



## Synthesis, crystal structure and computational chemistry research of the zinc(II) complex: $[\text{Zn}(\text{pt})(\text{Biim})_2]$

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**Abstract:** The title metal–organic coordination complex **1**,  $[\text{Zn}(\text{pt})(\text{Biim})_2]$  (pt = phthalate, benzene-1,2-dicarboxylate, Biim = 2,2'-biimidazole), was obtained by hydrothermal synthesis and characterized by single crystal X-ray diffraction. The complex crystallized as monoclinic, space group  $P2_1/n$  with  $a = 8.5466(15)$  Å,  $b = 11.760(2)$  Å,  $c = 20.829(4)$  Å,  $\beta = 95.56(2)^\circ$ ,  $V = 2083.5(6)$  Å<sup>3</sup>,  $M_r = 497.78$ ,  $D_c = 1.587$  g cm<sup>-3</sup>,  $\mu(\text{MoK}\alpha) = 1.226$  mm<sup>-1</sup>,  $F(000) = 1016$ ,  $Z = 4$ , the final  $R = 0.0564$  and  $wR = 0.1851$  for 3656 observed reflections ( $I > 2\sigma(I)$ ). The complex was also investigated by elemental analysis, IR spectroscopy, thermogravimetry and theoretical calculations.

**Keywords:** 2,2'-biimidazole; phthalic acid; zinc(II) complex; crystal structure; quantum chemistry.

### INTRODUCTION

The design and synthesis of metal–organic framework structures have been studied widely during the past decade not only because of their intriguing architectures but also because of their unexpected properties for potential practical applications in a wide number of fields, such as asymmetric catalysis, magnetism, photoluminescence, *etc.*<sup>1–3</sup> These novel structures can be rapidly and efficiently synthesized from some subunits, whereby the metal ion, bi- or multidentate organic ligand and coordinate bonding are the important factors for the self-assembly processes. Consequently, investigations in this field have led to many materials with interesting structures.<sup>4</sup>

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The structural characteristics of and characterization of some metal complexes, such as  $[\text{Cd}(\text{C}_8\text{H}_4\text{O}_4)(\text{C}_7\text{H}_6\text{N}_2)_3]_n$ , has been reported<sup>5</sup> and some metal complexes containing the pt ligand (pt = phthalate, benzene-1,2-dicarboxylate) were synthesized and characterized. 2,2'-Biimidazole (Biim), a good nitrogen and hydrogen donor, can regard as a robust heteromeric hydrogen-bonded synthon. As the five-membered rings also contain  $\pi$  electrons,  $\pi$ - $\pi$  interactions may be formed when the distance between the two rings is befitting.<sup>6,7</sup> In this article, a new Zn(II) complex with pt as the first ligand is reported.

#### EXPERIMENTAL

2,2'-Biimidazole was prepared according to a reported method.<sup>8</sup> Other chemicals from commercial sources were of reagent grade and used without further purification. Infrared spectra (KBr pellets) were taken on a Perkin-Elmer 240C spectrometer. The thermal analysis was performed on a Diamond DSC type thermal analyzer.

##### *Synthesis of bis(2,2'-biimidazole)phthalato zinc(II) [Zn(pt)(Biim)<sub>2</sub>] (I)*

Complex **1** was prepared from a mixture of  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  (0.109 g), phthalic acid (0.166 g), biimidazole (0.268 g) and  $\text{H}_2\text{O}$  (18 mL) in a 30 mL Teflon-lined autoclave under an autogenous pressure at 160 °C for six days. After cooling to room temperature, white block crystals of **1** were collected by filtration and washed with distilled water. Yield 73 % (based on Zn). Anal. Calcd. for  $\text{C}_{20}\text{H}_{16}\text{N}_8\text{O}_4\text{Zn}$ : C, 48.2; H, 3.2; N, 22.5 %. Found: C, 48.1; H, 3.2; N, 22.3 %.

