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FULL PAPER

Nano-Sized and Single Crystal of a 1D Copper(I) Coordination Polymer: Preparation, Characterization, Thermal and Structural Studies

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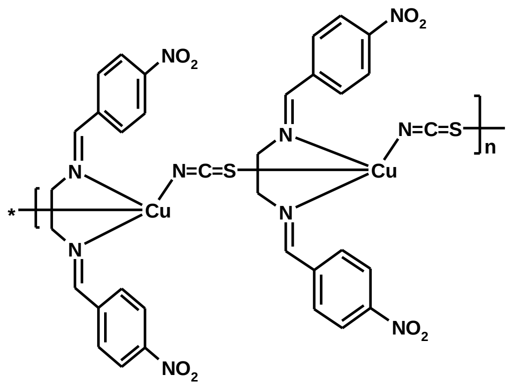
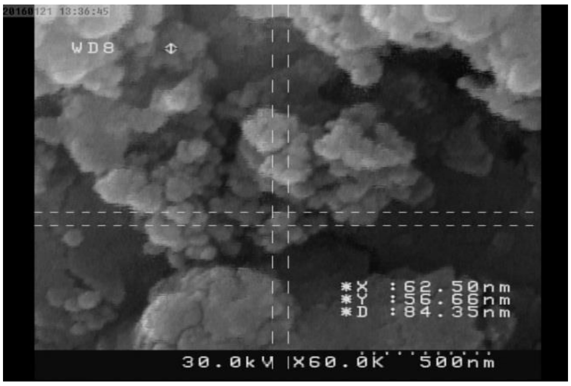
ABSTRACT: Nano-sized powder of a new 1D copper(I) coordination polymer, $[Cu(nba_2en)(NCS)]_n$ (**1**), (nba_2en = N,N′-bis(4-ntrobenzylidene)ethane-1,2-diamine, was synthesized using ultrasonic bath assisted and characterized by scanning electron microscopy (SEM), IR and ^{1}H-NMR spectroscopy, and elemental analyses. Thermal stability of **1** was studied using thermogravimetric (TG) and differential thermal analyses (DTA). The crystal structure was investigated by single-crystal X-ray diffraction. The structure of **1** consists of a 1D polymeric chain in which copper(I) ions are bridged by two thiocyanate group bonding in an end-to-end fashion, with Cu···Cu separation 5.556(4) Å.

KEYWORDS: Nano-Sized; Single-Crystal X-Ray Diffraction; 1D Polymeric Chain; Crystal Structure.

GRAPHICAL ABSTRACT:





1. Introduction

Transition metals coordination polymers are known for their interesting structures [1,2] and useful properties including third-order nonlinear optical response and luminescency [3,4]. They are also used as precursors for synthesis of the transition metal oxides in a nano size [5,6]. The copper(I) ion with d^{10} electronic configuration is suitable for the

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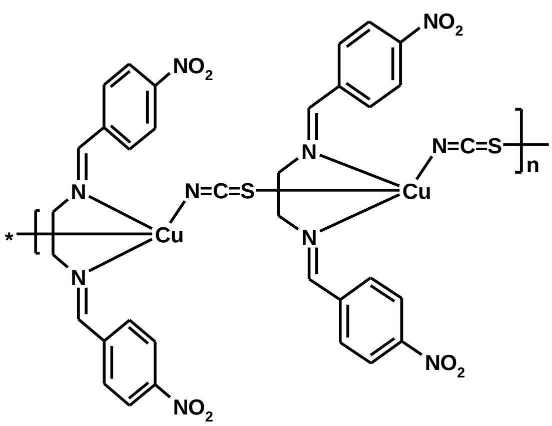
preparation of one, two and three-dimensional coordination polymers [7,8]. Different flexible ligands [9-11] as well as halides or pseudohalides [3,12-14] have been widely used for this purpose. Among them, we focused to Schiff bases with a flexible spacer between iminic nitrogen atoms, which are suitable for this matter [7-9], especially when completed with the pseudohalide NCS^- known to coordinate to copper(I) ions in an end-to-end bridging mode [3, 13, 14]. Here, we describe synthesis and characterization of a new 1D copper(I) coordination polymer, $[Cu(nba_2en)(NCS)]_n$ (**1**) (Scheme 1), prepared as a nanomaterial and as a single crystal.



