

Heteronuclear cadmium(II)/cobalt(III) cyanide coordination polymers with 1-methylimidazole and 1-ethylimidazole ligands: synthesis, characterization and catalytic activities

Güneş Süheyla Kürkçüoğlu^{a,*}, Seray Kekeç^a, Okan Zafer Yeşilel^b, Kutalmış Gökkuş^c, Hakan Ünver^d, Onur Şahin^e

^a Department of Physics, Faculty of Science, Eskişehir Osmangazi University, 26040 Eskişehir, Türkiye

^b Department of Chemistry, Faculty of Science, Eskişehir Osmangazi University, 26040 Eskişehir, Türkiye

^c Department of Environmental Engineering, Faculty of Engineering and Architecture, Kastamonu University, 37500 Kastamonu, Türkiye

^d Department of Chemistry, Faculty of Science, Eskişehir Technical University, 26555 Eskişehir, Türkiye

^e Department of Occupat Health & Safety, School of Health, Sinop University, 57000 Sinop, Türkiye

ARTICLE INFO

Keywords:

Hexacyanocobaltate(III) complex
1-Methylimidazole complex
1-Ethylimidazole complex
Cadmium(II) complex
Coordination polymer
Hydrogen production
Thymol oxidation

ABSTRACT

Two new heteronuclear Cd(II)/Co(III) compounds, $\{[\text{Cd}(\text{1-meim})_3\text{Cd}_{0.5}(\text{1-meim})\text{Co}(\mu\text{-CN})_4(\text{CN})_2]\}_n$ (**1**) and $\{[\text{Cd}(\text{1-etim})_3\text{Cd}_{0.5}(\text{1-etim})_2\text{Co}(\mu\text{-CN})_3(\text{CN})_3]\cdot\text{H}_2\text{O}\}_n$ (**2**) (1-meim: 1-methylimidazole, 1-etim = 1-ethylimidazole), have been synthesized and characterized using elemental analysis, FT-IR and Raman spectroscopy, single-crystal X-ray diffraction techniques. The single crystal X-ray study shows that the compound **1** exhibited a 1D double chain structure and is further linked into 3D supramolecular architectures through C—H...N and $\pi\cdots\pi$ interactions. Whereas the compound **2** displayed 2D network which is extended into a 3D supramolecular framework by O—H...N hydrogen bonds and C—H... π interactions. In **1** and **2**, each Co(III) ion is coordinated by six carbon atoms from cyanide ligands, thus showing an octahedral coordination geometry. Cd1 and Cd2 ions exhibited two different geometries, distorted trigonal bipyramidal and octahedral. Furthermore, phase purities, catalytic and thermal properties were investigated.

1. Introduction

Coordination compounds, also known as coordination complexes, are a class of compounds in which a central atom or ion (usually a metal) is surrounded by a set of molecules or ions, known as ligands, that are bonded to it. The central atom or ion and the ligands are connected via coordinate covalent bonds, where the ligands donate electron pairs to the metal atom or ion. One of the most well-known classes of coordination compounds is coordination polymers (CPs) [1]. CPs are formed by the assembly of two different building blocks: the metal entities (metal ion or metal complex) and the bridging ligands [1–8]. The selection of bridging ligands plays a very important role in the formation of CPs [9]. Therefore, this formation requires usually multidentate ligands with two or more donor atoms. Research on CPs bridged with cyanide ligands continues to attract interest [10–15]. Cyanide ligands are widely used due to their ability to act as both σ -donor and π -acceptor, their negative charge, and their dual character [16–19]. The

cyanide groups can partly or fully participate in the formation of coordination bonds with various transition metal ions to generate different structures by the combinations of them, which result in practically zero-, one-, two- and three-dimensional structures [20–22].

The versatility and wide-ranging applications of hexacyanometallates make them an important area of study in inorganic chemistry, materials science, and various applied fields. Hexacyanometallates serve as key examples in studies of coordination chemistry and crystal engineering. They often form well-defined structures, such as the famous Prussian blue analogues, which are used to understand metal–ligand interactions and coordination networks [23]. Many hexacyanometallates exhibit interesting magnetic properties, including ferromagnetism and ferrimagnetism [24]. It acts as a catalyst in various chemical reactions [25]. The ability of metals to stabilize different oxidation states makes them useful in redox reactions, including environmental applications such as organic transformations and degradation of pollutants. Hexacyanometallates are used in

* Corresponding author.

E-mail address: gkurkcuo@ogu.edu.tr (G.S. Kürkçüoğlu).

