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A New Highly Thermally Stable Co(II)-coordination polymer with Semi-flexible Bis(Imidazole) Directed Secondary Building Unit: Solvothermal Synthesis and Structure

Fatih SEMERCİ*

Department of Energy Systems Engineering, Technology Faculty, Kırklareli University, Kırklareli, Turkey

Abstract: A new thermally highly stable 2D coordination polymer, formulated as [Co(μ6-abtc)$_{0.5}$(μ-obix)]$_n$ (abtc = dioxygenated form of 3,3′,5,5′-azobenzenetetracarboxylate) obtained employing the semi-flexible 1,2-bis(imidazole-1-ylmethyl)benzene (obix) linker in hydro(solvo)thermal method. The complex was characterized by various techniques such as IR spectroscopy, elemental analysis, single crystal and powder crystal analysis. Crystallographic study of complex **1** reveal that two metal(II) ions are linked by O atoms of carboxylate groups of abtc ligand to build paddle-wheel SBU (secondary building unit). These SBUs are stabilized by the connection of obix ligand. The Co(II) ions are μ$_6$-bridged by hexadentate abtc ligand to generate 2D polymer layers with 3,4-connected binodal net (point symbol $\{4.6^2\}_2\{4^2.6^2.8^2\}$) and topological type is 3,4L13. Thermal analysis shows that complex **1** thermally stable up to 401 °C.

Keywords: Coordination polymers; bis(imidazole) ligands; 3,3′,5,5′-azobenzenetetracarboxylate ligand; SBU.

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Corresponding author. E-mails: fsemerci@klu.edu.tr; f_semerci@hotmail.com.

INTRODUCTION

The quickly expanding area of coordination polymers has attracted interest for the fascinating architectures and their potential applications (1-5). Many efforts have been given for constructing new structures, new topologies, as well as new functionalities (6-8). These materials can be synthesized relying on the mixture of metal salts, carboxylate-based ligand and N-donor bridging ligands (9-12). The coordination polymers can be synthesis by using highly symmetrical multifunctional organic ligands owing to their various coordination behavior and special topologies. Furthermore, secondary building units (SBUs) that can predict the structures of coordination polymers are largely utilized to construct them (13-15).

Properties of flexible coordination polymers can be synthesis practically at will by a preference of flexible ligands (16). The employment of flexible ligands often gives rise to increased disorder, which hampers the arrangement of self-assembly of coordination polymers. Nonetheless, flexible ligands can appropriate the coordinative demands of metal ions and form architecture in another way unavailable with rigid ligands (17).

Azobenzenecarboxylic acid compounds such as azobenzenedicarboxylic (18), azobenzene-tricarboxylic, (19) and azobenzenetetracarboxylic acids (20-30) were employed to synthesis functional materials. The rigid 3,3′,5,5′-azobenzenetetracarboxylate ($abtc^{4-}$) ligand has four carboxylate functional group, and they can be deprotonated and can be oxidized to generate an azoxy structure in the reaction media to build various architectures. In these architectures, highly strong metal-oxygen bonds can improve stability of the framework. Additionally, an important and useful strategy for synthesis coordination polymers with interesting structures is to employ semi-flexible imidazole-based ligands (31-33). The semi-flexible N-donor ligand, obix is a wise choice for the synthesis of coordination polymers (11, 34).

Taking all these into account, $abtcH_4$ and semi-flexible bis(imidazole) derivative ligands, namely obix, were prepared and their Co(II) coordination polymer, $[Co(\mu_6\text{-}abtc)_{0.5}(\mu\text{-}obix)]_n$ was synthesized. The synthesized complex was structurally characterized by various techniques such as elemental analysis, IR spectroscopy, and X-ray diffraction. Moreover, thermal and topological analysis were studied.

MATERIAL AND METHODS

All starting materials were commercially available and AR grade. Obix and $abtcH_4$ ligands were synthesized according to previous studies (34, 35). PerkinElmer 2400C Elemental Analyzer was used to elemental analyses (C, H and N). The IR spectrum was taken in the range of 4000–400 cm^{-1} with a Bruker Tensor 27 spectrometer. TG, DTG and DTA curves are recorded in the static air atmosphere in the range of 30–700 °C with platinum crucibles.