Scheme 1 Chemical structure of $[Cu(nba_2en)(NCS)]_n$ (**1**)

2. Experimental

2.1. Preparation of $[Cu(nba_2en)(NCS)]_n$ (1) (single crystals)

To a solution of nba_2en (0.01 mmol) in CH_3CN (5 mL) a solution of CuNCS (0.1 mmol) in CH_3CN (5 mL) were added. The reaction mixture was stirred for 10 minutes. With the slow evaporation of solvent, Yellow-orange crystals were formed, then filtered off and washed with Et_2O. Anal. Calcd. for $C_{17}H_{14}Cu_1N_5O_4S_1$: C, 45.54.; H, 3.12.; N, 15.63%. Found; C, 45.61.; H, 3.04.; N, 15.65%. FT-IR (KBr, cm^{-1}): 3442, 3092, 2892, 2073, 1591, 1574, 1514, 1493, 1312, 1267. ^1H NMR (DMSO-d_6, ppm): 3.97 (s, 4H, -C-C**H**$_2$-C**H**$_2$-C-), 7.97 (d, 4H, Ar-**H**), 8.26 (d, 4H, Ar-**H**), 8.52 (s, 2H, -C**H**=N-).

2.1. Preparation of $[Cu(nba_2en)(NCS)]_n$ (1) (nanoparticles)

To a solution of nba_2en (0.01 mmol) in CH_3CN (5 mL) positioned in an ultrasonic bath, a solution of CuNCS (0.1 mmol) in CH_3CN (5 mL) were added. The mixture was kept under the ultrasonic bath for 30

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min. After that, the obtained precipitates were filtered off, washed with Et_2O.

2.2. X-ray Structure Determination

A single crystal of the dimensions 0.40 mm × 0.19 mm × 0.06 mm of **1** was chosen for an X-ray diffraction study. Both experiments were done at 95K on a four-circle diffractometer SuperNova of Rigaku Oxford Diffraction using Cu-*K*α (λ = 1.54184 Å) microfocus mirror-collimated source and a CCD detector Atlas S2. Crystal structures were easily solved by charge flipping with program SUPERFLIP [15]. The symmetry analysis of the resulting electron density clearly indicated that the crystal has only the trivial symmetry. The structure model from charge flipping was completed and refined with the Jana2006 program package [16] by Full-matrix least-squares technique on F^2. The molecular structure plots were prepared by the Diamond 4.0 [17]. All hydrogen atoms are discernible in difference Fourier maps and could be refined to reasonable geometry. According to common practice, H atoms bonded to C were kept in ideal positions with C–H = 0.96 Å and with U_{iso}(H) set to 1.2U_{eq}(C). No hydrogen atoms were found on nitrogen. All non-hydrogen atoms were refined using harmonic refinement. Crystallographic data and details of the data collection and structure solution and refinement are listed in Table 1.

2.3. Materials and Instruments

All the used materials were commercially available and used as received without further purifications. Fourier transform infrared (FT-IR) spectra were recorded on a KBr disk on an FT-IR Perkin–Elmer spectrophotometer. The ^{1}H-NMR spectrum was recorded on a BRUKER DRX-400 AVANCE spectrometer at 400 MHz for the Schiff base ligand. All chemical shifts are reported in *δ* units downfield from TMS. Elemental analysis conducted using a Heraeus CHN-O-Rapid analyzer. The results of the elemental analysis agreed with the

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calculated values. The TGA was performed on a Perkin Elmer TG/DTA lab system 1 (Technology by SII) in an argon atmosphere with a heating rate of 20 ºC/min in the temperature span of 25 –700 ºC. The scanning electron microscopy (SEM) images of the complex were obtained using a Philips XL-30E SEM.

