



2D Cadmium(II) Coordination Polymer Based on 2,5-Furandicarboxylate and 1,4-Bis(1*H*-imidazol-1-yl)butane Linkers: Synthesis, Characterization and DFT Studies

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Received: 29 February 2024 / Accepted: 17 March 2024
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Abstract

As a result of hydrothermal synthesis of 2,5-furandicarboxylate (fdc^{2-}), Cd(II) ion and bis(imidazole) derivative 1,4-bis(1*H*-imidazole-1-yl)butane (bib) ligand, a novel two-dimensional Cd(II) coordination polymer $\{[\text{Cd}(\mu\text{-fdc})(\text{H}_2\text{O})(\mu\text{-bib})]\cdot\text{H}_2\text{O}\}_n$ (**1**) was synthesized. According to the results of single crystal X-ray diffraction analysis, the complex was crystallized in the monoclinic system and in the $P2_1/n$ space group. In addition, the thermal, luminescence and optical properties of the complex were investigated. The complex emits a maximum at 509 nm and also shows semi-conductor properties according to the solid-state UV–Vis diffuse reflection spectra results. To determine chemical structure, vibrational properties and some chemical properties of complex, theoretical calculations were carried out. All theoretical computations were performed using the DFT method at the B3LYP/LanL2DZ level of theory. The obtained experimental results were in good agreement with theoretical results. To calculate HOMO–LUMO energy values, which provided insights into the material's electronic properties, DFT calculations were used. Detailed information about the local and global chemical activity, as well as the electrophilic and nucleophilic nature of the complex, were also obtained.

Keywords Coordination polymer · 2,5-furandicarboxylic acid · 1,4-bis(1*H*-imidazole-1-yl)butane · DFT

1 Introduction

Great attention has been paid to the design and synthesis of new porous materials in the use of new coordination polymers that form 1, 2 and 3-dimensional networks due to their superior electronic, magnetic and structural properties. Coordination polymers represent a class of tunable materials that show promise in many applications such as gas storage [1–3], dye adsorption [4–6], sensor [7–11], catalysis [12, 13], adsorption of volatile organic compounds [14, 15], etc. Compared with conventional materials such as zeolites or

activated carbons, coordination polymers have higher potential due to their high microporosity, functionalizable frameworks and host designable organic linkers that bridge metal centres in various coordination geometries. Additionally, in the design and synthesis of coordination polymers, multidentate carboxylate and N-donor organic ligands are commonly preferred as bridging ligands to connect two metal centres. Designing mixed-ligand coordination polymers in this way increases structural and topological diversity [16–19]. Additionally, complex systems including Cd(II) have a particular interest, because Cd(II) is a highly adaptable metal ion that can form bonds with a wide variety of donor atoms, including N, O, and S atoms. This is because Cd(II) is a borderline acid in the hard-soft acid-base concept. The ability of Cd(II) ions to affect the emission wavelength and strength of organic materials is another reason why they are so attractive for the synthesis of polymeric compounds. Cd(II) ions can do this in several ways. On the other hand, coordination chemists are increasingly using organic molecules with nitrogen, oxygen, and sulfur atoms to build transition metal complexes with inorganic materials. These complexes have diverse applications due to their unique properties, like

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glowing in the dark, influencing magnetism, and speeding up chemical reactions. Scientists can fine-tune the structure of these complexes to achieve specific properties, which is useful for tasks like capturing molecules, developing new materials for light and electronics, and even fighting diseases. Moreover, research suggests that Cd(II) complexes have promising biological applications, including potential use in anticancer treatments, fighting bacterial and fungal infections, and offering antioxidant properties [20–22].

Herein we report the design and synthesis of a new 2D coordination polymer based on 2,5-furandicarboxylic acid (H_2fdc), Cd(II) ion and bis(imidazole) derivative N-donor 1,4-bis(1*H*-imidazol-1-yl)butane (bib). The fdc^{2-} ligand, which is included in the C_2 molecular symmetry group, acts as an anionic binder in the resulting complex and increases the stability of the complex with its angular geometry. The structure of $\{[\text{Cd}(\mu\text{-fdc})(\mu\text{-bib})(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$ (1) two-dimensional (2D) coordination polymer was characterized by elemental analysis, single crystal and powder X-ray diffraction analyses. Thermal, photoluminescence, optical and topological properties of the complex were studied. The obtained complex was characterized by FT-IR and Raman spectroscopic methods. Density functional theory (DFT) calculation is used to determine the structure analysis of the title complex. The DFT (B3LYP/LanL2DZ) approach has been used to interpret the vibrational properties and some theoretical properties of the complex.

2 Materials and Methods

2.1 Materials and Measurements

All chemicals were purchased from commercial sources. The ^1H -NMR spectrum of the bib ligand was captured on a 500 MHz JEOL ECZ 500R at room temperature. DMSO- d_6 and tetramethyl silane (TMS) was used as a solvent and internal standard, respectively FT-IR spectra of H_2fdc and complex were taken with a Bruker Tensor FT-IR spectrometer with the use of a KBr pellet in the range 4000–400 cm^{-1} . Elemental analyses of the complex for C, H and N were performed with a Perkin Elmer 2400 Series II device. A Perkin Elmer Diamond TG/DTA Thermal Analyzer was utilized for thermal analysis curves under a dry air atmosphere in the range of 30–1000 $^\circ\text{C}$. The diffuse reflectance spectra (DRS) were taken on a Shimadzu UV-2600 spectrophotometer using BaSO_4 as a reference in the wavelength range of 200–800 nm. Solid-state photoluminescence spectra of the complex and H_2fdc were measured with a Perkin-Elmer LS-55 spectrophotometer. A Panalytical Empirian X-ray diffractometer with Cu-K α radiation was used to record powder X-ray diffraction patterns. A Bruker Smart Apex II CCD diffractometer outfitted with Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$)

was used for single crystal X-ray diffraction (SCXRD) data collection. SHELXT-2015 program in conjunction with the OLEX2 was used to solve the structures with direct methods and the structure refinements were carried out by full-matrix least-squares on all F^2 data using SHELXL [23–25]. In the structures, all hydrogen atoms were calculated and refined using riding and free modes. The crystal structures were drawn using the Mercury program [26]. ToposPro software was used for topological analyses of the complex [27].