Suitable crystals of **1** were selected for data collections, which were performed on a Bruker D8-QUEST diffractometer equipped with graphite-monochromatic Mo-Kα radiation. The structure of complex **1** was obtained by direct methods using OLEX2 (36) and SHELXS-97 (37) software. All non-hydrogen atoms were refined anisotropically by full-matrix least squares methods in SHELXL-97 (37). The figures were drawn by using MERCURY (38). Topological analysis was performed using ToposPro software (39).

Synthesis of $[Co(\mu_6\text{-}abtc)_{0.5}(\mu\text{-}obix)]_n$ (1): A mixture of $abtcH_4$ (0.25 g, 0,69 mmol), obix (0,16 g; 0.69 mmol, $Co(NO_3)_2{\cdot}6H_2O$ (0.40 g; 1,38 mmol), DMF (10 mL) and two drops of conc. HNO_3 was mixed at 30 °C for half an hour. The obtained solution was sealed in a glass vial and heated at 120 °C for 3 days. Red-colored crystals of **1** were obtained (yield: 0.16 g, 12.17% based on $Co(NO_3)_2{\cdot}6H_2O$. Anal. Calcd. for $C_{22}H_{19}N_5O_4Co$: C, 55.47; H, 4.02; N, 14.70; Found: C, 56.03; H, 4.38; N, 13.84. IR data (KBr, cm^{-1}): 3142w, 3122w, 2955w, 2854w, 1622s, 1573sh, 1527sh, 1443m, 1408m, 1368s, 1233w, 1111w, 1090w, 937w, 829w, 780m, 707s, 654m, 615w, 566w, 490w, 471sh.

RESULTS AND DISCUSSION

Synthesis and Spectral Characterization: Obix and $abtcH_4$ ligands were synthesized, and its Co(II)-complex was obtained in acidic medium in DMF. Elemental analysis results agreed with single crystal X-ray results. FT-IR spectra of complex 1 is given in **Figure 1**. In the FT-IR spectrum of 1, the bands observed between 3142 and 2854 cm^{-1} are assigned to aromatic and aliphatic ν(C−H) stretching vibrations, respectively. The stretching vibrations of carboxylate groups of $abtc^{4-}$ ligand are seen at 1622 and 1443 cm^{-1}, respectively.

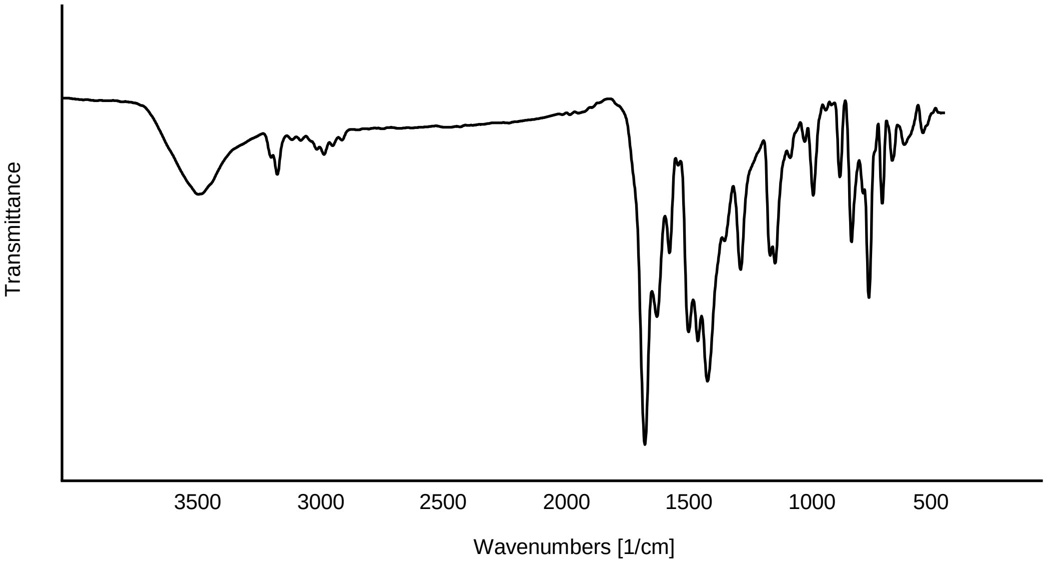


Figure 1. FT-IR spectrum of **1**.