Table 1. Crystallographic data and structure refinement details

Formula weight	$C_{17}H_{14}Cu_1N_5O_4S_1$	μ, mm^{-1}	3.04
Formula weight	447.9	R_{int}	0.045
Crystal system, Space group	Triclinic, *P*1	*S*	1.49
a, Å	5.5562 (3)	Measured reflections	6246
b, Å	7.4319 (5)	Measured independent	3084
c, Å	11.9363 (8)	Parameters	254
α, deg	97.113 (5)	Reflections with I > 3σ(I)	2987
β, deg	91.403 (5)	$R(F^2 > 3\sigma(F^2))$	0.044
γ, deg	108.341 (5)	$wR\ (F^2)$	0.105
V, $Å^3$	463.19 (5)	$\Delta\rho_{max}$, $\Delta\rho_{min}$	0.27, -0.35
Z	1	T_{min}, T_{max}	0.492, 0.838
		Size, mm	0.40 × 0.19 × 0.06

3. Results and Discussion

3.1. Spectroscopic Characterization

In the FT-IR spectrum of **1** (Figure 1), the weak absorption bands around 3000 cm^{-1} are assigned to the C-H vibration modes of the C-H aromatic and aliphatic atoms. The strong bands at 2073 cm^{-1} and 1591 cm^{-1} are assigned to υ(SCN) and υ(C=N) groups, respectively [13,14].

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The [1]H-NMR spectrum of **1** (Figure 2) displays two singlet signals at 3.97 ppm and 8.52 ppm which are assigned to ethylenic and iminc protons, respectively [7,9,13]. In addition, two doublet signals of the aromatic protons are appear at 7.97 and 8.26 ppm. The appearance of the unique signal for proton indicates that the shape of the molecule was retained in DMSO-d[6] solution [13].