2.2 Computational Details

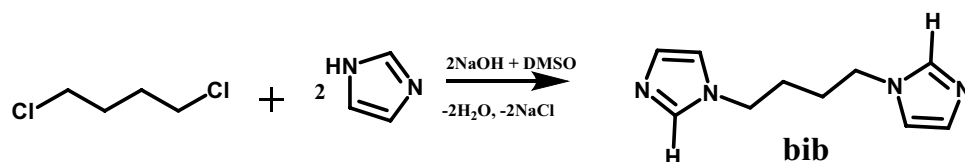
Molecular geometry optimizations, vibrational frequencies and geometric parameters of the complex were computed using the Gaussian 09 program package [28] using B3LYP DFT hybrid methods with Pople type basis set [29]. The valence triple-zeta basis set augmented with diffuse and polarization functions in both the hydrogen and weighty atoms 6–311 + +G(d,p) has been used for geometry optimization and vibrational frequency calculations. The LanL2DZ basis set augmented with polarization and diffuse functions was used for the Cd atom, with the core orbitals replaced by Effective Core Potentials (ECP) [30]. Vibrational frequencies were scaled with the SQM program [31, 32] to generate the corrected frequencies. The fundamental vibrational modes were assigned and the total energy distribution (TED) calculations were performed by the SQM.

2.3 Syntheses of the Compounds

1,4-bis(1*H*-imidazol-1-yl)butane (bib). The product was synthesized according to the procedure in the literature [33]. Imidazole (4.08 g, 60 mmol) and NaOH (2.40 g, 60 mmol) were added to the 60 mL of DMSO and stirred at 60 $^\circ\text{C}$. After 2 h 1,4-dichlorobutane (3.55 g, 28 mmol) was added to the reaction mixture and stirred at 60 $^\circ\text{C}$. After 1 day the mixture was cooled to room temperature and DMSO was removed by evaporation. The crude product was stirred in 100 mL of ice water and collected by filtration. The product was purified by crystallization from a methanol-water (1:4) mixture. ^1H -NMR (500 MHz, CDCl_3 , δ ppm): 7.55 (s, H, CH_{ar}), 7.09 (d, H, CH_{ar}), 6.82 (d, H, CH_{ar}), 3.91 (t, 2H, CH_2), 1.55 (m, 2H, CH_2) (Fig. S1) (Scheme 1).

$\{[\text{Cd}(\mu\text{-fdc})(\text{H}_2\text{O})(\mu\text{-bib})]\cdot\text{H}_2\text{O}\}_n$. A mixture of $\text{Cd}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (0.39 g, 1.28 mmol), H_2fdc (0.20 g, 1.28 mmol), bib (0.24 g, 1.28 mmol) and 30 mL water were stirred at 60 $^\circ\text{C}$. After 30 min the mixture was sealed in a 45 mL Teflon-lined autoclave and heated at 170 $^\circ\text{C}$ for 5 days. The mixture was cooled the room temperature and pale yellow crystals were obtained. Then the crystals were filtered and washed with water. Yield: 0.030 g (48%, based on Cd(II) cation). Anal. Calcd. for $\text{C}_{17}\text{H}_{23}\text{CdN}_4\text{O}_7$ (492.77 g/mol): C, 40.21; H, 4.57; N, 11.03%. Found: C, 39.87; H,

Scheme 1. Synthesis of bib



4.12; N, 10.97%. FT-IR (ν , cm^{-1}): 3453 (–OH), 3115, 2949 (–CH), 1585–1369 (–COO).

3 Results and Discussion

3.1 Descriptions of Crystal Structure

Crystal data and structure refinement parameters for complex **1** are presented in Table 1. The bond lengths (Å) and bond angles ($^\circ$) of complex **1** are given in Table S1. It crystallizes in the monoclinic space group $P2_1/n$, and the asymmetric unit contains one crystallographically independent cadmium (II) centre, one fdc^{2-} , one bib, one aqua ligands and one lattice water molecule. As shown in Fig. 1a, Cd(II) centre is seven-coordinated by four carboxylate oxygen atoms of two different fdc^{2-} ligands, one aqua ligand and two nitrogen atoms of bib ligands in a distorted pentagonal bipyramidal $[\text{CdO}_5\text{N}_2]$ coordination environment. The Cd–O/N bond lengths vary from 1.974 to 2.743 Å. These bond distances compare well to the literature values [34]. The fdc^{2-} ligand acted as a bridging ligand ($\mu\text{-}\eta^1\text{:}\eta^1\text{:}\eta^1\text{:}\eta^1$) between two Cd(II) centres and formed a straight 1D polymeric chain structure (Fig. 1b). The 1D polymeric chain structures were connected by the bib ligand and a 2D layer structure was formed (Fig. 1c). The 3D supramolecular structure is formed by hydrogen bonds and $\text{CH}\cdots\pi$ interactions (Fig. 2a). The lengths of the rectangular frame formed between the bib ligand, fdc^{2-} ligand and Cd(II) centres are $10.141 \times 12.287 \text{ \AA}^2$. The dihedral angle between the imidazole rings in the bib ligand is 9.69° (along N1–N2–N3–N4). Topologically, complex **1** is a uninodal (4)-connected 2D structure and displays sql topology with the point symbol of $\{4^4.6^2\}$ (Fig. 2b).

3.2 Geometrical Structure

The molecular structure of the complex belongs to the C1 point group. The energy value and dipole moment of the complex was calculated as $-1,052,748.3322558 \text{ kcal/mol}$ ($-1677.68658575 \text{ a.u.}$) and 7.5436 Debye, respectively. Single crystal data and the optimized chemical structure are shown in Fig. S2. Table 2 presents the optimized geometric parameters, including bond lengths and angles, obtained from theoretical calculations. These calculated values were

compared to the experimental results derived from the SCXRD analysis of the complex.

The calculated bond lengths and bond angles of the complex were consistent with the experimental results.

3.3 Vibrational Characterization

Infrared and Raman spectroscopic methods are two powerful techniques which can be used to characterize the vibrational properties of molecular systems. Quantum chemical computations can also be used to calculate the vibrational frequencies of molecules. These calculations can provide additional information about the molecular structure and dynamics and can be used to interpret the experimental IR and Raman spectra. The combination of IR and Raman spectroscopy with quantum chemical computations provides a powerful tool for the vibrational characterization of molecular systems [35, 36]. This combination of techniques can be used to study

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

Parameters	1
Empirical formula	$\text{C}_{17}\text{H}_{23}\text{CdN}_4\text{O}_7$
Formula weight	492.77
Crystal system	Monoclinic
Space group	$P2_1/n$
(Å)	8.65 (4)
b (Å)	10.141 (4)
c (Å)	22.882 (10)
α ($^\circ$)	90.00
β ($^\circ$)	90.00 (2)
γ ($^\circ$)	90.00
V (Å ³)	2007.2 (11)
Z	4
D_c (g cm ^{−3})	1.631
μ (mm ^{−1})	1.13
θ range ($^\circ$)	2.2–23.7
Measured refls	29,919
Independent refls	4213
R_{int}	0.055
S	1.06
$R1/wR2$	0.035/0.112
$\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}}$ (e Å ^{−3})	0.94/−0.54