<https://doi.org/10.1016/j.ica.2024.122400>

Received 4 July 2024; Received in revised form 27 September 2024; Accepted 30 September 2024

Available online 2 October 2024

0020-1693/© 2024 Elsevier B.V. All rights are reserved, including those for text and data mining, AI training, and similar technologies.

electrochemical applications such as batteries, electrochromic devices, and sensors [26–28]. Additionally, hexacyanometallates can be used to remove toxic metal ions from contaminated water and soil. It is used in the development of advanced materials, including nanoporous materials and frameworks [29,30]. These materials have potential applications in gas storage, separation and catalysis [31]. Some hexacyanometallates exhibit interesting photophysical properties such as luminescence and photochromism [32,33]. These properties are useful in the development of light-emitting devices, sensors, and molecular switches. Hexacyanocobaltate(III) complexes are an important class of coordination compounds characterized by their octahedral geometry, low-spin electron configuration, and significant stability due to the strong field strength of cyanide ligands. Transition metal hexacyanocobaltates(III) refer to CPs that also offer physical properties that can be exploited for technological applications. These properties make them useful in a variety of chemical and industrial applications [25,34]. Additionally, there are structures with two different centers containing Cd(II) ions [35,36].

The intensive use of fossil fuels for energy directly leads to air pollution and indirectly to water and soil pollution. In short, the use of fossil fuels seriously disrupts the all ecosystems at the same time. In this respect, it is the greatest danger that humans have discovered. Therefore, it is necessary to seriously reduce the use of fossil fuels. The main approach to minimize the impact of fossil fuels is the discovery or use of alternative energy sources. In this respect, hydrogen is one of the best alternatives to fossil fuels as a green, renewable and clean energy source [37]. Because the energy density of hydrogen (142 MJ/kg) is almost three times higher than the energy density of oil (47 MJ/kg) [38]. However, there are still significant challenges in the efficient production, storage and transportation of hydrogen [39–41].

Although a variety of methods are used in hydrogen production, one of the most commonly used ones is the production of hydrogen gas from NaBH_4 due to its high hydrogen capacity (10.8 wt%), high stability, non-toxicity, cheapness and easy accessibility, and its use in proton-exchange membrane fuel cells [42,43]. Under normal conditions, hydrogen gas can be produced from NaBH_4 by hydrolysis or methanolysis without the need for a catalyst. However, since this natural process is extremely slow, a catalyst is definitely needed. Apart from this, monoterpenes are also a certain class of compounds produced by plants for various purposes, including defense, attraction, etc. The various pharmaceutical properties exhibited by these compounds, such as anti-bacterial, anti-cancer, etc., make monoterpenes very valuable chemicals in synthetic chemistry. In addition, many compounds of commercial importance can be obtained by the reaction of monoterpenes as starting materials [44,45]. For this purpose, the catalytic properties of the coordination compounds synthesized in this study were investigated.

In the literature, the metal compounds utilizing the imidazole ligand and its derivatives have been studied [46–56]. However, specific research on hexacyanometallate(III) compounds with imidazole and its derivatives are scarce [57,58]. In our previous studies, tetracyanometallate(II) compounds were synthesized and structurally examined using metal(II) ($\text{M(II)} = \text{Cu, Zn or Cd}$), 1-meim and 1-etim ligands [59–65]. As a continuation of these studies, we present two new cadmium(II)/cobalt(III) cyanide bridged compounds with 1-meim and 1-etim ligands, $\{[\text{Cd}(1\text{-meim})_3\text{Cd}_{0.5}(1\text{-meim})\text{Co}(\mu\text{-CN})_4(\text{CN})_2]\}_n$ (1) and $\{[\text{Cd}(1\text{-etim})_3\text{Cd}_{0.5}(1\text{-etim})_2\text{Co}(\mu\text{-CN})_3(\text{CN})_3]\cdot\text{H}_2\text{O}\}_n$ (2). Their vibrational spectra (FT-IR and Raman), single-crystal and powder X-ray diffractions and thermal analytical properties were investigated. Furthermore, compounds 1 and 2 were tested as catalysts in both hydrogen productions by methanolysis of NaBH_4 and oxidation of Thymol (a monoterpene).

2. Materials and methods

2.1. Materials and instruments

Cadmium(II) acetate dihydrate ($\text{Cd}(\text{CH}_3\text{COO})_2\cdot 2\text{H}_2\text{O}$, Acros, 99 %),