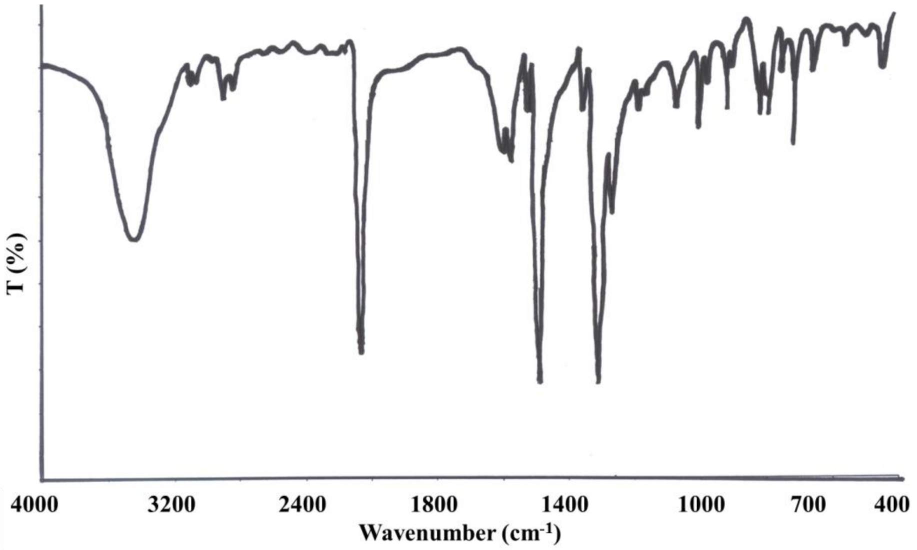

Fig .1. FT-IR spectrum of **1**

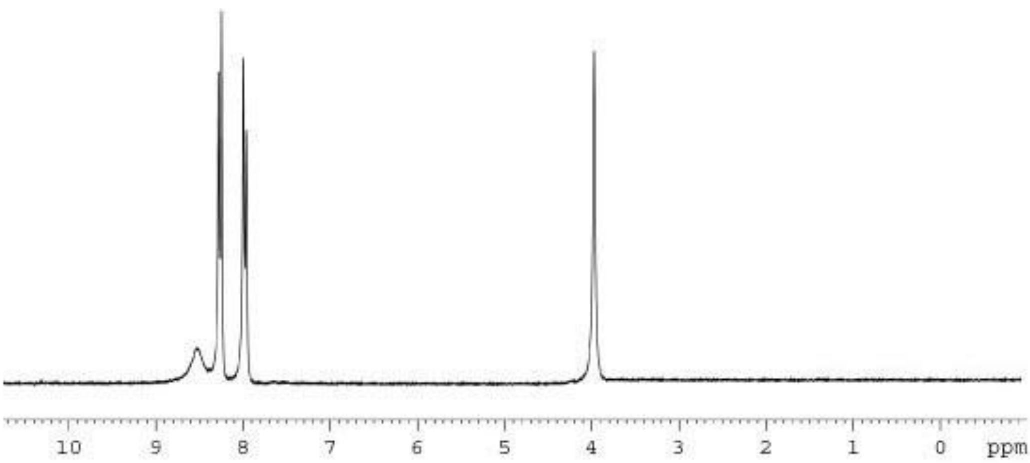

Fig. 2. [1]H-NMR spectrum of **1**

3.2. Thermal Analysis

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TG/DTA curve of **1** are demonstrated in Figure 3. The complex **1** is stable up to 190 °C, and over the further heating it will undergo decomposition in two stages. The first stage occurs at 190-335 °C, and it is associated with a mass loss of 19.93% (calcd. 20.51%) corresponding to the removal of two NO_2 groups. At the second stage from 335 to 700 °C, complex **1** illustrates a mass loss of 32.48% (calcd. 33.93%) corresponding to the removal of two C_6H_4-segments. The decomposition of **1** is not finished at 700 °C and continues beyond this temperature.

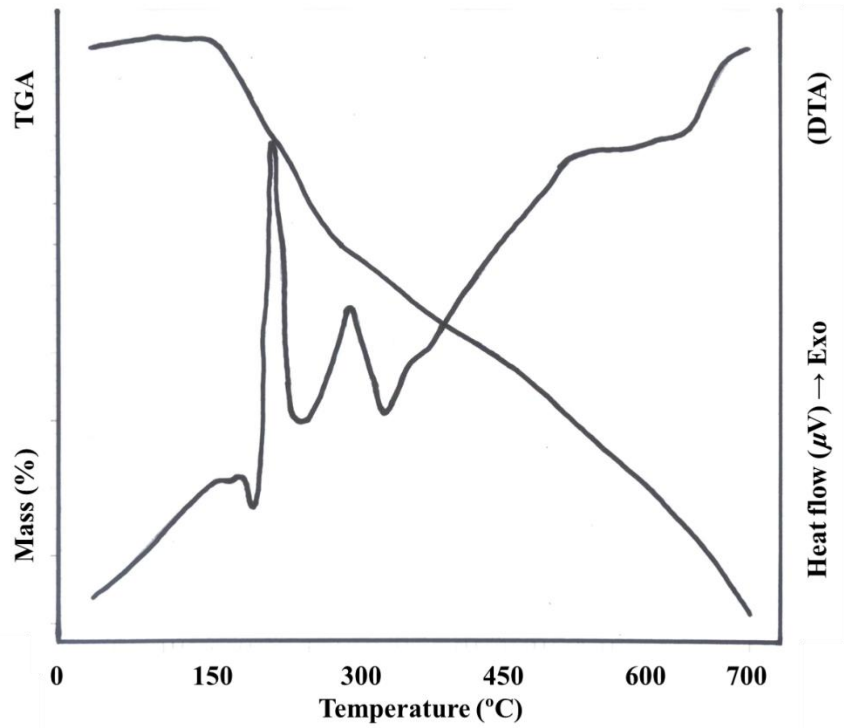
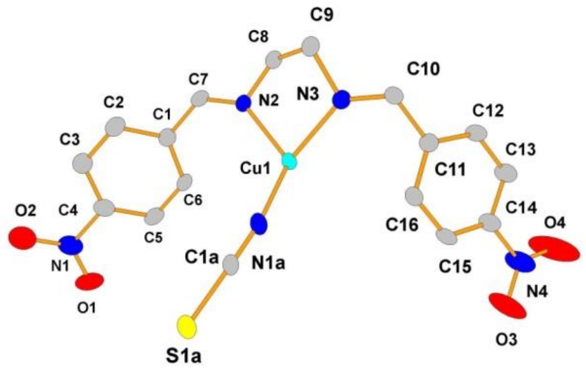


Fig. 3. TG/DTA curves of **1**.