##### *Crystal structure determination and physical measurements*

A single crystal with dimensions of 0.360 mm×0.316 mm×0.218 mm was mounted at 293(2) K. All measurements were performed on a Bruker CCD diffractometer using graphite-monochromated  $\text{MoK}_\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) radiation in the  $\omega$  scan mode ( $5.00 < 2\theta < 52.14^\circ$ ). A total of 17514 reflections were collected and 4134 were independent with  $R_{\text{int}} = 0.0252$ , of which 3656 were observed with  $I > 2\sigma(I)$ . A correction for  $Lp$  factors was applied. The structure was solved by direct methods using the SHELX-97 program and refined with SHELXL-97<sup>9</sup> by full-matrix least-squares techniques on  $F^2$ . All H atoms were positioned geometrically and refined as riding atoms, with C-H = 0.93 Å and N-H = 0.86 Å, and with  $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C,N})$ . All non-hydrogen atoms were refined anisotropically and hydrogen atoms isotropically. The final  $R = 0.0564$  and  $wR = 0.1851$ ,  $w = 1/(\sigma^2(F_o^2) + (0.1466P)^2 + 1.1882P)$  where  $P = (F_o^2 + 2F_c^2)/3$ .  $S = 1.057$ ,  $(\Delta\rho)_{\text{max}} = 0.70$ ,  $(\Delta\rho)_{\text{min}} = -0.71 \text{ e/\AA}^3$  and  $(\Delta/\sigma)_{\text{max}} = 0.002$ . The selected important bond parameters are given in Table I.

*Crystal structure deposition for complex I.* Supplementary crystallographic data for complex **1** is deposited at the Cambridge Crystallographic Data Centre under CCDC 739928. Further details of the crystal structure investigation may be obtained via [http://www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

#### RESULTS AND DISCUSSION

##### *Crystal structure of [Zn(pt)(Biim)<sub>2</sub>] I*

The single crystal X-ray diffraction analysis revealed that complex **1** crystallizes in the  $P2_1/n$  space group. There are one Zn(II) ion, one pt ligand and two Biim ligands in the asymmetric unit (Fig. 1).

TABLE I. Selected bond lengths (Å) and bond angles (°) of the title complex obtained from X-ray analysis and theoretical calculations at the B1B95/(6-311+G(2df,2p) (for C, H, N and O) and the Lan12dz (for Zn) level of theory, as well as the relative errors (%)

Bond	Experimental	Calculated	Error, %
Bond length, Å			
Zn–O(2)	2.265(4)	2.2653	0.004
Zn–N(1)	2.342(5)	2.3425	0.000
Zn–N(5)	2.333(4)	2.3327	0.029
Zn–O(3)	2.321(3)	2.3219	0.026
Zn–N(4)	2.266(4)	2.2658	0.026
Zn–N(8)	2.265(5)	2.2647	0.035
Bond angle, °			
N(4)–Zn–O(2)	86.31(15)	86.2986	0.015
O(2)–Zn–N(8)	165.09(17)	165.0567	0.021
O(2)–Zn–O(3)	78.26(15)	78.2608	0.001
N(4)–Zn–N(5)	92.29(16)	92.3217	0.033
N(8)–Zn–N(5)	74.76(15)	74.7555	0.008
N(4)–Zn–N(1)	74.69(14)	74.6713	0.027
N(8)–Zn–N(1)	89.54(14)	89.5631	0.024
N(5)–Zn–N(1)	155.52(14)	155.5279	0.004
N(4)–Zn–N(8)	108.41(16)	108.4539	0.039
N(4)–Zn–O(3)	163.03(15)	163.0163	0.009
N(8)–Zn–O(3)	87.40(16)	87.3638	0.043
O(2)–Zn–N(5)	103.00(14)	102.9839	0.017
O(3)–Zn–N(5)	97.97(14)	97.9603	0.011
O(2)–Zn–N(1)	96.86(14)	96.8661	0.005

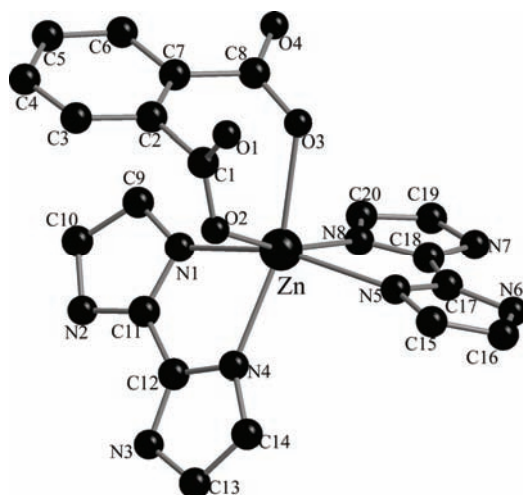


Fig. 1. The coordination geometry of complex **1**.