Crystal Structure Description of [Co(μ$_6$-abtc)$_{0.5}$(μ-obix)]$_n$ (1): The X-ray crystal structural analysis shows that complex **1** is a two-dimensional (2D) coordination polymer. Complex **1** has monoclinic system and it has space group of $P2_1/n$. The asymmetric unit of **1** includes Co(II) ion, half abtc anionic ligand and one obix ligand (**Figure 2**). Each Co(II) ion in **1** shows a distorted trigonal bipyramidal environment composed of three carboxylic O atoms from different abtc^{4-} anions [Co1−O1 = 1.980 (3); Co1−O2^{i} = 2.009 (3) and Co1−O3^{ii} = 1.958 (3) Å ((i) −x+1, −y+1, −z; (ii) x+1, y, z)] and two nitrogen atoms from two different obix ligands [Co1−N1 = 2.106 (3) and Co1−N4^{i} = 2.101 (3) Å]. Secondary building units (SBU) in complex **1** were formed by two Co(II) ions that are bridged by carboxylate groups of abtc ligands. In SBU units obix ligands exhibit chair-conformation and these SBUs are stabilized by the coordination of obix ligand (34). The Co···Co distance in SBU is 3.917 (4) Å. The SBU units are bridged by oxygen atoms of anionic ligands to generate 1D structures of **1** (Figure 3). Adjacent 1D structures are bridged by other carboxylate atoms of abtc ligands to achieve layered 2D unit (Figure 4). The neighboring 2D units are further connected via van der Waals interaction, thus generating the 3D supramolecular structure (Figure 5). Topologically, complex **1** is 3,4-connected binodal net with point symbol $\{4.6^2\}_2\{4^2.6^2.8^2\}$ (Figure 6).

