

A new 2D Ni(II) coordination polymer: synthesis, crystal structure, and electrochemical properties

*Liying Yu*¹, *Hongxu Bai*¹, *Jiamu Song*²,
*Heyun Zhu*², *Jiao Guan*², *Yanan Luo*²

¹College of Chemical and Pharmaceutical Engineering, Jilin Institute of Chemical Technology, 45 Chengde Str., 132022 Jilin, P. R. China

²College of Pharmacy, Jilin Medical University, 5 Jilin Str., 132013 Jilin, P. R. China

Received June 26, 2023

One Ni(II) metal organic coordination polymer based on H₃L (H₃L = 5-amino-8-hydroxyquinoline), $\{[Ni(H_2L^-)_2] \cdot H_2O\}_n$ (**1**), has been synthesized. This compound has an infinite 2D layer structure. Compound **1** is the first example of a TiO₂ photoanode co-sensitized by the H₃L coordination compound with N719. In the tandem structure of compound 1/N719/TiO₂, compound **1** reorganizes the energy levels due to its single-crystal structure, which improves the photoelectric conversion efficiency. The results show that the compound 1/N719/TiO₂ solar cell has excellent photovoltaic performance with a photovoltaic conversion efficiency of 3.34 % under standard solar irradiation conditions of AM 1.5. The electrochemical properties of compound **1** were studied.

Keywords: metal organic coordination polymer, hydrothermal conditions, supramolecular network, electrochemical property.

Новий двовимірний координаційний полімер Ni(II): синтез, кристалічна структура та електрохімічні властивості. *Liying Yu, Hongxu Bai, Jiamu Song, Heyun Zhu, Jiao Guan, Yanan Luo*

Синтезовано металоорганічний координаційний полімер Ni(II) на основі H₃L (H₃L = 5-аміно-8-гідроксихінолін), $\{[Ni(H_2L^-)_2] \cdot H_2O\}_n$ (**1**). Ця суміш має структуру нескінченних двовимірних шарів. Сполука **1** є першим прикладом координаційної сполуки H₃L, спільно сенсibilізованої фотоанодом TiO₂ з N719. У тандемній структурі 1/N719/TiO₂ сполука **1** реорганізує енергетичні рівні завдяки своїй монокристалічній структурі, що сприяє підвищенню ефективності фотоелектричного перетворення. Результати демонструють, що сонячна батарея 1/N719/TiO₂ має чудову фотоелектричну продуктивність з ефективністю фотоелектричного перетворення 3,34 % за стандартних глобальних умов сонячного опромінення AM 1,5. Визначено електрохімічні властивості сполуки **1**.

1. Introduction

Organometallic coordination polymers refer to supramolecular compounds in which central ions or ionic clusters are linked to organic ligands by ionic-covalent or covalent bonding through a self-assembly process [1]. There are both metal ions and organic ligands in organometallic coordination

polymers, therefore, they have the activity characteristics of inorganic metals, the structural characteristics of organic compounds, and the characteristics of functional groups [2, 3]. Organometallic coordination polymers have rich and diverse properties and have a wide range of applications in catalysis, electrochemical energy storage, fluorescence and chemical sensing [4–6]. Or-

ganometallic materials are applied in battery electrodes and supercapacitor electrode materials due to their excellent characteristics such as controllable morphology, high specific surface area, abundant pores and multi-function [7, 8]. In recent years, organometallic compounds and their composites have been widely used, including lithium-ion batteries (LiBs), lithium-sulfur batteries (Li-S), dye-sensitized solar cells (DSSC) and supercapacitors (SC) [9, 10]. As for the porous open skeletal structure of organometallic compounds of 5-amino-8-hydroxyquinoline, it has a good rigid structure and can increase the stability of the compounds [11]. In addition, when the organic ligands containing O and N functional groups form metal compounds, the delocalization of electrons is further increased; this can not only greatly increase the maximum absorption wavelength of the ligand, but also improve its photoelectric conversion efficiency [12]. Therefore, the exploration and design of coordination polymers with novel structures and excellent properties as new materials has become one of the important topics in the field of optoelectronics.

In this paper, we describe the synthesis of a new compound, $\{[Ni(H_2L^-)_2] \cdot H_2O\}_n$ (**1D**). Its electrochemical properties have been investigated. This is the first example of a metal coordination polymer based on the H_3L ligand cosensitizing TiO_2 photoanodes with N719; and the reason of the improving the photoelectric conversion efficiency is also investigated. The compound **1**/N719/ TiO_2 tandem structure shows much higher photoelectric conversion efficiency. The results show that the compound **1** may have potential applications in the field of photoactive materials.