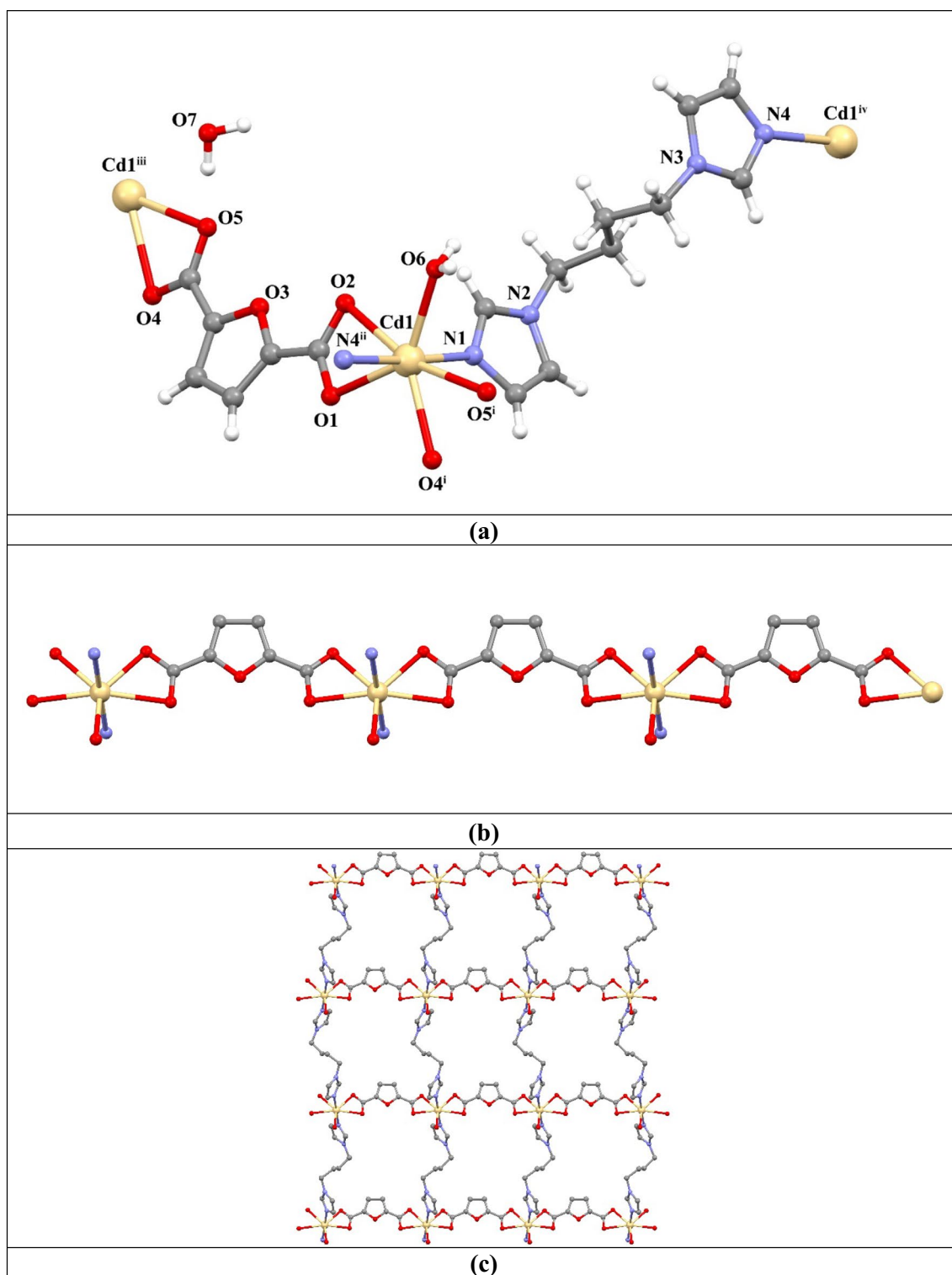


Fig. 1 (a) View of the molecular structure for 1 showing the atom numbering scheme. (b) 1D chain structure of 1. (c) 2D structure of 1 along bc layer

a wide variety of molecular systems, including small molecules, polymers, and biological molecules. Some theoretical and experimental vibrational frequencies and vibrational assignments of the complex are given

in Table 3. Moreover, experimental and theoretical IR and Raman spectra are shown in Fig. 3 and Fig. 4. In addition, some characterization vibrational peaks of the complex are given in Table 3.

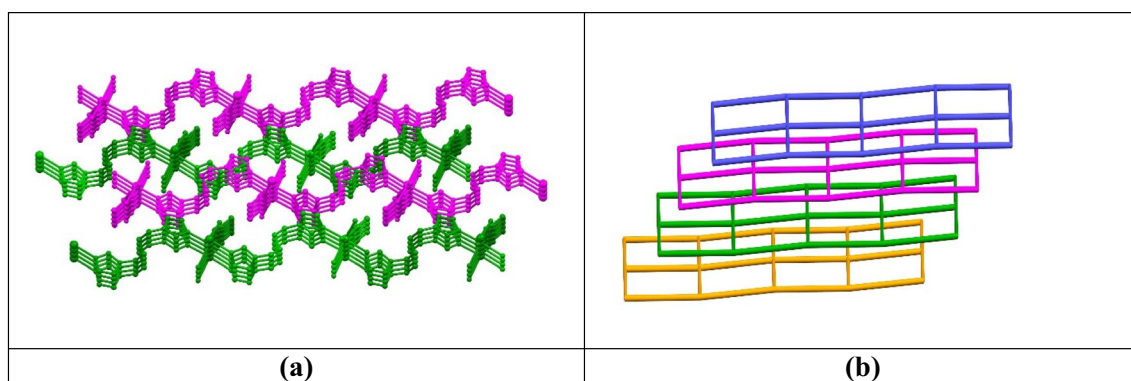


Fig. 2 (a) 3D supramolecular structure of **1** (b) A schematic view of the 2D structure of **1**

Table 2 Values of some selected geometrical parameters of the complex

Parameters	Experimental	Calculated
Bond Lengths (Å)		
Cd1—O2	2.607	2.588
Cd1—O6	2.360	2.345
Cd1—O4	2.446	2.438
Cd1—O1	2.347	2.345
Cd1—O5	2.488	2.485
Cd1—N1	2.263	2.265
Cd1—N4	2.322	2.318
Cd1—O5	2.488	2.485
Bond Angles (°)		
O6—Cd1—O2	85.49	85.38
O6—Cd1—O4	134.41	135.02
O6—Cd1—O5	81.68	81.65
O4—Cd1—O2	140.09	140.00
O4—Cd1—O5	53.48	53.45
O1—Cd1—O2	52.75	52.85
O1—Cd1—O6	134.84	135.85
O1—Cd1—O4	88.64	86.59
O1—Cd1—O5	142.00	140.35
O5—Cd1—O2	164.50	165.20
N1—Cd1—O2	82.05	82.39
N1—Cd1—O6	92.19	91.25
N1—Cd1—O4	95.09	95.40
N1—Cd1—O1	97.39	96.67
N1—Cd1—O5	89.76	90.04
N1—Cd1—N4	176.41	179.25
N4—Cd1—O2	97.33	97.62
N4—Cd1—O6	84.24	85.37
N4—Cd1—O4	87.66	87.96
N4—Cd1—O1	84.97	85.34
N4—Cd1—O5	90.03	89.65