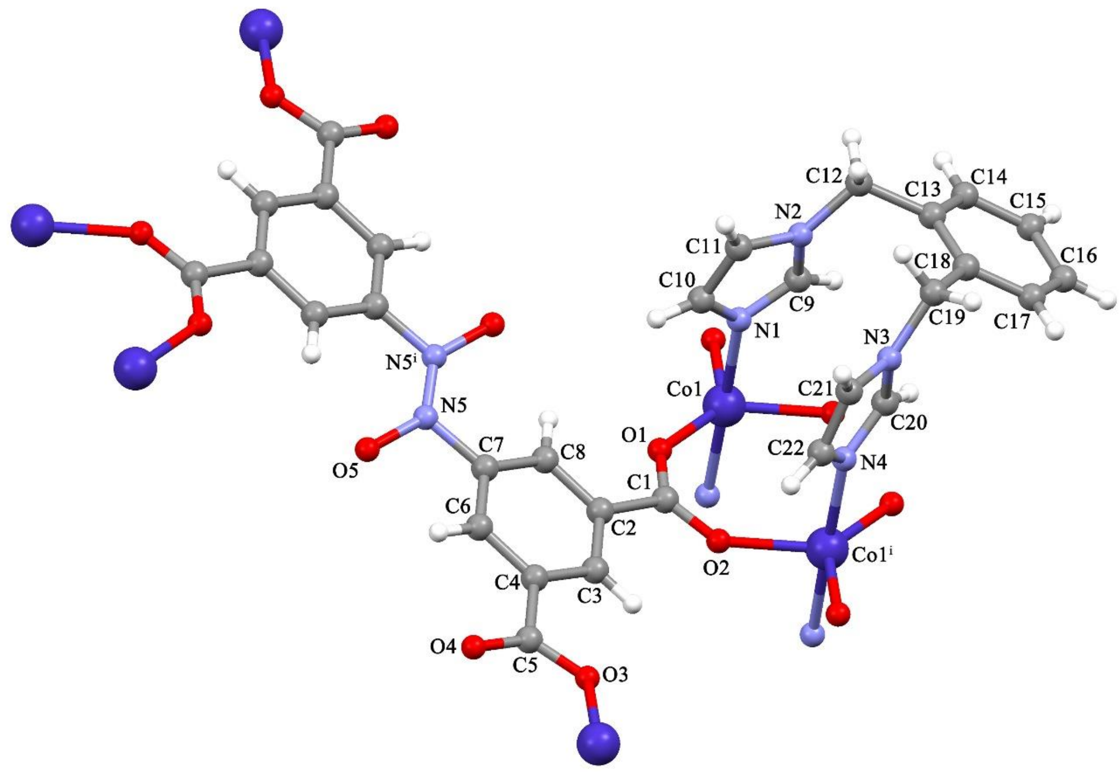


Figure 2. The molecular structure of **1**.

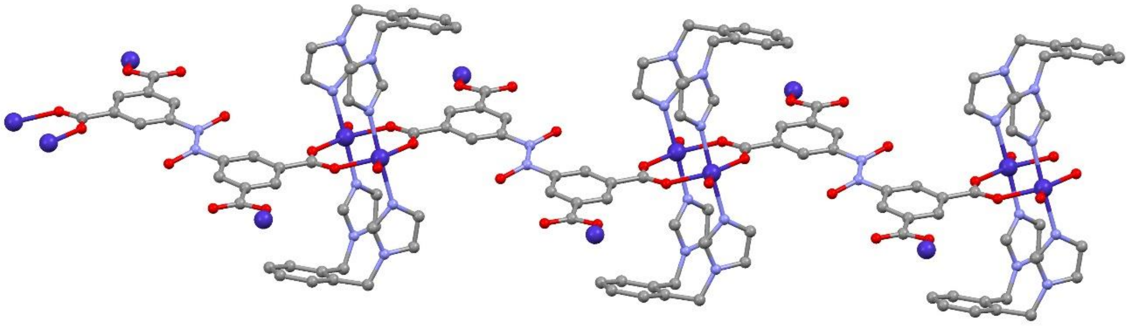


Figure 3. 1D structure of complex **1**.

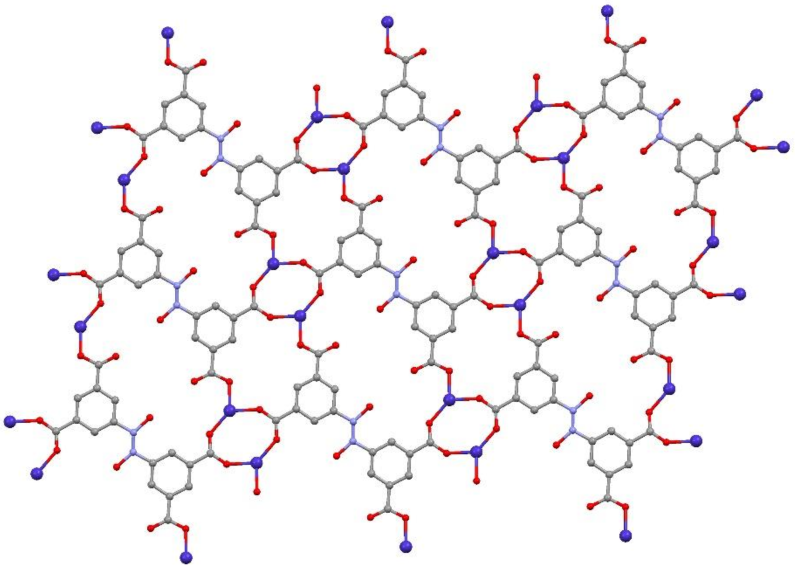


Figure 4. 2D structure of complex **1**.

