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Synthesis, Crystal Structure, and Electrochemical Properties of the Complex [Ni(imidazole)$_6$](DBSH)$_2$ · 2DMF[1]

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Abstract—The title complex [Ni(Im)$_6$](DBSH)$_2$ · 2DMF (H_2DBSH = 3,5-dibromosalicylaldehyde, Im = imidazole, DMF = N,N-dimethylformamide) has been prepared and characterized by X-ray diffraction analysis. It crystallizes in the monoclinic system, space group $P2_1/c$ with a = 14.7271(13), b = 9.0221(8), c = 18.1143(16) Å, β = 100.408(2)°, V = 2367.2(4) Å^3, Z = 2, M_r = 1171.22, F(000) = 1172, ρ_c = 1.643 g/cm^3 and μ(MoK_α) = 3.844 mm^{-1}. The structure was refined to R = 0.0425 and wR = 0.1052 for 3646 observed reflections. The X-ray crystal structure analysis revealed that the center nickel(II) cation is bonded to six nitrogen atoms from six imidazole to form a six-coordinated elongated octahedron. The complex includes a DBSH^{2-} anion and two DMF solvates. The intramolecular and intermolecular hydrogen bonds in the crystal structure play remarkably important role in the thermostability of the title complex. The electrochemical properties were studied in DMF with an electrochemical analyzer.

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INTRODUCTION

In a recent issue of Inorganic Chemistry, the synthesis and the crystal structures of polymeric iron, cobalt, and nickel pyrazolates peared [1]. Most of the known binary phases of M(Pz)$_n$, and M(Pymo)$_n$ (HPz = pyrazole, HPymo = 2- or 4-hydroxypyrimidine) are formed only as powders, thus leaving XRD as the only viable tool for structural characterization [2].

Polymorphic complexes such as Ni(Pz)$_2$ and Ni(Im)$_2$ (Im – imidazole), which bear photomechanical [3], magnetic [4], anticorrosive [5], and antimicrobial [6] significance, had been reported.

Due to the weak coordination bond of dibromosalicylaldehydenate anions with transition metals, dibromosalicylaldehydenate usually acts as the counterbalance of the charge [7]. Herein we report the synthesis, structure, and electrochemical study of a mononuclear nickel(II) complex with H_2DBSH and Im (**I**). The nickel(II) center is in a slightly distorted octahedron environment. The intramolecular and intermolecular hydrogen bonds play important roles in the thermostability of the title complex. Cyclic voltammetry of the complex indicated an irreversible cathodic peak in DMF.

[1] The article is published in the original.

EXPERIMENTAL

Synthesis [Ni(Im)$_6$](DBSH)$_2$ · 2DMF (I) (H_2DBSH – 3,5-dibromosalicylaldehyde). Ni(Ac)$_2$ · 2H_2O (0.110 g, 0.5 mmol) was added to a solution of H_2DBSH (0.122 mg, 0.5 mmol) in methanol (20 ml) and DMF (20 ml). After stirring the mixture for 2 h at 80°C, the resulting brown solution was cooled to room temperature. The mixture was filtered and the filtrate was allowed to stand for 1 week, during which brown crystals were formed. The yield was 92.1%.

For $C_{38}H_{44}Br_4N_{14}Ni$			
anal. calcd, %:	C, 38.96;	H, 3.79;	N, 16.74.
Found, %:	C, 39.01;	H, 3.91;	N, 16.79.

IR (KBr; ν, cm^{-1}): 2750 m (C–H in –CHO), 1721 m (C=O), 1430 br (C–N), 1261 br (Ar–O), 1066 m (Im), 700 m (C–Br), 630 m (Im), 520 m (Ni–N).

Structure X-ray determination. A brown crystal of the title complex with dimensions of 0.25 mm × 0.20 mm × 0.20 mm was mounted on a Siemens SMART-CCD diffractometer using a graphite MoK_α (λ = 0.071073 nm) radiation at room temperature. A total of 13447 reflections were collected in a range of 1.41° ≤ 2θ ≤ 27.00°. The raw data were corrected and the structure was solved using the SHELX–97 program. Non-hydrogen atoms were located by direct phase determination and subjected to anisotropic refinements. The unit cell parameters along with data collection and refinement details for **I** are listed in Table 1. Atomic coordinates

Table 1. Crystallographic parameters and summary of data collection for structure **I**