3.3. Crystal Structure of 1

Figure 4 reveals the asymmetric unit of the crystal structure of **1**, and the way molecules are connected into a 1D coordination polymer. The crystallographic details are given in Table 1, selected bond distances and angles are given in Table 2. The Schiff base ligand nba$_2$en coordinates to copper(I) ion as a bidentate NN chelating ligand, giving rise to Cu(nba$_2$en) units. These units are bridged by NCS anions to form a neutral 1D copper(I) complex **1**. The copper(I) ion is coordinated to two nitrogen atoms from Schiff base ligand nba$_2$en, and one nitrogen and one sulfur atom from two distinct bridging thiocyanates [13,14]. The differences between bond distances (Cu1-N3 = 2.050(3), Cu1-N2 = 2.141(2) and Cu1-N1a = 1.922(4) Å) and angles (N2-Cu1-N3 = 83.78(6), N3-Cu1-S1 = 108.27(5), N2-Cu1-S1 = 106.86(7), N3-Cu1-N1a = 133.03(14) and N2-Cu1-N1a = 119.42(5)º) around copper(I) ion confirmed distortion of the tetrahedral geometry.

a



b

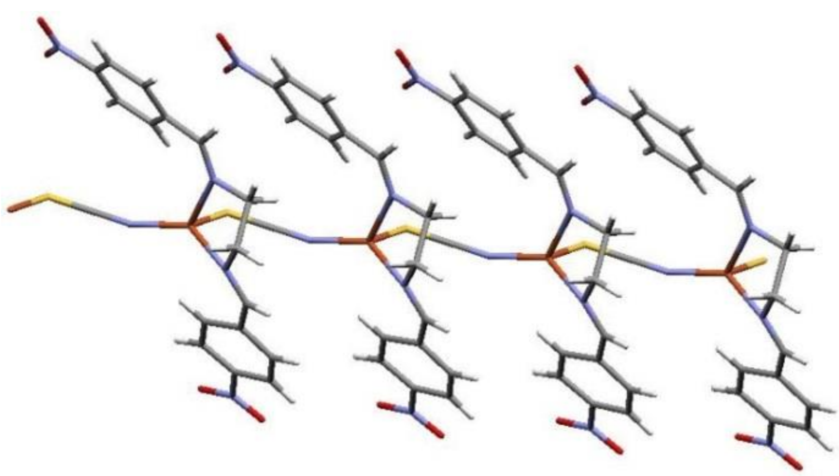


Fig. 4. The crystal structures of maker unit (a) and 1D coordination polymer of **1** (b).

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The 1D chains of the molecules are extended along a. These chains are connected by C-H…O hydrogen bonds and O…centroid interaction (Table 3, Table 4, Figure 5).

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

Cu1-N3	2.050(3)	Cu1-N2	2.141(2)
Cu1-N1a	1.922(4)	S1a-C1a	1.649(4)
N1-C4	1.465(6)	N4-C14	1.468(6)
N2-C7	1.281(6)	N3-C10	1.274(6)
N2-C8	1.455(5)	N3-C9	1.467(5)
N3-Cu1-N1a	133.03(14)	N2-Cu1-N1a	119.42(5)
C7-N2-C8	117.8(3)	C9-N3-C10	117.3(3)
Cu1-N3-C9	108.0(2)	Cu1-N3-C10	132.3(3)
Cu1-N2-C7	135.93(5)	Cu1-N2-C8	106.55(3)
Cu1-N1a-C1a	163.5(3)	S1a-C1a-N1a	178.8(4)
N2-C7-C1	123.7(3)	N3-C10-C11	124.7(3)
N2-C8-C9	109.0(3)	N3-C9-C8	108.9(3)

Table 3. Hydrogen-bond geometry (Å, °)

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
C3—H1*c*3⋯O4^{i}	0.96	2.35	3.281 (8)	163.77
C12—H1*c*12⋯O3^{ii}	0.96	2.31	3.219 (5)	156.69

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

Table 4: Y-X…centroid geometry (Å, °)