The coordination number of each zinc(II) atom is six. The Zn is coordinated by two carboxylate oxygen atoms from the two carboxyls of one pt (Zn–O(2)),

2.266(5) Å and Zn–O(3), 2.317(5) Å), the other two oxygen atoms were deprotonated, and four nitrogen atoms from two different Biim ligands, giving a distorted octahedron geometry. The Zn–N bond distances range from 2.259(5) to 2.331(6) Å, the O(N)–Zn–O(N) angles range from 74.89(18) to 165.1(2)° (Table I).

Each carboxyl group of pt is in a single-dentate coordination mode, *i.e.*, the two carboxyl groups are both deprotonated; this was proved by the absence of the characteristic double peak at around 1600 cm<sup>-1</sup> in the IR spectrum. In this coordination mode, the title complex formed a monomeric structure.

In the crystal lattice of the title complex, strong N–H...O hydrogen bonds exist (Table II). The nitrogen atoms N(2), N(3), N(6) and N(7) of the biimidazole ligands act as donors, while the acceptor O atoms come from the carboxyl oxygen of the pt ligands. The individual structures linked by strong hydrogen bonds form a two dimensional planar grid structure (Fig. 2).

TABLE II. The hydrogen bonds of the title complex (symmetry transformations used to generate the equivalent atoms: #1:  $-x+3/2, y+1/2, -z+1/2$ ; #2:  $-x+1, -y, -z$ ; #3:  $x-1/2, -y+1/2, z+1/2$ )

D–H...A	$d(\text{D–H}) / \text{Å}$	$d(\text{H...A}) / \text{Å}$	$d(\text{D...A}) / \text{Å}$	$\angle(\text{DHA}) / ^\circ$
N(3)–H(3B)...O(1)#1	0.86	1.91	2.736(6)	161.2
N(7)–H(7A)...O(3)#2	0.86	1.91	2.722(6)	155.8
N(2)–H(2A)...O(2)#1	0.86	1.86	2.702(6)	165.1
N(6)–H(6B)...O(4)#2	0.86	1.88	2.736(6)	173.3
C(13)–H(13A)...O(4)#3	0.93	2.38	3.273(7)	160.4

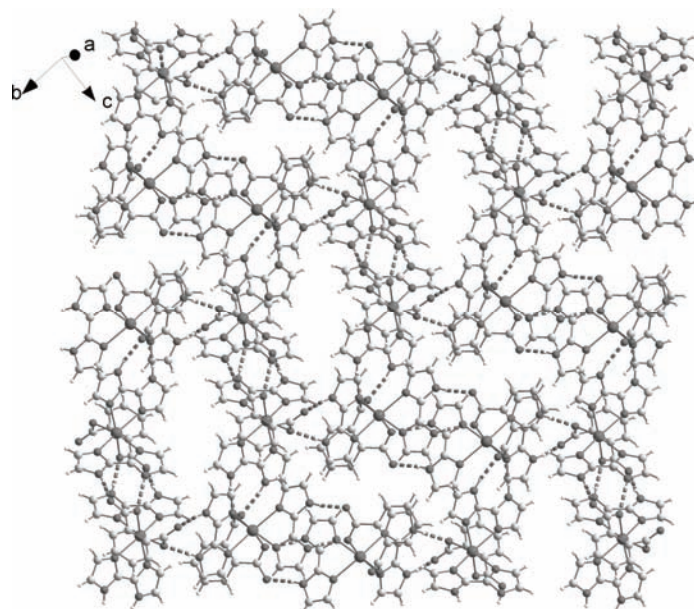


Fig. 2. The two-dimensional planar grid structure extended parallel to the plane (the dotted single lines indicate hydrogen bonds).

In addition, C(13)–H...O(4)# (#:  $-1/2+x$ ,  $1/2-y$ ,  $1/2+z$ ) hydrogen bond interactions exist.<sup>10</sup> These inter-molecular contacts link neighboring two-dimensional planar structures to a three dimensional supramolecular structure. Complex **1** also contains  $\pi$ – $\pi$  interactions and C–H... $\pi$  interactions (Table III). These intermolecular interactions stabilize the crystal structure.

