discussion

3.1. *Crystal structure*

X-ray crystallographic analysis reveals that **1** has a three-dimensional supramolecular structure. The basic structure is shown in figure 1. Each asymmetric unit contains

Table 1. Crystal data and refinement parameters for **1**.

Compound	$[Co(imi)_6]\cdot(NBA)_2\cdot2H_2O$
Empirical formula	$C_{32}H_{36}N_{14}O_{10}Co$
Formula weight	835.68
Temperature (K)	293(3)
Wave length (Å)	0.71073
Crystal system	Triclinic
Space group	$P1$
a (Å)	8.0057(16)
b (Å)	9.2327(18)
c (Å)	13.618(3)
α (°)	95.89(3)
β (°)	101.27(3)
γ (°)	103.71(3)
Volume (Å^3)	947.2(3)
D_{Calcd} (g cm^{-3})	1.465
Z	1
μ (mm^{-1})	0.528
F_{000}	433.0
Reflections collected/unique	9442/7095 [R(int) = 0.0353]
Data/restraints/parameters	7095/3/530
Θ range (°)	3.04–27.47
GOF on F^2	0.964
R_1, wR_2 [$I > 2\sigma(I)$]	$R_1 = 0.0453$, $wR_2 = 0.1261$
R_1, wR_2 (all data)	$R_1 = 0.0686$, $wR_2 = 0.1481$
Largest difference peak and hole (e Å^{-3})	0.301, −0.356

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

Co(1)–N(1)	2.161(6)	N(1)–Co(1)–N(5)	90.7(2)	C(14)–N(9)–Co(1)	125.4(6)
Co(1)–N(3)	2.158(8)	N(3)–Co(1)–N(5)	89.0(3)	C(11)–N(7)–Co(1)	126.9(5)
Co(1)–N(5)	2.189(6)	N(7)–Co(1)–N(11)	89.8(3)	C(10)–N(7)–Co(1)	129.8(6)
Co(1)–N(7)	2.138(7)	N(1)–Co(1)–N(11)	90.1(2)	C(1)–N(1)–Co(1)	128.3(5)
Co(1)–N(9)	2.232(7)	N(3)–Co(1)–N(11)	91.6(3)	C(2)–N(1)–Co(1)	127.4(6)
Co(1)–N(11)	2.188(7)	N(5)–Co(1)–N(11)	179.1(3)	O(8)–C(26)–O(7)	123.5(8)
O(4)–C(19)	1.227(10)	N(7)–Co(1)–N(9)	89.7(2)	O(8)–C(26)–C(27)	119.2(7)
O(8)–C(26)	1.255(9)	N(1)–Co(1)–N(9)	90.1(2)	O(7)–C(26)–C(27)	117.3(8)
O(7)–C(26)	1.263(11)	N(3)–Co(1)–N(9)	79.3(4)	O(4)–C(19)–O(3)	125.4(7)
O(3)–C(19)	1.253(10)	N(5)–Co(1)–N(9)	90.4(3)	O(4)–C(19)–C(20)	119.0(8)
O(6)–N(14)	1.258(15)	N(11)–Co(1)–N(9)	89.0(3)	O(3)–C(19)–C(20)	115.6(7)
O(5)–N(14)	1.174(15)	C(7)–N(5)–Co(1)	127.5(6)	O(5)–N(14)–O(6)	122.7(9)
N(13)–O(2)	1.128(17)	C(8)–N(5)–Co(1)	124.4(5)	O(5)–N(14)–C(30)	122.7(12)
N(13)–O(1)	1.274(19)	C(16)–N(11)–Co(1)	129.2(6)	O(6)–N(14)–C(30)	114.5(11)
N(7)–Co(1)–N(1)	179.8(4)	C(17)–N(11)–Co(1)	129.4(5)	O(2)–N(13)–O(1)	124.7(10)
N(7)–Co(1)–N(3)	90.6(2)	C(4)–N(3)–Co(1)	126.7(6)	O(2)–N(13)–C(23)	121.9(13)
N(1)–Co(1)–N(3)	89.6(3)	C(5)–N(3)–Co(1)	130.4(6)	O(1)–N(13)–C(23)	113.4(14)
N(7)–Co(1)–N(5)	89.4(3)	C(13)–N(9)–Co(1)	128.6(6)		

a $[Co(imi)_6]^{2+}$ cation, two uncoordinated deprotonated NBA and two molecules of water. In $[Co(imi)_6]^{2+}$, cobalt(II) coordinates to nitrogen atoms of six distinct imidazole molecules, and the coordination geometry is normal octahedral. All imidazoles act as monodentate ligands, and Co–N bond lengths are in the range 2.138(7)–2.232(7) Å. N–Co–N bond angles of two adjacent imidazoles vary from 89.0(3) to 91.6(3)°, while N–Co–N bond angles of imidazoles *trans* to each other are 179.8(4), 179.1(3) and

Table 3. Hydrogen bonding details (Å, °) for **1**.