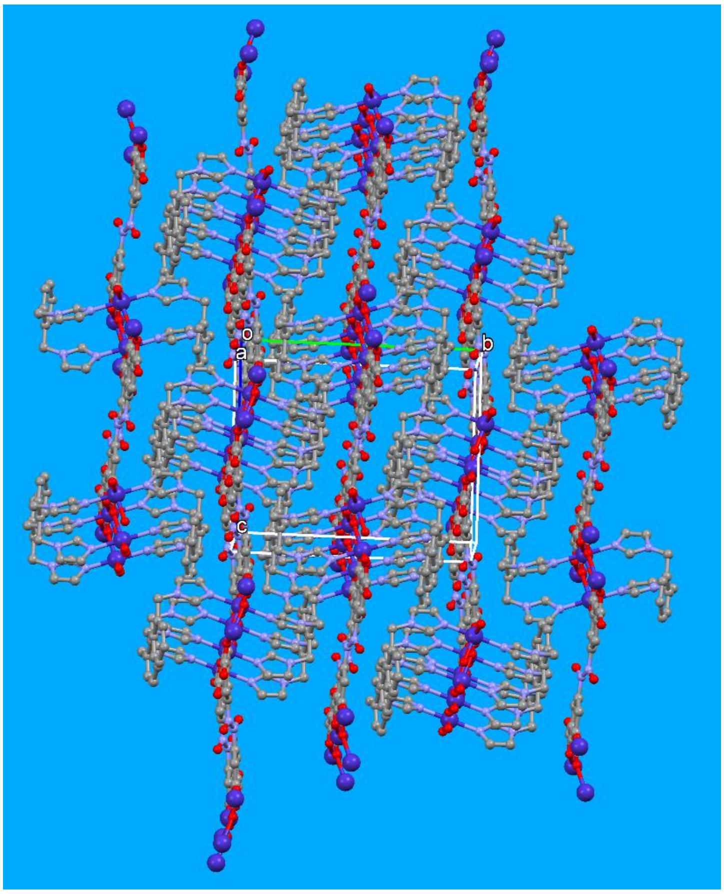
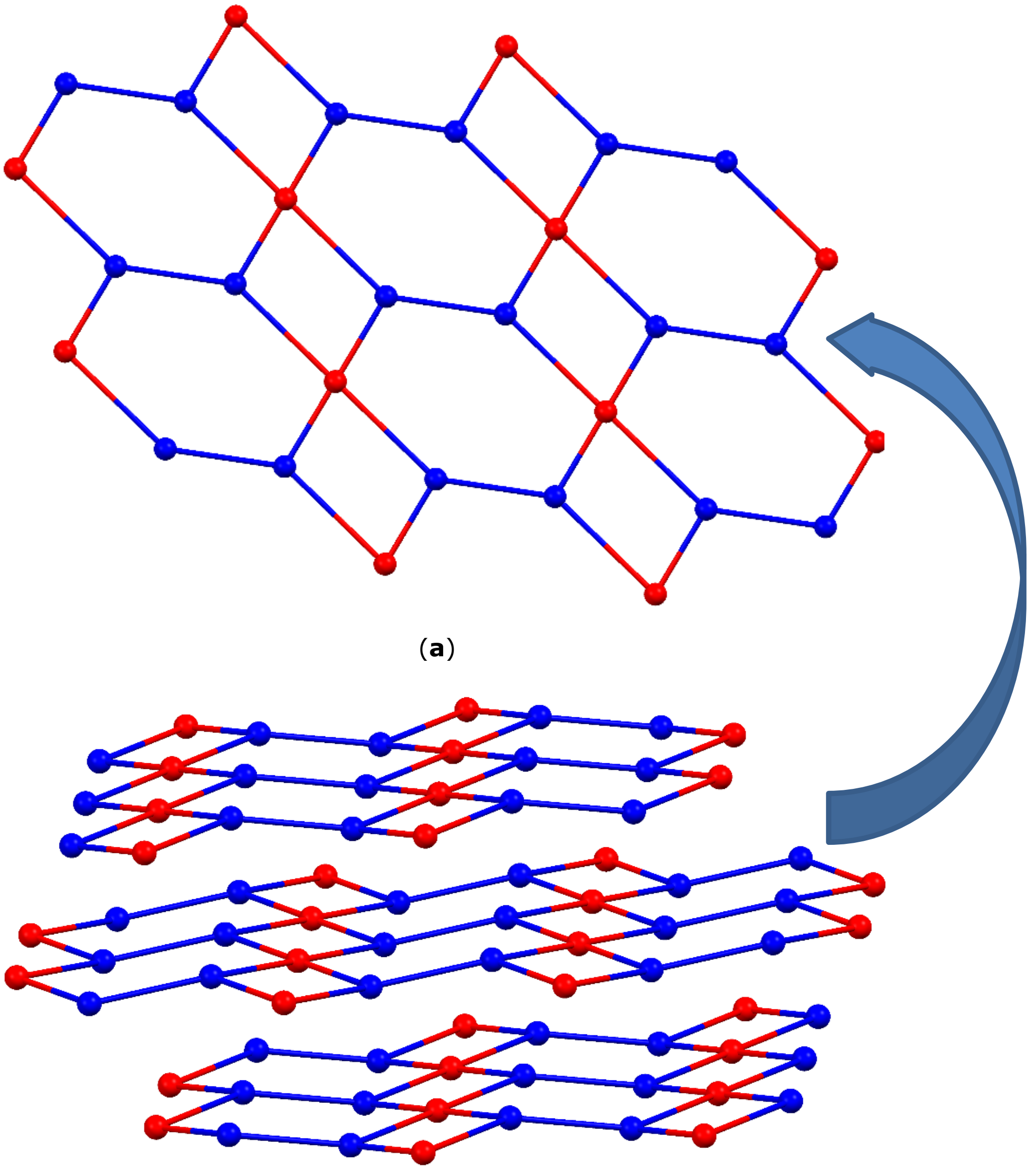