Parameter	Value
Formula weight	1171.22
Temperature, K	293(2)
Crystal system	Monoclinic
Space group	$-P2_1/c$
a, Å	14.7271(13)
b, Å	9.0221(8)
c, Å	18.1143(16)
β, deg	100.408(2)
V, Å^3	2367.2(4)
Z	2
ρ_{calcd}, g cm^{-3}	1.643
$F(000)$	1172
$\mu(MoK_\alpha)$, mm^{-1}	1.013
Crystal size, mm^3	0.25 × 0.20 × 0.20
Limiting indices	$-18 \le h \le 10, -11 \le k \le 10, -23 \le l \le 23$
Reflections collected	13477
Independent reflections	5147 (R_{int} = 0.0310)
Observed reflections ($I > 2\sigma(I)$)*	3646
GOOF	1.011
R_1, wR_2 ($I > 2\sigma(I)$)	0.0425, 0.1052
R_1, wR_2 (all data)	0.0671, 0.1128
Largest diff. peak and hole, e Å^{-3}	0.568 , –0.319

* $wR = 0.1052$ ($w = 1/[\sigma^2(F_o^2) + (0.0625P)^2]$, $P = (F_o^2 - 2F_c^2/3)$.

Table 2. Selected bond lengths and bond angles for complex **I**

Bond	d, Å	Angle	ω, deg
Ni(1)–N(1)	2.138(2)	N(5)Ni(1)N(3)	88.59(9)
Ni(1)–N(3)	2.128(2)	N(5)Ni(1)N(1)	90.14(9)
Ni(1)–N(5)	2.121(2)	N(3)Ni(1)N(1)	88.52(9)

Table 3. Geometric parameters of hydrogen bonds in structure **I***

Contact D–H···A	Distance, Å			Angle DHA, deg
	D–H	H···A	D···A	
N(2)–H(2A)···O(3)$^{\#1}$	0.86	1.92	2.764(5)	168.8
N(4)–H(4A)···O(2)$^{\#2}$	0.86	1.85	2.703(3)	170.3
N(6)–H(6A)···O(2)$^{\#3}$	0.86	1.97	2.772(3)	154.7

* Symmetry transformations used to generate equivalent atoms: $^{\#1}$ $-x+1, y-1/2, -z+1/2$; $^{\#2}$ $-x+1, y+1/2, -z+1/2$; $^{\#3}$ $x, -y+1/2, z-1/2$.

and thermal parameters are given in Table 2. Selected bond lengths and bond angles are listed in Table 3. Full atomic data of the title complex are available as a file in CIF format deposited with the Cambridge Crystallographic Data Center (no. 603381); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The molecular structure of the title complex is shown in Fig. 1. The six-coordinated Ni(II) (in inversion center) is in an elongated distorted octahedral geometry, four nitrogen atoms (N(3), N(3a), N(5) N(5a)) comprise the equatorial plane, whereas the other two nitrogen atoms (N(1), N(1a)) occupy the axial positions. The two DBSH anions are distributed around the central cation uniformly. Two DMF solvent molecules exist in the complex.

The octahedral geometry mentioned above is consistent with the similar distortions found in the related compounds [8]. Bond lengths Ni(1)–N(1), Ni(1)–N(3), and Ni(1)–N(5) (mean distances 2.129 Å) are longer than that of an analogous complex (2.0749 Å) [9]. The bond length Ni(1)–N(1) 2.138(2) Å is longer than the other Ni–N bond lengths, so the coordinated atoms around nickel form an elongated octahedron. Bond lengths and bond angles of Ni–N and NNiN in this complex are somewhat different from the reported compounds [10, 11] due to the effects of the DBSH anions and DMF molecule.

As shown in Figs. 2 and 3, an inorganic cationic layer is linked to an organic anionic layer through a series of N–H···O, C–H···O and C–H···N hydrogen bonds (Table 3), and adjacent DBSH anions are antiparallel. The uncoordinated N(2) atom of axial imidazoles and acyl oxygen O(3) in DMF form N–H···O hydrogen