Table 3 Some vibrational frequencies (cm^{-1}) of complex

Assignment	Experimental		Calculated
	FT-IR	Raman	
$\nu(\text{O-H})$ (stret.)	3149	3250	3503
$\nu(\text{C-H})_{\text{arom.}}$ (stret.)	3114	3108	3122
$\nu(\text{CH}_2)$ (stret.)	2949	2952	2951
$\nu(\text{C=O})_{\text{asym.}}$ (stret.)	1713	1705	1728
	1585	1586	1585
$\nu(\text{C=O})_{\text{sym.}}$ (stret.)	1695	1694	1692
$\nu(\text{C-C})$ (stret.)	1611	1615	1618
	1601	1608	1610
	1585	1586	1590
	1530	1532	1535
	1512	1515	1520
	1290	1296	1298
$\nu(\text{C-N})$ (stret.)	1549	1535	1538
$\nu(\text{C-O})$ (stret.)			
$\delta(\text{C-H})_{\text{arom.}}$ (bend.)	1197	1188	1192
	965	966	970
$\nu(\text{Cd-O})$	578	588	590
$\nu(\text{Cd-N})$	522	525	526

The FT-IR spectrum of the H_2fdc ligand indicates a broad band observed at 3453 cm^{-1} attributable to OH stretching. Moreover, CH aromatic stretching, CO stretching and CC stretching vibrational bands of ligand were observed at 3092 cm^{-1} , 1695 cm^{-1} and 1421 cm^{-1} , respectively (Fig. S3).

OH stretching vibration of the carboxylic acid group of the complex was observed at 3149 cm^{-1} as a broad peak in the FT-IR spectrum, at 3250 cm^{-1} in the Raman spectrum and calculated as 3503 cm^{-1} . Moreover, OH stretching vibrations of the crystal water molecule and aqua ligand in the structure of the complex were observed in the range of 3452 cm^{-1} in the spectra. Weak peaks expressing aliphatic and aromatic $\nu(\text{C-H})$ stretching vibrations were observed in the range of $3114\text{--}2949 \text{ cm}^{-1}$ in the IR and Raman

Fig. 3 Experimental (a) and theoretical FT-IR spectra of complex

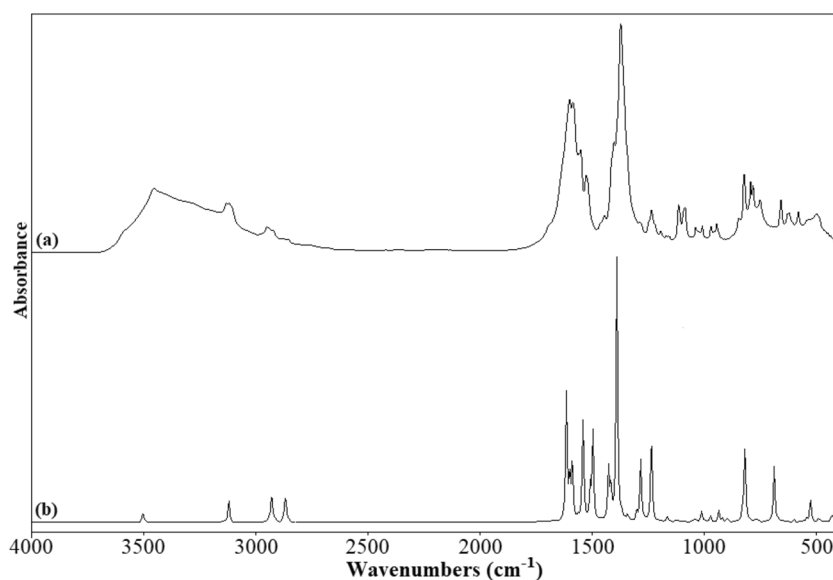
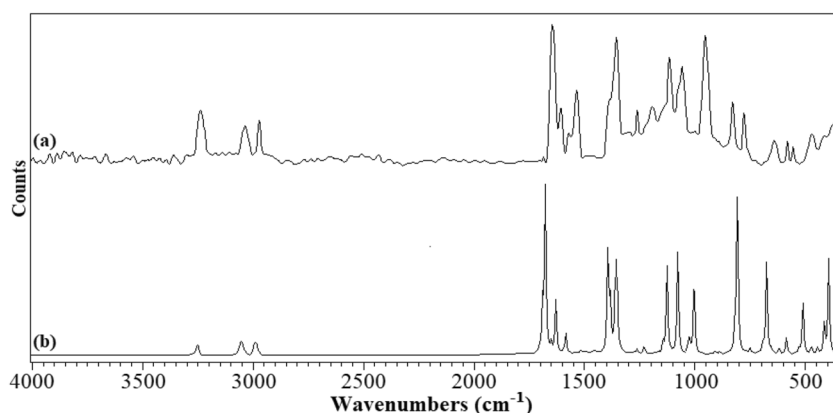


Fig. 4 Experimental (a) and theoretical Raman spectra of complex



spectra. CH stretching vibrations were calculated as 3122 and 2951 cm^{-1} .

Symmetrical ($\nu_s\text{COO}$) and asymmetrical ($\nu_{as}\text{COO}$) stretching vibrations of the carboxylate groups attached to the furan ring were observed at 1695 cm^{-1} and 1713 cm^{-1} in the IR spectrum and 1694 cm^{-1} and 1705 cm^{-1} in the Raman spectrum, respectively. These vibrations were calculated as 1692 cm^{-1} and 1728 cm^{-1} , respectively.

Aromatic C–C stretching modes were observed ranging from 1295 to 1620 cm^{-1} of the complex in the IR and Raman spectra. These modes are in agreement with experimental data after scaling using SQM. In plane CCC modes appeared at 738 , 672 and 645 cm^{-1} in the infrared spectrum, observed at 728 cm^{-1} in the Raman spectrum and these modes were calculated as 735 , 678 and 649 cm^{-1} .