2. Experimental

Synthesis of $\{[Ni(H_2L^-)_2] \cdot H_2O\}_n$ (1**).** An aqueous solution (12 mL) containing H_3L (5 mg, 0.031 mmol), $NiCl_2$ (30 mg, 0.23 mmol), H_2O (2 mL), methanol (10 mL) and dimethylamine (0.025 mL) was stirred at room temperature for 1 h until a clear green solution formed, finally transferred into a Parr Teflon lined stainless steel vessel (25 mL) and heated to 120°C for 72 h under autogenous pressure. Afterwards, it was cooled to 25°C at a rate of 4°C·h⁻¹. Green block crystals were obtained after washing with methanol and drying in air, in about 45 % yield (based on Ni). A similar calculation for $C_{18}H_{16}N_4NiO_3$ (395.06): C

54.72; H 4.08; N 14.19 %; found: C 4.02; H 2.70; N 14.23 %.

Structure determination. Reflection intensity data for compound **1** was measured at 293 K on a diffractometer Bruker Apex II with a CCD area-detector (Mo $K\alpha$, 0.71073 Å). An empirical absorption correction was applied to the data using the SAD-BAS program. The structure was solved by the direct method (SHELXS-97) and refined by the full matrix least squares method [13]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located geometrically by the program OLEX 2 [14]. The final formula was derived from crystallographic data combined with elemental and thermogravimetric analyses data. The CCDC number of compound **1** is 2267800.

Testing the electrochemical properties. The average cell of the TiO_2 film was 0.25 cm². The film electrodes were soaked in the compound **1** solution (concentration: 5·10⁻⁴ M, solvent: absolute ethanol) for 3 h and N719 solution (concentration: 5·10⁻⁴ M, solvent mixture: acetonitrile and absolute ethanol in the volume ratio of 1:1) for 20 h at room temperature, respectively. Then, the co-sensitized films were dry in air. The counter electrodes were a thermally platinized conducting glass (5 mM H_2PtCl_6 in dry isopropanol, heated at 400°C for 10 min). The electrolyte was consisted of 0.5 M LiI, 0.05 M I_2 , 0.1 M 4-tert-butylpyridine in a 1:1 volume ratio of acetonitrile-propylene carbonate. The photocurrent-photovoltage ($J-V$) curve of the sealed cells was measured under AM 1.5 illumination (100 mW·cm⁻² using a solar simulator. Based on the $J-V$ curve, the fill factor (FF) is defined as: $FF = (J_{max} \cdot V_{max}) / (J_{sc} \cdot V_{oc})$ where J_{max} and V_{max} are the photocurrent density and photovoltage for maximum power output (J_{sc} and V_{oc} are the short-circuit photocurrent density and open-circuit photovoltage, respectively). $\eta = (FF \cdot J_{sc} \cdot V_{oc}) / P_{in}$ is the photoelectric conversion efficiency (P_{in} is the power of incident light).

3. Results and discussion

$\{[Ni(H_2L^-)_2] \cdot H_2O\}_n$ (**1**) was synthesized by the traditional hydrothermal method with $NiCl_2$ and H_3L . Single-crystal X-ray diffraction analysis reveals that compound **1** crystallizes in the orthorhombic crystal system, space group $Pbcn$, which exhibits an infinite 2D layer structure (Table 1). In addition,

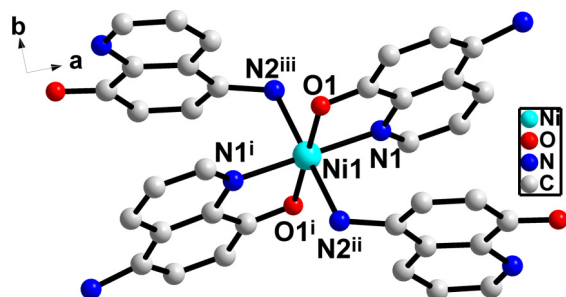


Fig. 1. Coordination environments of Ni1 in compound **1** (symmetry codes for compound **1**: i, $-x, 1-y, 1-z$; ii, $0.5-x, -0.5+y, z$; iii, $-0.5+x, 1.5-y, 1-z$. All hydrogen atoms are omitted for clarity).

the asymmetric structural unit of compound **1** contains a Ni(II) ion, two H_2L^- ligands and one molecule of crystallization water (Fig. 1).