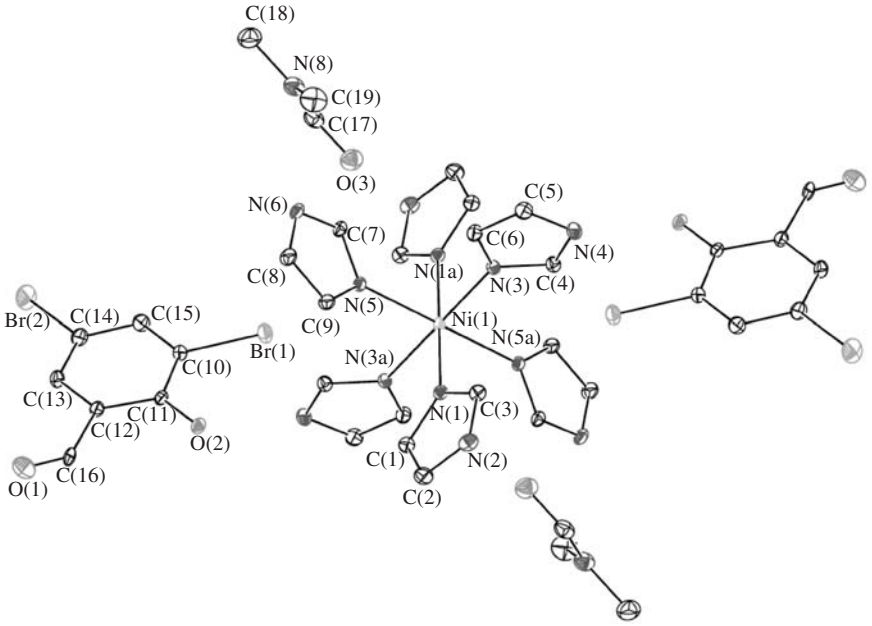

Fig. 1. Structure of the title complex with the atom numbering scheme.

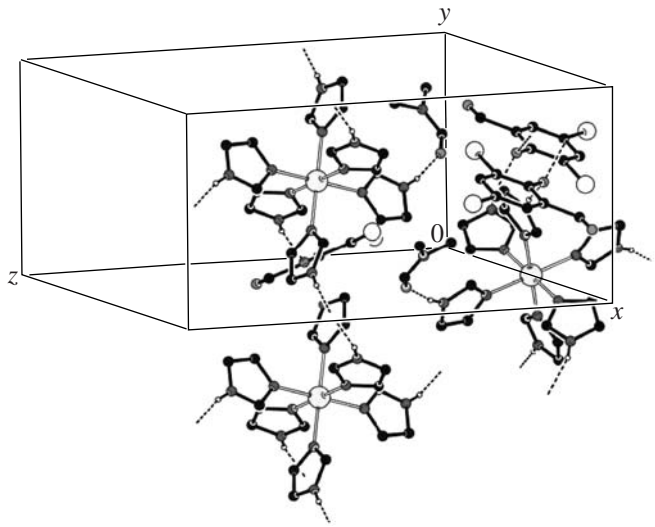

Fig. 2. Packing diagram of the title complex with hydrogen bonds.

bonds. The hydroxybenzene oxygen atom in DBSH and two nitrogen atoms (N(4), N(6)) of imidazole in the adjacent $[Ni(Im)_6]^{2+}$ cations are linked through N–H···O hydrogen bonds to give a 3D supramolecular network (Fig. 2), which forms a Ni_2O_2 cavum via hydrogen bonds with the distance of Ni···Ni 9.022 Å (Fig. 3). The different sites of hydrogen bonds lead to the different Ni–N bond distance from 2.121(2) to 2.138(2) Å. So, the six-coordinated Ni(II) is in an elongated distorted octahedral geometry. The hydrogen bonds stabilize the crystal structure.

TG–DTG thermal analyses have been carried out for the complex with the TG–DTG curves illustrated in Fig. 4. There are three continuous mass loss steps from 150 to 700°C in the TG–DTG curve. The first one starts at 260°C, finishes at 336°C, and reaches the a maximum at 284°C with a loss of 12.33% of the total weight, which is assigned to the removal of two DMF molecules (calcd 12.48%). The second step (about 47.00%) from 381 to 431°C with the largest weight loss at 437°C corresponds to the release of two DBSH (47.63%). The third step is about 30.67% in the range from 520 to