It was concluded that the asymmetric stretching vibrations shifted to a lower wavenumber compared to the asymmetric stretching vibration found in the H_2fdc ligand. This showed that the H_2fdc ligand lost both protons in its

structure and coordinated from oxygen atoms to metal centres. On the other hand, upon coordination, the CN stretching vibration (1571 cm^{-1} of the free ligand) was shifted to a lower frequency at 1549 cm^{-1} indicating the coordination of nitrogen atoms to the Cd(II) ion.

In the IR spectra of ligand molecule, the sharp bands observed at 968 cm^{-1} and 749 cm^{-1} belong to in plane and out of plane CH bending vibrations. In the spectra of the complex, these vibrations were observed at 965 and 751 cm^{-1} in the IR spectrum and at 966 and 749 cm^{-1} in the Raman spectrum, respectively. No significant variation was observed between such vibrational frequencies of both the ligand and the complex. Finally, the new peak observed at 522 cm^{-1} in the IR spectrum and 525 cm^{-1} in the Raman spectrum of the complex was attributed to Cd–N vibration. The bands observed at 578 cm^{-1} in the IR spectrum and 588 cm^{-1} in the Raman spectrum belong to the Cd–O vibrational mode. These wavenumbers are in good agreement with literature [37–39].

3.4 Thermal Analysis

The thermal stability of the complex was determined by simultaneous thermal analysis (STA) techniques (TG and DTA). Thermal analysis of complex **1** was carried out at a temperature range of 30–1000 °C, respectively, in a dry air atmosphere, with a heating rate of 10 °C/min, and the curves obtained are given in Fig. S4. The water molecules in the structure of the complex moved away from the structure at about 150 °C (Fig. S4). It was determined that the complex degrades in three steps. A strong exothermic peak was seen in the third step, *fdc* and *bib* ligands were observed to burn away from the structure. The thermal decomposition product is CdO. It was determined that the mass losses of the decomposition product were in agreement with the calculated values (exp.: 31%, theo.: 26%).

3.5 Powder X-Ray Diffraction, Luminescence and Optical Absorption Results

To determine the phase purity of the obtained complex, powder X-ray diffraction (PXRD) analysis was performed. Experimental and theoretical PXRD patterns of the complex were given in Fig. S5. It has been determined that the theoretical PXRD patterns simulated from the single crystal structure and the experimental PXRD patterns are compatible.

The luminescence properties of H_2fdc and the resulting complex were investigated in a solid state and at room temperature. The emission spectra of H_2fdc and the complex are given in Fig. 5. When the H_2fdc ligand was excited at 320 nm, it emitted intensely at 381 nm. This emission

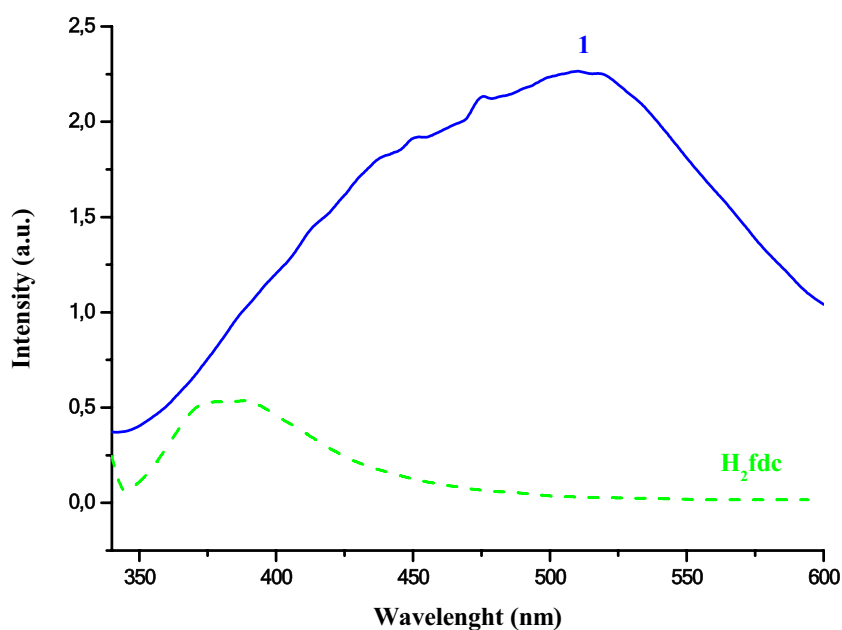
band is thought to originate from $\pi^* \rightarrow n$ or $\pi^* \rightarrow \pi$ transitions in the H_2fdc ligand. Emission maxima at 509 nm for the complex is observed upon excitation at 320 nm. It was determined that the emission band in the complex was redshifted compared to free H_2fdc . This emission may be assigned to ligand-to-metal charge transfer (LMCT) or coordination of the *fdc* ligand to the Cd(II) centres, which significantly increases the rigidity and asymmetry of the ligand.

Solid-state UV–Vis diffuse reflection spectra were obtained to determine the optical absorption properties of the complex and to evaluate the semiconductor properties. The calculated optical band gaps of the complex as a result of the data obtained at room temperature (E_g) are given in Fig. S6. To determine the E_g values of the complex using the Kubelka–Munk theory, the data in the reflection spectrum is converted into absorption values using Kubelka–Munk functions ($(F(R) = (1-R)^2/2R)$). Using the data obtained as a result of the measurements, the optical band gap (E_g) of the complex was determined with the photon energy (eV) versus $h\nu(F(R))^{1/2}$ curve. Here $F(R)$ is the Kubelka–Munk function. E_g value was calculated from the point where the linear parts intersect the x-axis by extrapolating the absorption curves obtained [40]. $BaSO_4$ was used as the reference material in the measurements. The E_g value determined for the complex is 3.80 eV. According to this result, it was determined that the complex may be a semiconductor.

3.6 HOMO–LUMO Energy Gap

The energy values of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular

Fig. 5 Luminescence spectra of **1** and H_2fdc



orbital (LUMO) of a molecule have been used to determine many important properties such as optical properties, chemical stability, and molecular electrical transport properties of the molecule. The knowledge of the HOMO–LUMO energy gap of a molecule can be used to design materials with specific optical, chemical, and electrical properties. For example, materials with a large HOMO–LUMO gap can be used to make organic solar cells, while materials with a small HOMO–LUMO gap can be used to make organic light-emitting diodes (OLEDs) [41, 42]. In this study, the energy values of HOMO and LUMO of the complex were calculated by the B3LYP/LanL2DZ level of theory. The relevant molecular orbital plots of the HOMO and LUMO for the complex are given in Fig. 6. HOMO and LUMO energies values of the complex were calculated as -4.98 eV and -2.17 eV, respectively (Table 4). The energy gap between HOMO and LUMO was computed as 2.81 eV. Nodes of HOMO were located on the oxygen atoms and furan ring and also in the C10, C19, C48 and C49 atoms, while nodes of LUMO were located on the nitrogen atoms and imidazole ring.