D–H	D (D–H)	d(H···A)	d(D···A)	∠DHA
N10–H18···O7[a]	0.860	1.947	2.748	154.53
N8–H14···O7	0.860	2.010	2.826	158.00
N2–H2···O4	0.860	2.015	2.812	153.52
N4–H6···O4[b]	0.860	1.944	2.734	152.19
N6–H10···O8[c]	0.860	2.039	2.888	168.84
N12–H22···O3[d]	0.860	2.075	2.901	160.76
O2W–H2A···O3[e]	0.989	2.317	2.933	119.49
O2W–H2B···O8	0.924	2.150	2.971	147.42
O1W–H1AA···O8[f]	1.139	1.807	2.921	164.55
O1W–H1BA···O3	0.722	2.275	2.947	155.24

Symmetry transformations used to generate equivalent atoms are a: $x, y-1, z$; b: $x, y+1, z$; c: $x+1, y, z$; d: $x-1, y, z$; e: $x-1, y, z-1$; f: $x+1, y, z+1$.

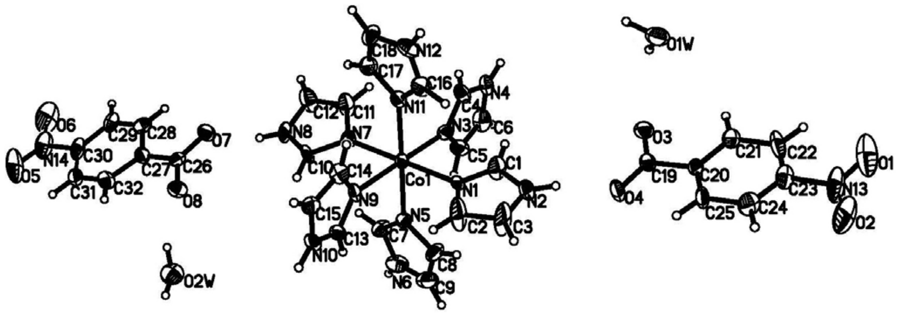

Figure 1. An ORTEP view of $[Co(imi)_6]\cdot(NBA)_2\cdot 2H_2O$ with the atom numbering scheme. Thermal ellipsoids are drawn at the 30% probability level.

179.3(4)° for N1–Co–N7, N5–Co–N11 and N9–Co–N3, respectively. Iidazole rings *trans* to each other are almost coplanar with dihedral angles of 9.1, 2.0 and 1.6° for I–IV, II–V, III–VI rings, respectively (plane I: N1, N2, C1, C2, C3; plane II: N3, N4, C4, C5, C6; plane III: N5, N6, C7, C8, C9; plane IV: N7, N8, C10, C11, C12; plane V: N9, N10, C13, C14, C15; plane VI: N1, N12, C16, C17, C18). For balancing the charge, two deprotonated NBA are present. The carboxyl and the nitro groups are uncoordinated.

A complicated hydrogen bonding scheme is a prominent feature in the crystal structure of **1**. As shown in figures 2 and 3, $[Co(imi)_6]^{2+}$ cations units, NBA anions and neutral water molecules are held together via O–H···O and N–H···O hydrogen bonds to form an extensive three-dimensional network. Each $[Co(imi)_6]^{2+}$ ion forms six N–H···O H-bonds with carboxyl group oxygen atoms of adjacent NBA anions. One of the oxygen atoms of the carboxyl group (O4, O7) forms two N–H···O hydrogen bonds with two nitrogen atoms of different $[Co(imi)_6]^{2+}$ units to form a $[Co(imi)_6]$–NBA chain along the *b* axis, while another carboxyl oxygen (O3, O8) forms three hydrogen bonds with nitrogen atoms of a third $[Co(imi)_6]^{2+}$ ion and two oxygen atoms of water. Thus the carboxyl groups of the join $[Co(imi)_6]^{2+}$ ions along the *a* and *b* axes to form a hydrogen bonded sheet.