A Ni(II) ion is six coordinated by two oxygen atoms and four nitrogen atoms. Among them, Ni1 is coordinated by O1, O1ⁱ, N1 and N1ⁱ of the 8-hydroxyquinoline rings from two H_3L^- ligands and two nitrogen atoms (N1ⁱⁱ and N1ⁱⁱⁱ) from the amino groups of the other two H_3L^- ligands, forming a distorted octahedral geometry. In compound **1**, each H_2L^- ligand acts as the μ_2 -tridentate ligand binding to two adjacent Ni (II) atoms via an amino group and a quinoline group. The amino group and quinoline group of H_2L^- ligand exhibit two different types of coordination modes. The first category, due to the amino group (N2) adopts a monodentate coordination mode. The second category due to the quinoline group (O1 and N1) shows a chelation coordination mode. In addition,

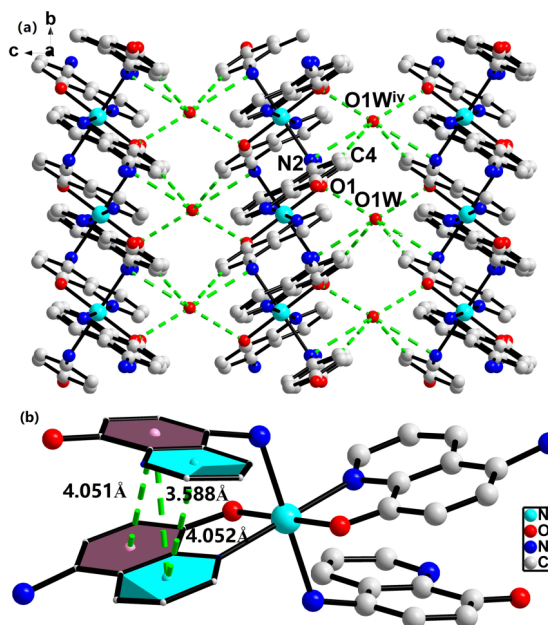


Fig. 2. (a) Compound **1** formed during the crystallization of the H_2O molecule due to the interaction of hydrogen bonds with the formation of a three-dimensional supramolecular network; (b) π - π interactions of compound **1** (symmetry code: iv, $0.5+x, 0.5+y, 1.5-z$. All hydrogen atoms are omitted for clarity).

the bond angle range of O/N–Ni1–O/N is $[81.83(2)^\circ-180.0^\circ]$. The distances of Ni–O/N $[0.2028(3)-0.2220(4)$ nm] are comparable with those found in other related Ni(II) compounds (Table 2).

In the crystalline construction, the 2D structure is connected into a three-dimensional (3D) supramolecular network structure by hydrogen bonding (Table 3). O1W

Table 1. Compound **1**: crystal data collections and structure refinements

Compound 1			
Formula	$C_{18}H_{16}N_4NiO_3$	<i>Fw</i>	395.06
Crystal system	Orthorhombic	<i>V</i> , nm ³	1.6187(2)
Temperature, K	293(2)	Space group	
α , °	90	ρ_{calc} , Mg·m ⁻³	1.621
β , °	90	μ , mm ⁻¹	1.226
γ , °	90	Reflections collected	1479
<i>a</i> , nm	1.3157(5)	<i>Z</i>	4
<i>b</i> , nm	0.8101(3)	<i>F</i> (000)	816
<i>c</i> , nm	1.5186(7)	θ range, °	3.10–25.34
Final $R^{a,b}$ indices	$R_1 = 0.0479$	<i>R</i> indices (all data)	$R_1 = 0.0671$
$[I > 2\sigma(I)]$	$wR_2 = 0.1229$		$wR_2 = 0.1413$
Independent reflections (R_{int})	1054(0.0295)	GOF	1.072