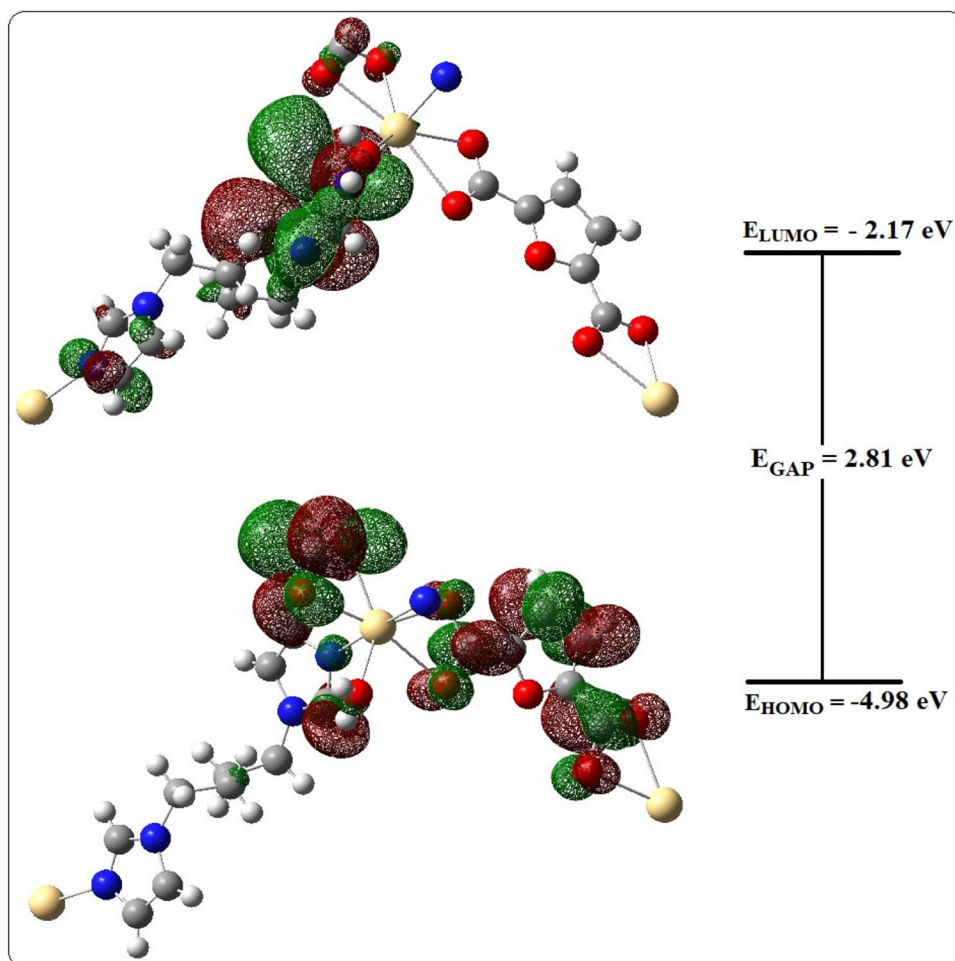
Table 4 Calculated energy values of complex using B3LYP/LanL2DZ method

Calculated Energies	Values
E_{HOMO} (eV)	-4.98
E_{LUMO} (eV)	-2.17
Ionization potential (I)	4.98
Electron affinity (A) (eV)	2.17
Energy gap (ΔE) (eV)	2.81
Electronegativity (X) (eV)	3.575
Chemical potential (μ) (eV)	-3.575
Chemical hardness (η) (eV)	1.405
Chemical softness (S) (eV)	0.356
Electrophilicity index (W) (eV)	4.548
Max. charge transfer (ΔN_{max})	1.272

3.7 Mulliken Atomic Charges

As the Mulliken atomic charges have been used to determine many important properties of molecules, including electronic structure, dipole moment and molecular

Fig. 6 Molecular orbital surfaces for the HOMO and LUMO of complex



polarizability, Mulliken atomic charges give very important information about the characterization of molecular systems [43].

The distribution of electrical charges across the atoms in a molecule provides valuable insights into the location of donor–acceptor pairs, the tendency of atoms to achieve similar electronegativity values, and the transfer of electrons during chemical reactions. Donor–acceptor pairs are formed when two atoms or molecules have different electronegativities. Electronegativity is a measure of how strongly an atom attracts electrons. An atom with a higher electronegativity will attract electrons more strongly than an atom with a lower electronegativity. Mulliken atomic charge calculations were performed on the complex in the gas phase using the B3LYP/LanL2DZ level of theory. The Mulliken atomic charges revealed that C11, C13, C20, C22, C24, C26, C28, C30, C33, C36, C38, C41, Cd47, oxygen atoms, and nitrogen atoms possess negative atomic charges, indicating their propensity for electrophilic attack. Cd1, C8, C10, C15, C19, Cd46, and all hydrogen atoms bear positive atomic charges, suggesting their susceptibility to nucleophilic attack. These calculations demonstrate the complex's predominantly electrophilic nature compared to its nucleophilic character. The calculated atomic charges are given in Table S2.

3.8 Global Chemical Activity

Frontier molecular orbitals (FMOs) are very important in the electrical properties, optical properties, UV–VIS spectra, and chemical reactions of molecules [41]. Overall, FMOs are a very important tool for understanding and predicting the properties of molecules. They are used in a variety of fields, including materials science, chemistry, and physics. Molecules with low energy gap values between HOMO and LUMO have high chemical reactivity. The high values of chemical potential (μ) and electrophilicity index (w) indicate a strong tendency for chemical reactivity. The electrophilicity index (w) is a measure of the molecule's ability to accept electrons, reflecting the ease with which electrons can escape from the molecule. Chemical reactivity provides insights into global chemical hardness (η), chemical potential (μ), and global electrophilicity index (W). Global chemical hardness (η) quantifies the molecule's resistance to electron redistribution. Chemical potential (μ) is associated with the force acting on an electron. Additionally, ionization potential (I) and electron affinity (A) can be calculated using the equations $I = -E_{\text{HOMO}}$ and $A = -E_{\text{LUMO}}$, respectively. These values are determined by the energies of the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) [44];