TABLE III. Intermolecular  $\pi$ – $\pi$  interactions (dist. centroids  $< 4.0$  Å) and C–H... $\pi$  interactions ( $H\cdots Cg < 3.0$  Å,  $\gamma < 30.0^\circ$ ) parameters of complex **1** (Cg(1): N(5)→C(15)→C(16)→N(6)→C(17)→5, Cg(2): N(7)→C(18)→N(8)→C(20)→C(19)→6, Cg(3): C(2)→C(3)→C(4)→C(5)→C(6)→C(7)→7, Cg(4): N(3)→C(12)→N(4)→C(14)→C(13)→4; Cg(I) = plane number I (= ring number in () above), dihedral angle = dihedral angle between planes I and J ( $^\circ$ ), dist. centroids = distance between ring centroids (Å), CgI\_Perp = perpendicular distance of Cg(I) on ring J (Å), CgJ\_Perp = perpendicular distance of Cg(J) on ring I (Å),  $\gamma$  = angle Cg(I)→Cg(J) vector and normal to plane J ( $^\circ$ ), symmetry codes: a =  $1-x$ ,  $-y$ ,  $-z$ ; b =  $-1+x$ ,  $y$ ,  $z$ ; c =  $1+x$ ,  $y$ ,  $z$ )

Cg(I)→Cg(J)	Dist. centroids, Å	Dihedral angle, $^\circ$	CgI_Perp, Å	CgJ_Perp, Å
Cg(1)→Cg(2)	3.677(4)	6.04	3.327	3.344
Cg(2)→Cg(1)	3.677(4)	6.04	3.345	3.327
Cg(2)→Cg(3)	3.916(4)	18.72	3.670	3.612
Cg(3)→Cg(2)	3.916(4)	18.72	3.611	3.670
C–H(I)→Cg(J)				
C(3)–H(3A)→Cg(4)	Distance H...Cg, Å	H-Perp $\gamma$ / $^\circ$	C–H...Cg angle, $^\circ$	
	2.90	8.68	131	

### IR Spectrum of complex **1**

The IR spectrum of complex **1** contained a weak band at  $3144\text{ cm}^{-1}$  of  $\nu_{N-H}$  and  $\nu_{C-H}$ , which is a characteristic absorption of Biim. The medium bands at  $1608$  and  $1397\text{ cm}^{-1}$  are, respectively, the asymmetric and symmetric stretch vibration of the carboxylate groups;  $\Delta > 200\text{ cm}^{-1}$  shows the presence of monodentate linkages of the carboxylates in the dianions, which is consistent with the X-ray diffraction results. The bands at  $1559w$ ,  $1483w$ ,  $1424w$  and  $1257s\text{ cm}^{-1}$  can be attributed to C=C and C=N<sup>11–13</sup> stretch vibrations of the imidazole ring. The band at  $827s\text{ cm}^{-1}$  arises from N–H bend vibrations, and those at  $771w$ ,  $758w$ ,  $745w\text{ cm}^{-1}$  can be attributed to C=C and C=N bend vibrations of imidazole. The band at  $445w\text{ cm}^{-1}$  is in the low frequency region and can be regarded as arising from the metal coordinated to the Biim ligand (Zn–N stretching vibration).<sup>13</sup>

### Thermal analysis

The TG measurement was performed under a N<sub>2</sub> atmosphere at a heating rate of  $10\text{ }^\circ\text{C min}^{-1}$ . The TG curve of complex **1** is shown in Fig. 3. TG curve of complex **1** shows a first weight loss of 31.4 % from  $190$  to  $310\text{ }^\circ\text{C}$ , corresponding to the removal of the pt ligand molecules (calcd. 32.9 %). Upon further heating, a weight loss (54.6 %) occurred in the temperature range of  $510$ – $595\text{ }^\circ\text{C}$ , corres-

ponding to the release of the organic ligand Biim (calcd. 53.9 %). After 600 °C, no weight loss was observed, which indicates the complete decomposition of complex **1**. The residual weight of 16.8 % (calcd. 16.4 %) corresponds to ZnO.