Table 2. Selected bond lengths (nm) and angles (°) for compound 1

Compound 1			
Ni1–O1	0.2028(3)	Ni1–O1 ⁱ	0.2028(3)
Ni1–N1 ⁱ	0.2073(4)	Ni1–N1	0.2073(4)
Ni1–N2 ⁱⁱ	0.2220(4)	Ni1–N2 ⁱⁱⁱ	0.2220(4)
O1–Ni1–O1 ⁱ	180.0	O1–Ni1–N1 ⁱ	98.17(2)
O1–Ni1–N1	81.83(2)	O1 ⁱ –Ni1–N1 ⁱ	81.83(2)
O1 ⁱ –Ni1–N1	98.17(2)	O1 ⁱ –Ni1–N2 ⁱⁱ	90.36(2)
O1 ⁱ –Ni1–N2 ⁱⁱⁱ	89.64(2)	O1–Ni1–N2 ⁱⁱⁱ	90.36(2)

Table 3. Hydrogen bond distances [nm] and angles [°] in compound 1

D–H	<i>d</i> (D–H)	<i>d</i> (H...A)	DDHA	<i>d</i> (D–A)	Å
O1W–H1W	0.085	0.186	171	0.2702(4)	O1
N2–H2A	0.097(6)	0.223(6)	148(5)	0.3092(5)	O1W ^{iv}
C4–H4	0.093	0.258	144	0.3377(5)	O1W ^{iv}

Symmetry code for compound 1: iv, 0.5+x, 0.5+y, 1.5-z.

Table 4. Selected $\pi\cdots\pi$ interactions geometry for compound 1

Cg(I) → Cg(J)	Cg–Cg, Å	α , °	β , °	γ , °	CgI_Perp, Å	CgJ_Perp, E
Cg3 → Cg3 ⁱⁱ	4.052(2)	21	31.04	30.05	3.507(2)	-3.472(2)
Cg3 → Cg4 ⁱⁱ	3.588(2)	20.41(2)	13.43	11.62	3.514(2)	-3.490(2)
Cg4 → Cg4 ⁱⁱ	4.051(2)	20	30.02	29.86	3.513(2)	-3.508(2)

Cg(I) = Plane number I (= ring number in () above) (Cg3 = N1 → C6 → C5 → C9 → C7 → C8; Cg4 = C1 → C2 → C4 → C3 → C5 –C6) (Symmetry code for compound 1: ii, 0.5-x, -0.5+y, z)

Cg–Cg = Distance between ring Centroids (Ang.)

Alpha = Dihedral Angle between Planes I and J (Deg)

Beta = Angle Cg(I) → Cg(J) or Cg(I) → Me vector and normal to plane I (Deg)

Gamma = Angle Cg(I) → Cg(J) vector and normal to plane J (Deg)

CgI_Perp = Perpendicular distance of Cg(I) on ring J (Ang.)

CgJ_Perp = Perpendicular distance of Cg(J) on ring I (Ang.)

acts as a hydrogen bond donor and acceptor bonds to O1, N2 and C4 atoms in a H₂L⁻ ligand molecule [*d*(O1W...O1) = 0.2702(4) nm, ∠O1W–H1W...O1 = 171°; *d*(N2...O1W^v) = 0.3092(5)nm, ∠N2–H2A...O1W^v = 148°; *d*(C4...O1W^v) = 0.3377(5) nm, ∠C4–H4...O1W^v = 144°] to connect two adjacent layers to form a three-dimensional supramolecular network (Fig. 2(a)). In the crystalline structure, due to the H₂L⁻ ligand containing 8-hydroxyquinoline rings, there are a large number of $\pi\cdots\pi$ stacking interactions (Fig. 2(b)). The range of center distance between 8-hydroxyquinoline rings was calculated by the Platon program as [3.588(2)–4.052(2) Å] (Table 4). Non-covalent bonding forces such as hydrogen bonding and $\pi\cdots\pi$ stacking interaction play an important role in building and stabilizing

the supramolecular grid structure of compound 1.

The phase purity of the bulk material was confirmed by comparison of its PXRD patterns with the simulated pattern from the single-crystal X-ray diffraction study (Fig. 3).

The TGA curve (Fig. 4) shows weight losses of compound 1. The weight loss of 4.50 % (calc. 4.56 %) from 126°C to 163°C is attributed to the release of one molecule of crystallization water. The total weight loss of 76.62 % from 234 to 516°C can be attributed to the release of H₂L⁻ (calc. 76.53 %). According to weight loss analysis, the final product may be NiO (exp. 18.82 %, calc. 18.91 %).