$$X = \frac{(I + A)}{2}$$

$$\mu = -\frac{(I + A)}{2}$$

$$\eta = \frac{(I - A)}{2}$$

$$S = \frac{1}{2\eta}$$

$$W = \frac{\mu^2}{2\eta}$$

$$\Delta N_{\text{max}} = \frac{(I + A)}{2(I - A)}$$

3.9 Molecular Electrostatic Potential (MEP) Surface

Molecular Electrostatic Potential (MEP) is a valuable tool for identifying regions of a molecule that are susceptible to nucleophilic or electrophilic attack, as well as potential hydrogen bonding sites. Additionally, MEP provides insights into the molecular shape and size. To evaluate the reactive sites of the complex, MEP calculations were performed on its optimized structure. Molecular electrostatic potential (MEP) surfaces provide valuable insights into the chemical reactivity of molecules. By visualizing the electrostatic potential distribution around a molecule, we can identify regions that are susceptible to electrophilic or nucleophilic attack. This information is crucial for understanding and predicting molecular reactivity [43]. MEP is related to the electrostatic interaction energy of a molecule with a proton [41]. The color-coding of MEP surfaces provides a wealth of information about molecular properties. Blue regions indicate areas of negative electrostatic potential, which are susceptible to electrophilic attack. Conversely, red regions represent positive electrostatic potential, indicating areas that are prone to nucleophilic attack. The distribution of these colours across the molecule helps us visualize its size, shape, and overall electrostatic potential distribution. This information is crucial for understanding the molecule's physicochemical properties, including its reactivity, stability, and interactions with other molecules [41, 44].

Figure S7 presents two-dimensional (2D) and three-dimensional (3D) representations of the molecular

electrostatic potential (MEP) surfaces of the complex. The MEP map utilizes a color scale to visualize the electrostatic potential distribution, with red indicating regions of low potential (negative charge) and blue indicating regions of high potential (positive charge). The blue regions represent areas of strongest electron density, which are attractive to positively charged particles (electrophiles), while the red regions represent areas of electron deficiency, which are attractive to negatively charged particles (nucleophiles). This color-coding scheme provides valuable insights into the electrostatic properties of the complex and can be used to predict its reactivity and interactions with other molecules.

The MEPs map of complex showed that near CH and CH₂ groups have positive potential, while over the oxygen and nitrogen atoms have negative potential. Accordingly, this results, near the especially hydrogen atoms bonded to nitrogen atoms indicate the strongest attraction (because of blue color), O6, O3, O2, O5, O7 atoms indicates the strongest repulsion. The 2D MEPs are represented in the molecular plane of complex. While the oxygen atoms are surrounded by regions of high electron density, while the hydrogen atoms are surrounded by regions of low electron density (Fig. S7).

3.10 NBO Analysis

Natural bond orbital (NBO) analysis is a powerful tool for understanding and quantifying intramolecular and intermolecular interactions, charge transfer, and conjugative interaction in molecular systems. NBO analysis is a post-Hartree–Fock method that transforms the molecular wave function into a set of localized orbitals that are more chemically intuitive than the canonical Hartree–Fock orbitals. NBOs are constructed by maximizing the occupancy of the orbitals and minimizing their variance. Once the NBOs have been constructed, NBO analysis can be used to calculate a variety of properties, including intramolecular interactions, intermolecular interactions, charge transfer and conjugative interaction [45, 46]. Intermolecular delocalization arises from the interaction of occupied orbitals of one subsystem with unoccupied orbitals of another subsystem. This interaction leads to the stabilization of the system, which is quantified by the delocalization energy, $E(2)$. The delocalization energy can be calculated using the following equation [44];

$$E^{(2)} = q_i \frac{F^2(i, j)}{S_j - S_i}$$

The delocalization energy ($E(2)$) is calculated using an equation that incorporates donor orbital occupancy (q_i), off-diagonal elements of the NBO Fock matrix ($F(i, j)$), and diagonal elements (S_j , S_i). A higher $E(2)$ value indicates a stronger interaction between electron donors and acceptors.

Table 5 Some significant donor–acceptor interactions of the complex

Type	Donor	Type	Acceptor	Energy (kcal/mol)
LP(1)	N9	LP*(7)	Cd	12.28
LP(1)	N50	LP*(8)	Cd	11.64
LP(2)	O3	LP*(7)	Cd	13.47
LP(2)	O4	LP*(8)	Cd	11.96
LP(2)	O6	LP*(7)	Cd	11.35
LP(2)	O48	LP*(8)	Cd	11.19
LP(2)	O49	LP*(7)	Cd	11.28

Table 5 lists significant interactions between donor and acceptor NBOs. Additional perturbation energies for donor and acceptor orbitals are also presented in Table 5. NBO analysis reveals that electron delocalization occurs from lone pairs (n) of oxygen and nitrogen orbitals to anti-lone pairs (n^*) of cadmium orbitals. Due to the presence of $n \rightarrow n^*$ interactions, delocalization effects play a crucial role in shaping the coordination environment of the cadmium atom in this complex. As shown in Table 5, the strongest donations involve LP(2)O4 to the antibonding orbital of LP*(7)Cd with an energy of 13.47 kcal/mol and LP(1)N9 to the antibonding orbital of LP*(7)Cd with an energy of 12.28 kcal/mol.

4 Conclusions

In this study, 2D {[Cd(μ -fdc)(H₂O)(μ -bib)]·H₂O}_n (**1**) coordination polymer was obtained by hydrothermal reaction of H₂fdc, bib and Cd(II). The structure of the synthesized complex was characterized by FT-IR spectrometry, UV–Vis spectrophotometer, single crystal and powder X-ray diffraction analysis methods. In addition, the luminescence, thermal and optical properties of the complex were also investigated. According to the results of X-ray diffraction analysis, the complex crystallized in the monoclinic system and in the $P2_1/n$ space group. The vibrational spectra (IR and Raman) and geometric properties of the complex were calculated using DFT/B3LYP/LanL2DZ theory, and excellent agreement was found between the computational and experimental results. The energies of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) were also determined using the same basis set. The HOMO–LUMO energy gap was calculated to be 2.81 eV. Based on this energy gap, the chemical reactivity, electronegativity, hardness, and softness of the complex were evaluated. The results indicate that the complex exhibits its low intramolecular charge transfer and chemical reactivity, suggesting high kinetic stability. Natural bond orbital

(NBO) analysis revealed the presence of intramolecular charge transfer, delocalization, and stabilization energies within the complex.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s10904-024-03083-7>.

Author Contributions SD: Formal analysis, Investigation, Validation, Software, Methodology, Writing-Review and Editing. GD: Conceptualization, Methodology, Formal analysis, Investigation, Validation, Software, Writing-Original draft. HE: Supervision, Conceptualization, Methodology, Validation, Software, Writing-Review and Editing. All authors have read and agreed to the published version of the manuscript.

Funding Open access funding provided by the Scientific and Technological Research Council of Türkiye (TÜBİTAK). This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Data Availability Not applicable.