Figure 5. 3D structure of complex **1** with unit cell.



(**a**)

(b)

Figure 6. Topological presentation of complex **1.**

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

Item	**Value**
Crystal data	**1**
Empirical formula	$C_{22}H_{17}CoN_5O_5$
Formula weight	490.34
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	9.9166 (2)
b (Å)	15.6800 (4)
c (Å)	14.0749 (3)
α (°)	90
β (°)	109.3028(11)
γ (°)	90
V (Å^3)	2065.51 (8)
Z	4
D_c (g cm^{-3})	1.577
μ (mm^{-1})	0.88
θ range (°)	2.5–27.5
Measured refls.	34803
Independent refls.	4727
R_{int}	0.034
S	1.06
R1/wR2	0.056/0.159
$\Delta\rho_{max}/\Delta\rho_{min}$ (eÅ^{-3})	2.05 /−1.24

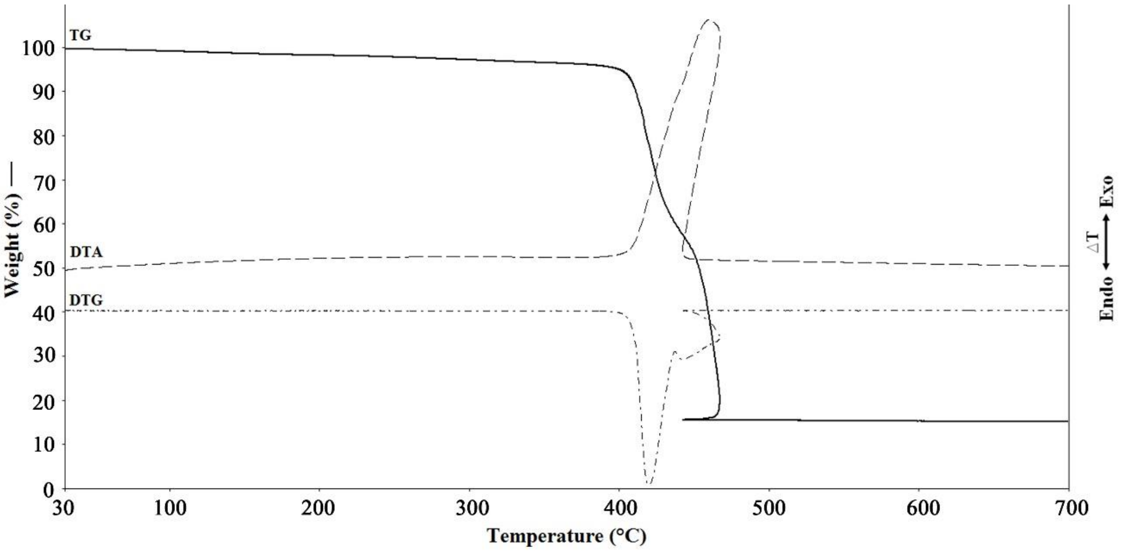
Table 2. Selected bond distances (Å) and angles (°) for **1.**