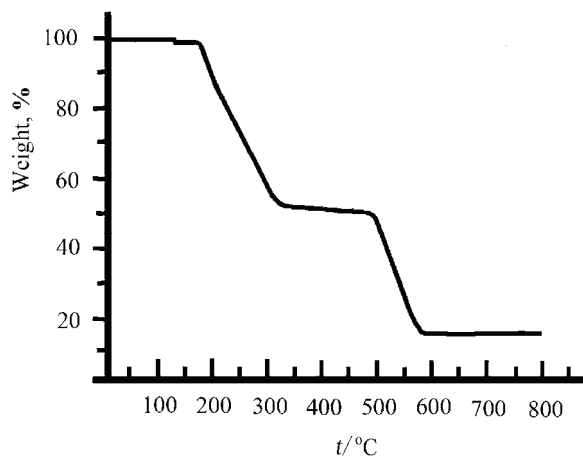


Fig. 3. The TG curve for the title complex **1**.

#### Computational chemistry research

The geometric structure with real frequency was optimized by the density functional theory (DFT)<sup>14</sup> method with a Becke one parameter hybrid functional (B1B95).<sup>15</sup> There were no symmetry constraints on the complex. In the calculation, the effective core potentials of Zn atoms proposed by Hay and Wadt<sup>16</sup> were employed, and a “double- $\zeta$ ” quality basis set LANL2DZ was adopted for the Zn metal. There are lone-pair electrons and a conjugated system in the complex, the 6-311++G(2df, 2p) basis set was employed for C, H, O, N optimization, which involved 49 atoms, 1266 basis functions, 1895 primitive Gaussians, 118 alpha electrons and 118 beta electrons. All calculations were performed with the Gaussian 09 software package<sup>17</sup> and Natural Bond Orbital (NBO)<sup>18</sup> analyses were obtained based on the optimized geometries.

From Table I, it can be seen that the relative errors of the bond lengths and bond angles were all in the range of 0.00–0.04 %. This led to the belief that the employed theoretical method was suitable for complex **1**.

The atomic net charges for complex **1** calculated in the NBO analysis are listed in Table IV. The results of calculation show that electronic arrangement of the central zinc atom is  $4s^{0.273}d^{9.984}p^{0.42}$ . The covalent valence of zinc is +2, but the zinc partially obtains electrons from the pt and Biim ligands, illustrating that the charge of the central Zn metal for complex **1** is 1.31799. The net charges of the other coordinated N and O atoms (N1, N4, N5, N8, O2 and O3) are  $-0.53277$ ,  $-0.51940$ ,  $-0.53279$ ,  $-0.51939$ ,  $-0.86153$  and  $-0.86151$ , respectively. Thus, the net charges of the coordinated O atoms are more negative than those of the coor-



minated N atoms. The calculated Weiberg bond orders (Zn–O (0.2220), Zn–N4, Zn–N8 (0.1707) and Zn–N1, Zn–N5 (0.1579)) indicate that the bonds around the metal are covalent in nature.

TABLE IV. Selected atom net charges and electronic configuration of the title complex at the BIB95/(6-31+G(2df)) (for C, H, N and O) and the Lan12dz (for Zn) level

Atom	Charge	Electronic c
Zn	1.31799	[core] 4s(0.27) 3d( 9.98) 4p(0.42)
N1	-0.53277	[core] 2s(1.35) 2p(4.14) 3d(0.02) 4p(0.01)
N2	-0.55498	[core] 2s(1.23) 2p(4.30) 3d(0.01) 4p(0.01)
N3	-0.55533	[core] 2s(1.23) 2p(4.30) 3d(0.01)
N4	-0.51940	[core] 2s(1.35) 2p(4.13) 3d(0.02) 4p(0.01)
N5	-0.53279	[core] 2s(1.35) 2p(4.14) 3d(0.02) 4p(0.01)
N6	-0.55498	[core] 2s(1.23) 2p(4.30) 3d(0.01) 4p(0.01)
N7	-0.55532	[core] 2s(1.23) 2p(4.30) 3d(0.01)
N8	-0.51939	[core] 2s(1.35) 2p(4.13) 3d(0.02) 4p(0.01)
O1	-0.71567	[core] 2s(1.70) 2p(4.98) 3p(0.01) 3d(0.02)
O2	-0.86153	[core] 2s(1.68) 2p(5.15) 3p(0.01) 3d(0.02)
O3	-0.86151	[core] 2s(1.68) 2p(5.15) 3p(0.01) 3d(0.02)
O4	-0.71569	[core] 2s(1.70) 2p(4.98) 3p(0.01) 3d(0.02)