Declarations

Conflict of Interest The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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References

1. A. Dinh, H. Yang, F. Peng, T.C. Nguyen, A. Hong, P. Feng, X. Bu, *Cryst. Growth Des.* **20**, 3523 (2020)
2. Q. Zhuang, S. Chen, K. Xu, L. Kang, Z. Li, G. Li, *Inorg. Chem.* **62**, 11570 (2023)
3. H.-Q. Tian, T. Jiang, C. Huang, D.-M. Chen, B.-X. Zhu, *Inorganica Chim. Acta* **545**, 121242 (2023)
4. T.G. Qu, X.M. Hao, H. Wang, X.G. Cui, F. Chen, Y.B. Wu, D. Yang, M. Zhang, W.L. Guo, *Polyhedron* **156**, 208 (2018)
5. E. Çiftçi, T. Alp Arıcı, M. Arıcı, H. Erer, and O. Z. Yeşilel, *J. Solid State Chem.* **311**, 123111 (2022)
6. Y. Samav, S. Demir, G. Solmaz, C. Tuncer, and H. Erer, *J. Inorg. Organomet. Polym. Mater.* **34**, 1092–1103 (2023)
7. P. Köse Yaman, Ö. Demir, S. Demir, M. Zeyrek Ongun, S. Oğuzlar, and H. Erer, *ACS Omega* **9**, 3193–3203 (2024)
8. M. Şevik, S.M. Sezdi, E. Kavak, T.A. Arıcı, M. Arıcı, *Cryst. Growth Des.* **23**, 5163 (2023)
9. D.K. Singha, P. Majee, S. Hui, S.K. Mondal, P. Mahata, *Dalt. Trans.* **49**, 829 (2020)
10. X.S. Zeng, H.L. Xu, Y.C. Xu, X.Q. Li, Z.Y. Nie, S.Z. Gao, D.R. Xiao, *Inorg. Chem. Front.* **5**, 1622 (2018)
11. M. Riasat, S. Sharif, S. Khurshid, S. Farid, R. Bano, M.A. Gilani, O. Şahin, F. Perveen, *J. Coord. Chem.* **75**, 431 (2022)
12. J. Zhao, Z. Dang, M. Muddassir, S. Raza, A. Zhong, X. Wang, and J. Jin, *Molecules* **28**, 6848 (2023)
13. P. Köse Yaman, S. Demir, S. Denizaltı, H. Erer, and O. Z. Yeşilel, *New J. Chem.* **48**, 1850–1855 (2024)
14. X. Li, L. Zhang, Z. Yang, P. Wang, Y. Yan, J. Ran, *Sep. Purif. Technol.* **235**, 116213 (2020)
15. S. Bolat, S. Demir, H. Erer, F. Pelit, R. Dzingelevičienė, T. Ligor, B. Buszewski, L. Pelit, *J. Hazard. Mater.* **466**, 133607 (2024)
16. P. Yao, *J. Inorg. Organomet. Polym. Mater.* **24**, 568 (2014)
17. J.N. Xing, J.Z. Guo, B. Li, *Crystallogr. Reports* **63**, 581 (2018)
18. H. Erer, O. Z. Yeşilel, and M. Arıcı, *Cryst. Growth Des.* **15**, 3201–3211 (2015)
19. W. Wu, L. Lu, D. Liao, B. Li, X. Liu, M. Muddassir, H. Sakiyama, J. Wang, *J. Inorg. Organomet. Polym. Mater.* **32**, 875 (2022)
20. H.L. An, Y. Duan, T.T. Chen, L.Y. Xu, L.Q. Chai, *J. Mol. Struct.* **1301**, 137297 (2024)
21. L.Q. Chai, Q. Hu, K.Y. Zhang, L. Zhou, J.J. Huang, *J. Lumin.* **203**, 234 (2018)
22. G. Kumaravel, P. Ponya Utthra, and N. Raman, *Bioorg. Chem.* **77**, 269–279 (2018)
23. G.M. Sheldrick, *Acta Crystallogr. Sect. C. Struct. Chem.* **71**, 3 (2015)
24. O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **42**, 339 (2009)
25. G.M. Sheldrick, *Acta Crystallogr. Sect. A Found. Crystallogr.* **71**, 3 (2015)
26. C.F. Macrae, P.R. Edgington, P. McCabe, E. Pidcock, G.P. Shields, R. Taylor, M. Towler, J. Van De Streek, *J. Appl. Crystallogr.* **39**, 453 (2006)
27. V.A. Blatov, A.P. Shevchenko, D.M. Proserpio, *Cryst. Growth Des.* **14**, 3576 (2014)
28. M. J. Frisch, G. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. Sonnenberg, M. Hada, and D. Fox, *Gaussian 09 Revision A.1.* Gaussian Inc. (2009)
29. M.J. Frisch, J.A. Pople, J.S. Binkley, *J. Chem. Phys.* **80**, 3265 (1984)
30. S.R. Whittleton, R.J. Boyd, T.B. Grindley, *J. Phys. Chem. A* **110**, 5893 (2006)
31. J. Baker, A.A. Jarzecki, P. Pulay, *J. Phys. Chem. A* **102**, 1412 (1998)
32. G. Rauhut, P. Pulay, *J. Phys. Chem.* **99**, 3093 (1995)
33. S. Ying-Hung, *Macromolecules* **25**, 516 (1992)
34. C.L. White, R.L. LaDuca, *Inorganica Chim. Acta* **451**, 171 (2016)
35. Y. Yang, H. Gao, *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **85**, 303 (2012)
36. W.-Z. Lee, H.-S. Tseng, M.-Y. Ku, and T.-S. Kuo, *Dalt. Trans.* 2538–2541 (2008)
37. B. Khalili, M. Rimaz, *Can. J. Chem.* **94**, 501 (2016)
38. B. Borah, T.G. Devi, *J. Mol. Struct.* **1223**, 128972 (2021)
39. S. Bahçeli, N. Öztürk, Ü.U. Akduman, Süleyman Demirel Univ. Fac. Arts Sci. J. Sci. **6**, 99 (2011)
40. S. Demir, H. Erer, *J. Mol. Struct.* **1295**, 136502 (2024)
41. M. Prabhakaran, A.R. Prabakaran, S. Gunasekaran, S. Srinivasan, *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **136**, 494 (2015)
42. P. Rajesh, S. Gunasekaran, T. Gnanasambandan, S. Seshadri, *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **137**, 1184 (2015)
43. G. Dikmen, İ Kani, *J. Mol. Struct.* **1209**, 127955 (2020)
44. G. Dikmen, D. Hür, *Chem. Phys. Lett.* **716**, 49 (2019)
45. H. Tanak, A. Açar, M. Yavuz, *Int. J. Quantum Chem.* **111**, 2123 (2011)
46. V. Arjunan, I. Saravanan, P. Ravindran, S. Mohan, *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **74**, 375 (2009)

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