Bond Lengths (Å)			
Co1—O1	1.980 (3)	Co1—N1	2.106 (3)
Co1—O2^{i}	2.009 (3)	Co1—N4^{i}	2.101 (3)
Co1—O3^{ii}	1.958 (3)		
Angles (°)			
N4^{i}—Co1—N1	176.37(11)	O2^{i}—Co1—N4^{i}	91.87 (11)
O3^{ii}—Co1—O1	136.8 (3)	O2i—Co1—N1	89.45 (11)
O3^{ii}—Co1—N1	93.24 (14)	O1—Co1—N4^{i}	89.75 (11)
O3^{ii}—Co1—O2^{i}	93.9 (3)	O1—Co1—O2^{i}	129.26 (18)
O3^{ii}—Co1—N4^{i}	90.05 (15)	O1—Co1—N1	86.79 (11)

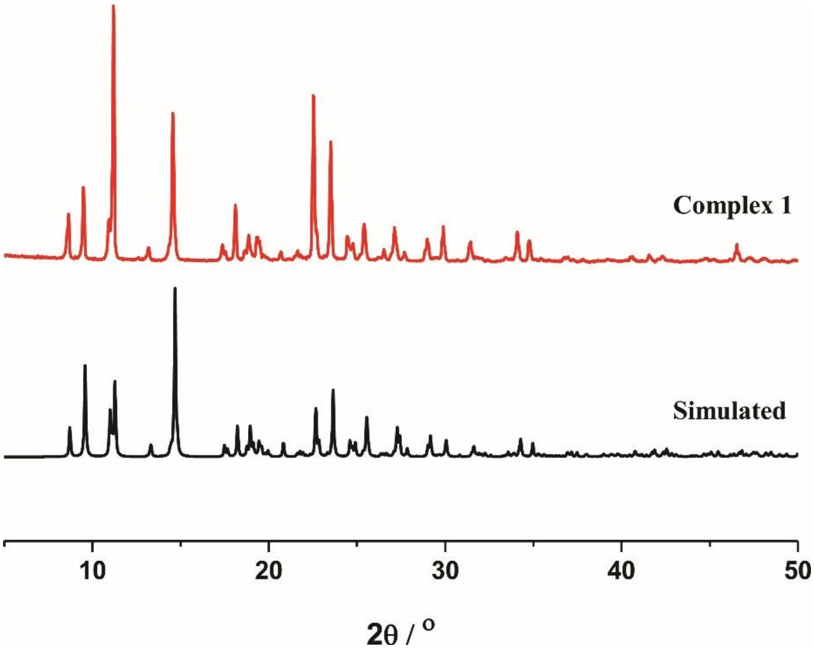
Symmetry codes: (i) −x+1, −y+1, −z; (ii) x+1, y, z; (iii) −x+1, −y+1, −z+1; (iv) x−1, y, z.

Thermal Analysis and X-ray Powder Diffraction: The thermal behaviors and thermal stability of complex **1** were investigated by TG/DTA techniques in a dry air atmosphere with a heating rate of 10 °C/min in the temperature range 30-700 °C (Figure 7(a)). Complex **1** is thermally stable up to 401 °C, respectively. For complex **1**, on further heating, the complex is exothermically decomposed. The final residual product of complex **1** is possible CoO (obsd.: 15.21%, calcd.: 15.73%).

The crystalline product of **1** was characterized by powder X-ray diffraction (PXRD) (**Figure 7(b)**). The experimental XRD pattern is comparable with the results simulated from the single crystal data. This is show that the purity of the synthesized samples.



(**a**)



(**b**)

Figure 7. (**a**) Thermal analysis (TG, DTG and DTA) curves (**b**) XRPD pattern of complex **1.**

CONCLUSION

A new 2D Co(II)-coordination polymer with 3,3′,5,5′-azobenzenetetracarboxylate and semi-flexible obix was synthesized and structurally characterized. μ_6-bridged by hexadentate abtc ligands are coordinated by Co(II) ions to generate 2D polymer chains with 3,4-connected binodal net (point symbol $\{4.6^2\}_2\{4^2.6^2.8^2\}$) and topological type is 3,4L13.

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