Y—X⋯*Cg*	X⋯*Cg*	*Y*—X⋯*Cg*

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N1—O2⋯Cg3[i]	3.202(4)	86.6(3)

Symmetry codes: (i) *x*, *y*, *z*−1; Cg3 = centroid of C11, C12, C13, C14, C15, C16

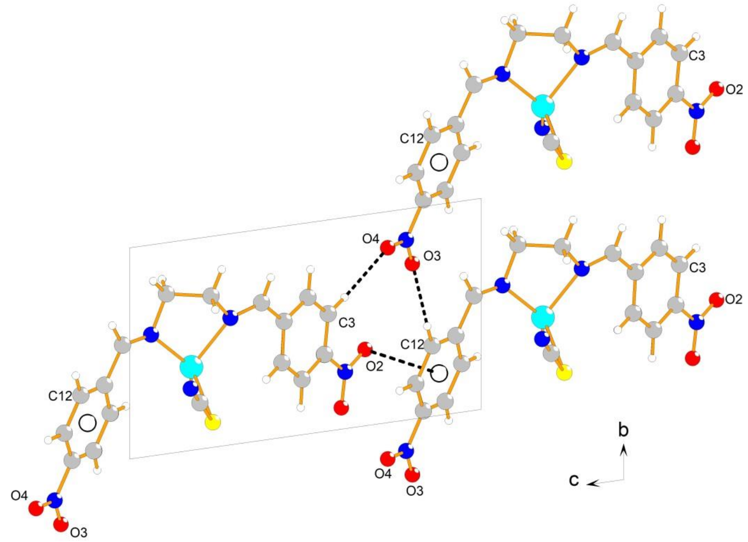

Fig. 5. Chains of molecules connected by C-H…O hydrogen bonds and N1-O2…Cg3 interactions. Centroids of C11, C12, C13, C14, C15, and C16 rings are visualized as open white circles. For symmetry codes and distances, refer to Tables 3 and 4.

3.4. Nano-form of 1

Nano-form of **1** was prepared by an ultrasonic bath assisted synthesis in an acetonitrile solution and characterized by FT-IR and SEM. The FT-IR spectrum of nanoparticles with the same crystals spectrum is similar, although there is a slight shift in the peaks. The method of preparation of nanoparticles and crystals is not the same. Therefore, only nanoparticles are characterized by SEM (Fig. 6). The SEM image showed the particles have practically uniform shapes and sizes. The nanoparticle size is less than 60 nm.

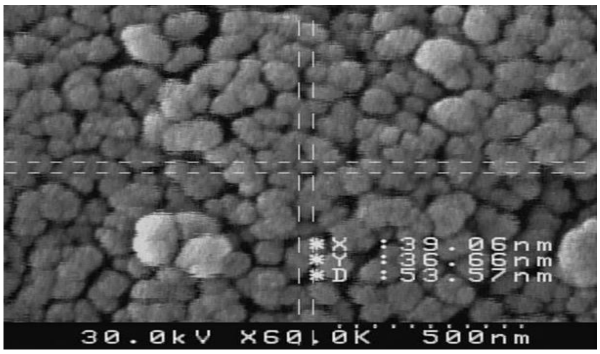

Fig. 6. SEM image of nano-sized of **1**.

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Conclusions

A new 1D copper(I) complex $[Cu(nba_2en)(NCS)]_n$ (**1**), was prepared and characterized using elemental analysis, FT-IR and ^{1}H-NMR spectroscopy. The thermal analysis gravimetry was studied, as well The crystal structure of the title compound was determined using the single crystal X-ray diffraction. The geometry around the copper(I) in **1** distorted tetrahedron, and completed by two nitrogen atoms from bidentate Schiff base ligand and one sulfur atom and one nitrogen atom from two bridging NCS. The azide bridges formed a one-dimensional structure for this complex.

Supplementary Data

Crystallographic data (excluding structure factors) for the structure reported in this paper has been deposited with the Cambridge Crystallographic Center, CCDC No. 1821073. Copy of the data can be obtained free of charge on deposit@ccdc.cam.ac.uk

Acknowledgments

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