The photoelectric performances are important and significant to coordination polymers, so we performed photoelectric conversion efficiency measurements for

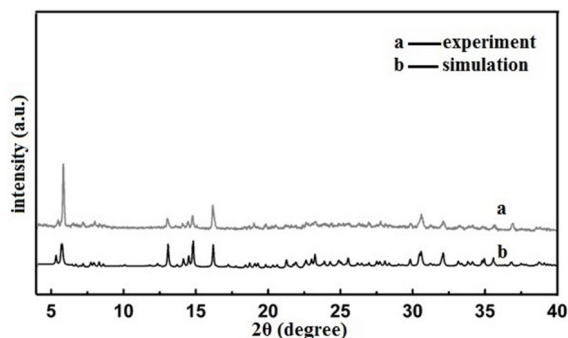


Fig. 3. Experimental (a) and calculated (b) powder X-ray diffraction patterns for compound **1**.

compound **1**. Fig. 5 shows the curves of current density versus voltage for DSSC based on the N719/TiO₂ films and compound **1**/N719/TiO₂ under illumination at 100 mW·cm⁻². The photovoltaic performances of N719/TiO₂-based DSSC, namely, the short photocurrent density (J_{sc}), the open circuit voltage (V_{oc}), the fill factor (FF), and overall energy conversion efficiency (η) are 4.25 mA·cm⁻², 0.65 V, 0.64 and 1.77 %, respectively. For the DSSC compound based on compound **1**/N719/TiO₂, J_{sc} , V_{oc} , FF , and η values are 8.17 mA·cm⁻², 0.67 V, 0.61 and 3.34 %, respectively. V_{oc} is the potential difference between the electrochemical potential of the redox couple in the electrolyte and the conduction band edge of TiO₂ photoanode. V_{oc} value of co-sensitized device increased slightly compared with single N719. This indicated that compound **1** led to the upward shift of the conduction band edge of TiO₂. The photovoltaic performance of DSSC based on the compound **1**/N719/TiO₂ is clearly higher than that of a single N719. J_{sc} of the DSSC based on the compound **1**/N719/TiO₂ is remarkably higher than that of a single N719. This increase in J_{sc} indicates that the compound **1**/N719 effectively sensitizes the TiO₂ photoanode and leads to higher light collection. This co-sensitization of the compound **1** and N719 is an efficient method of improving efficiency. The overall solar conversion efficiency of DSSC based on the compound **1**/N719/TiO₂ tremendously increases to 3.34 %.

The method of cyclic voltammetry was used to study the electrochemical properties of the compound **1**, the mechanism of electron injection from the compound **1** into the conduction band of TiO₂, and the oxidation and reduction regeneration of the compound **1** in the electrolyte. Fig. 6 shows the results

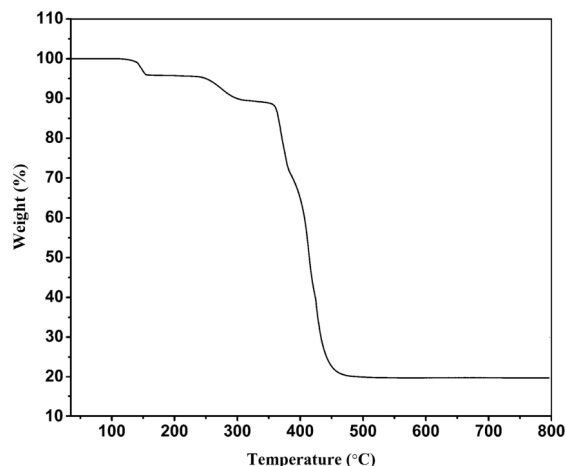


Fig. 4. TGA curve of compound **1**.

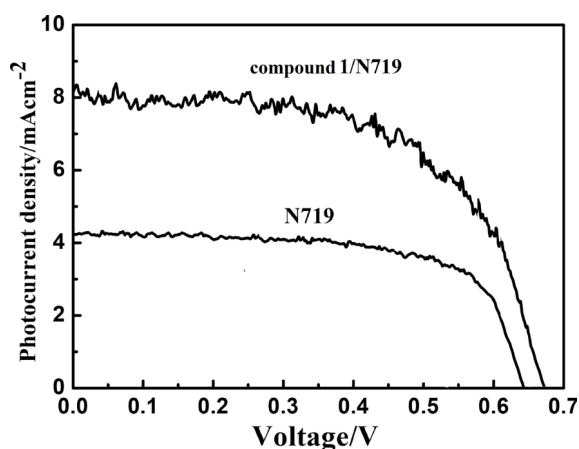


Fig. 5. Photocurrent-photovoltaic curves of dye-sensitized solar cell based on photoanodes of **1**/N719/TiO₂ and N719/TiO₂.

of cyclic voltammetry for the compound **1** in the CH₂Cl₂ solution. The compound **1** exhibits a reversible oxidation-reduction behavior. The excited state oxidation potential of the compound **1** is -1.256 V relative to supercapacitors (SCE), which is sufficiently more negative than the conduction band edge level of the TiO₂ at approximately -0.7 V relative to SCE (Liu et al., 2002). The negative offset of E^* provides the thermodynamic driving force for electron injection from the excited dyes into the conduction band of TiO₂.