The water molecules play an important role in the assembly of the complex. They form four hydrogen bonds between two NBA sheets, and bridge them to yield a 3D motif. Furthermore, there are strong π–π interactions between aromatic groups of NBA

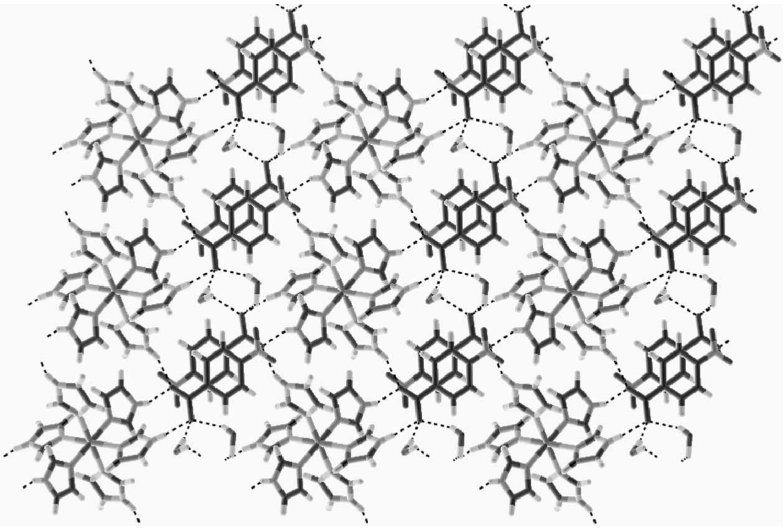

Figure 2. The structure of **1** viewed along the *a* axis.

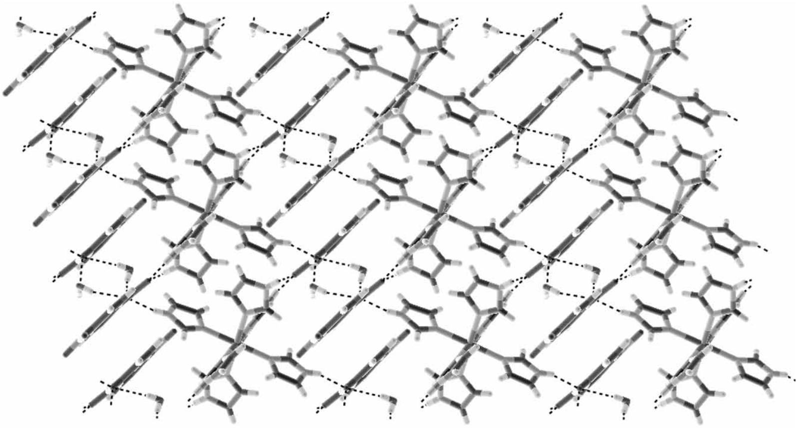

Figure 3. The structure of **1** viewed along the *b* axis.

molecules of adjacent $[Co(imi)_6]$–NBA sheets. The average distance between the aromatic groups is 3.4 Å. The hydrogen bonding pattern and the π–π interactions between two sheets enhance the stability of the lattice. Compared with complexes of $[Co(imi)_6]^{2+}$ and simple anions, the introduction of the NBA into the $[Co(imi)_6]^{2+}$ system gives a complex and novel structure.

3.2. *Spectroscopic properties*

The IR spectrum of **1** displays a broad band centred at 3432 cm^{-1} that can be assigned to $\nu(OH^-)$ of lattice water molecules; its broadness is indicative of hydrogen bonding in accord with the crystal structure. Bands at 3049 and 725 cm^{-1} can be assigned to stretching and out-of-plane bending C–H vibrations of NBA. The absence of a band at 1730–1690 cm^{-1} confirms that all NBA molecules are deprotonated. The asymmetric $\nu_{as}(COO^-)$ stretch at 1577 cm^{-1} and the symmetric $\nu_s(COO^-)$ stretch at 1385 cm^{-1} are observed, and the difference, of the order of 200 cm^{-1}, indicates that carboxylate groups are either free or coordinated to the metal as monodentates; the former is consistent with the crystal structure.

Supplementary material

Complete tables of bond lengths and angles, coordinates and displacement parameters have been deposited at the Cambridge Crystallography Data Centre. Supplementary data are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK on request, quoting the deposition number 294149 (Fax: + 44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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