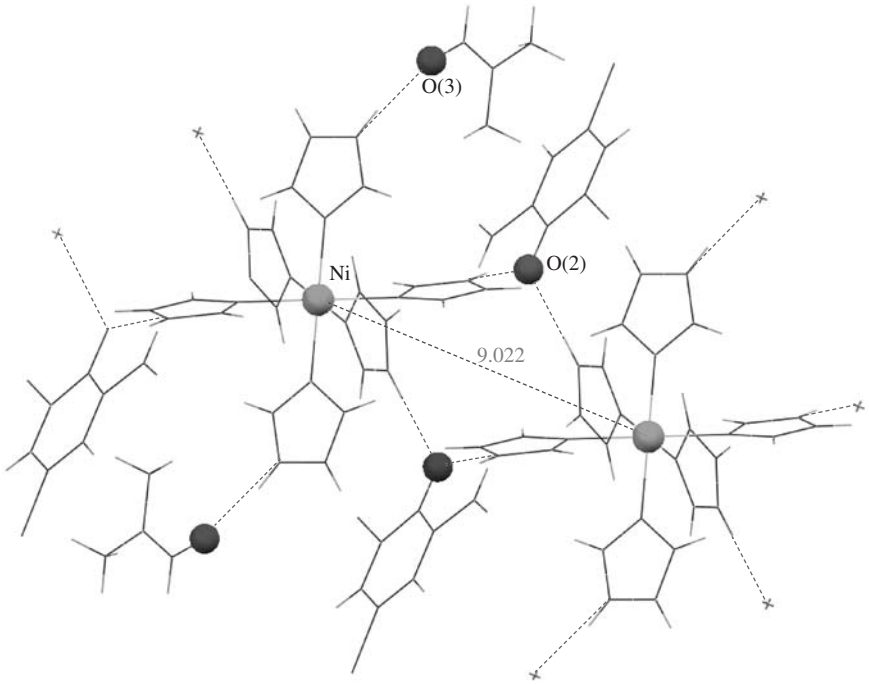

Fig. 3. Part of the crystal structure showing hydrogen bonds.

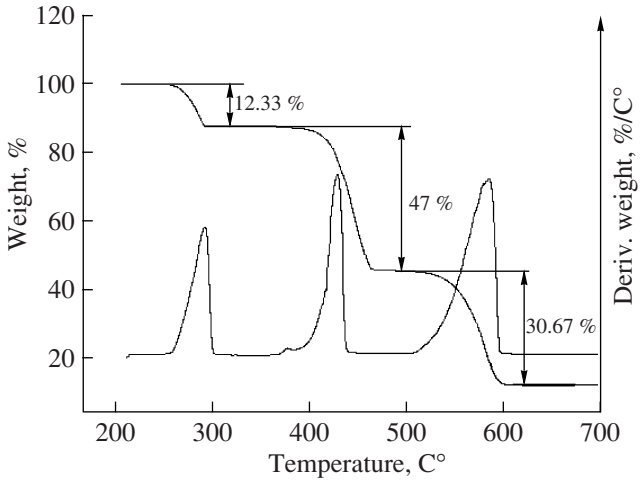

Fig. 4. Thermal analyses curves of the title complex.

620°C with the highest rate at 591°C. This step is assigned to the loss of six coordinated imidazole molecules (calcd 34.88%). The final product of the decomposition process is the metal oxide.

Cyclic voltammetric experiments were performed with an electrochemical analyzer (CH Instrument 650a). A standard three-electrode cell was used with a graphite–working electrode, a platinum auxiliary electrode, and an Ag/AgCl as a reference electrode. The potential of this electrode was calibrated vs. SCE using the $[Fe(C_5H_5)_2^+]/[Fe(C_5H_5)_2]$ redox couple as an internal standard. All the experiments were performed in a high-purity DMF solution with 0.001 M tetra-*n*-butyl ammonium chloride as a supporting electrolyte.

The CV obtained in DMF solvent at 10^{-3} mol/l concentration at a scan rate of 50 mV s^{-1} in the +1500 mV to –1500 mV potential range is shown in Fig. 5. The results show that only one couple of oxidation/reduction peaks appears, which corresponds to the electron transfer of Ni(III)/Ni(II). Electric potentials of cathode and

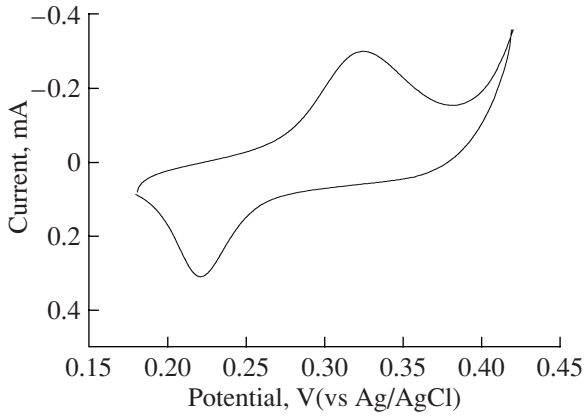

Fig. 5. Cyclic voltammogram of the complex in DMF.

anode are: E_{pa} = 0.32V and E_{pc} = 0.22V, and $i_{pe}/i_{pa} \approx 1$. A conclusion is that the electron transfer in the electrolysis reaction is quasireversible.

Thus, the reaction of nickel(II) with six imidazole ligands gave the six-coordinate complex. The structure of the complex forms a distorted rectangular pyramidal configuration of nickel. Electrochemical studies of the complex using cyclic voltammetry in DMF indicate an irreversible cathodic peak from 0.22 to 0.32 V (versus Ag/AgCl) corresponding to the reduction of Ni(II) to Ni(III).

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