4. Conclusion

In this paper, a Ni(II)-based coordination polymer {[Ni(H₂L⁻)₂·H₂O]_n with a 2D structure was successfully synthesized by hydrothermal synthesis using H₃L ligand and Ni(II) ions. The 2D structure is connected into a 3D supramolecular network structure

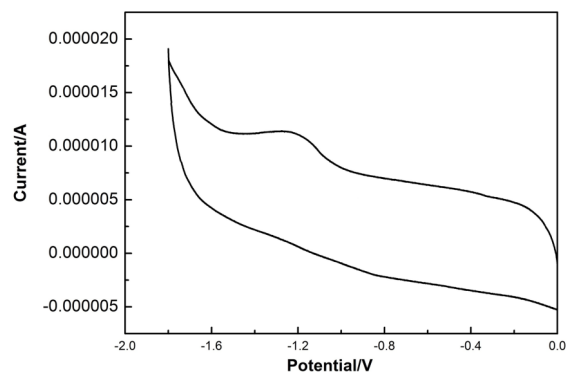


Fig. 6 Cyclic voltammograms of compound **1** in CH_2Cl_2 solution

by hydrogen bonding interaction. Compound **1** exhibited excellent photovoltaic performance with the photoelectric conversion efficiency of 3.34 %. This also indicates that the crystalline material of compound **1** may have potential applications in the field of photoactive materials.

Acknowledgment. This work was supported by the National Science Foundation of China (grant No. 21902058), the Project in Jilin Medical University (No. JYBS2021019LK), Project of Science and Technology Development of Jilin City (No. 20190104161), the Science and Technology Project in Jilin Province Department of Education (No. JJKH20220458KJ), Industrial Technology Research and Development

Project of Jilin Provincial Development and Reform Commission (No. 2023C038-5).

References

1. D.K.Singha, P.Majee, S.K.Mondal et al., *Inorg. J. Photoch Photobio A.*, **365**, 389 (2018).
2. B.Zhang, J.Ying, X.Zhang et al., *New J. Chem.*, **45**, 13340 (2021).
3. G.N.Gui, L.L.Wang, W.B.Liu et al., *J. Solid State Chem.*, **304**, 122562 (2021).
4. N.J.Shamle, A.C.Tella, A.C.Whitwood et al., *J. Coord Chem.*, **74**, 125 (2021).
5. A.Haider, B.S.Bassil, Z.G.Lin et al., *Dalton T.*, **50**, 3923 (2021).
6. X.C.Chai, H.Li, M.Z.Li et al., *Z. Naturforsch B.*, **76**, 319 (2021).
7. Y.N.Wang, S.D.Wang, L.Xu et al., *J. Mol. Struct.*, **1233**, 99 (2021).
8. P.Ju, H.Yang, L.Jiang et al., *Spectrochim Acta A.*, **246**, 118962 (2020).
9. M.Yan, P.Zhu, S.Yang et al., *Crystengcomm*, **23**, 4370 (2021).
10. M.Abedi, S.S.Abolmaali, R.Heidari et al., *Int. J. Pharmaceut.*, **602**, 120685 (2021).
11. J.J.Jiang, Y.Wang, D.S.Wang et al., *Chinese J. Chem.*, **39**, 2789 (2021).
12. B.Safarkoopayeh, A.Abbasi, A.Shayesteh, *Inorg. Chem. Commun.*, **127**, 502 (2021).
13. O.V.Dolomanov, L.J.Bourhis, R.J.Gildea et al., *J. Appl. Crystallogr.*, **42**, 339 (2009).
14. G.M.Sheldrick. SHELXTL NT Crystal Structure Analysis Package[CP]. Version 5.10; Bruker AXS, Analytical X-ray System: Madison, WI (1999).