It can be seen from Fig. 4 that in the highest molecular occupied orbital (HOMO, Orbital No. 118, Fig. 4a), the electron is mainly located at the pt ligand,

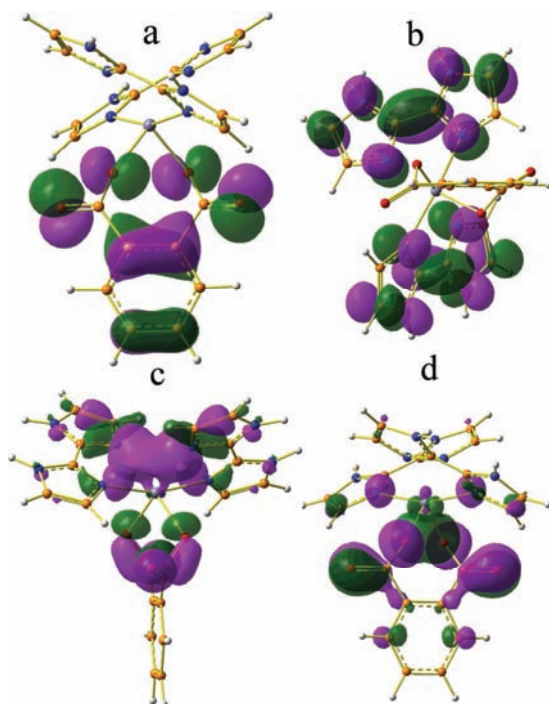


Fig. 4. The LUMO No. 94 0.036 (a) and No. 109 0.029 isosurface (b), HOMO 0.034 (c) and LUMO 0.030 isosurface (d) orbitals of the title complex **1**.

while in the lowest unoccupied molecular orbital (LUMO, Orbital No. 119, Fig. 4b), the electron is mainly situated on the two Biim ligands. There are four Zn–N coordinate bonds and two Zn–O coordinate bond around the central Zn. After examination of both molecular orbital graphs, it is known that the Zn–N bonds are related to the orbital No. 94 (Fig. 4c), correspondingly, the Zn–O bonds are related to the orbital No. 109 (Fig. 4d). These two orbitals reveal that the Zn center uses its d orbitals to interact with N or O p orbital to form the coordinate bonds of the title complex.

### CONCLUSION

In this article, the metal–organic coordination complex **1**, [Zn(pt)(Biim)<sub>2</sub>], which exhibits a three-dimensional network structure, is reported. The complex was investigated by IR spectroscopy, elemental analysis and TG analysis. The density functional theory (DFT) calculation was performed at the B1B95 level. Analysis of the orbitals revealed that the Zn center mainly uses its d orbitals to coordinate to the ligands. The net charges and the bond orders were also investigated. The obtained results are consistent with the X-ray diffraction results.

### ИЗВОД

#### СИНТЕЗА, КРИСТАЛНА СТРУКТУРА И ТЕОРИЈСКА ИСПИТИВАЊА ЦИНК(II) КОМПЛЕКСА [Zn(pt)(Biim)<sub>2</sub>]

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Хидротермалном синтезом изолован је цинк(II) комплекс **1**, [Zn(pt)(Biim)<sub>2</sub>] (pt = фталат, бензен-1,2-дикарбоксилат, Biim = 2,2'-биимидазол). Карактеризација комплекса је извршена на основу дифракције X-зрака са монокристала. Моноклинични кристали комплекса имају просторну групу *P*2<sub>1</sub>/*n* са вредностима: *a* = 8,5466(15) Å, *b* = 11,760(2) Å, *c* = 20,829(4) Å, β = 95,56(2)°, *V* = 2083,5(6) Å<sup>3</sup>, *Mr* = 497,78, *D<sub>c</sub>* = 1,587 g/cm<sup>3</sup>, μ(MoK<sub>α</sub>) = 1,226 mm<sup>-1</sup>, *F*(000) = 1016, *Z* = 4, коначни фактор поузданости *R* = 0,0564 и *wR* = 0,1851 за 3656 употребљених рефлексија (*I* > 2σ(*I*)). Поред тога, за карактеризацију комплекса употребљени су елементална анализа, IR, TG и теоријска израчунавања.

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