Table 1

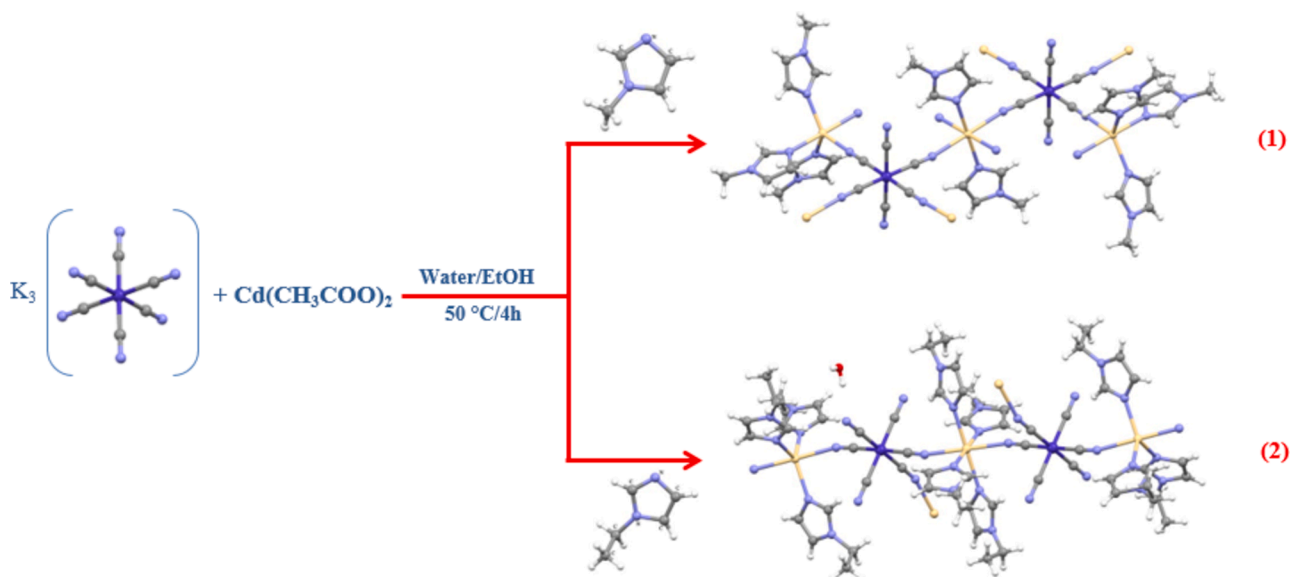
Crystal data and structure refinement parameters for compounds 1–2.

Crystal data	1	2
Empirical formula	$\text{C}_{44}\text{H}_{48}\text{Cd}_3\text{Co}_2\text{N}_{28}$	$\text{C}_{62}\text{H}_{84}\text{Cd}_3\text{Co}_2\text{N}_{32}\text{O}_2$
Formula weight	1424.16	1764.67
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$Pbca$
<i>a</i> (Å)	7.5320 (4)	17.4403 (18)
<i>b</i> (Å)	22.6223 (13)	15.5105 (14)
<i>c</i> (Å)	16.5707 (9)	28.968 (3)
β (°)	98.122 (2)	90.00
<i>V</i> (Å ³)	2795.2 (3)	7836.0 (13)
<i>Z</i>	2	4
<i>D_c</i> (g cm ^{−3})	1.692	1.496
μ (mm ^{−1})	1.76	1.28
θ range (°)	2.5–28.4	1.8–28.3
Measured refls.	65,890	244,354
Independent refls.	6950	9743
<i>R_{int}</i>	0.049	0.056
<i>S</i>	1.03	1.11
<i>R1/wR2</i>	0.029/0.058	0.037/0.090
$\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}}$ (e Å ^{−3})	0.39/−0.50	0.41/−0.57
CCDC	2,355,652	2,355,653

potassium hexacyanocobaltate(III) ($\text{K}_3[\text{Co}(\text{CN})_6]$, Acros, 95 %), 1-methylimidazole ($\text{C}_4\text{H}_6\text{N}_2$, Merck, 99 %), 1-ethylimidazole ($\text{C}_5\text{H}_8\text{N}_2$, Fluorochem, 99 %) and ethanol ($\text{C}_2\text{H}_5\text{OH}$, Merck) were purchased from commercial sources and were used as received. Elemental analyses were carried out on LECO, CHNS-932 analyzer for C, H and N at the Middle East Technical University Central Laboratory. The FT-IR spectra of the compounds were carried out as KBr pellets in the range of 4000–400 cm^{-1} (4 cm^{-1} resolution) on a Perkin Elmer spectrum 100 FT-IR spectrometer which was calibrated using polystyrene and CO_2 bands (Fig. S1). Raman spectra of the compounds were recorded in the region 4000–400 cm^{-1} on a Bruker Senterra Dispersive Raman instrument using laser excitation of 785 nm line of a 3B diode laser (Fig. S2). Powder X-ray diffractions (PXRD) were carried out with $\text{Cu-K}\alpha$ irradiation using a PANalytical Empyrean device. PXRD patterns of the compounds were recorded to control their phase purities. Powder X-ray diffraction (PXRD) plots are usually recorded in reflection geometry. This is the standard technique used in most powder XRD analyses. In powder XRD measurements, the reflection geometry is more commonly used with instruments such as the PANalytical Empyrean because it is simpler and has a wider range of applications. The experimental PXRD patterns of the complexes are well-matched with simulated patterns from the single crystal structure with the use of Mercury program (Fig. S3). Thermal analyses of the compounds were performed in a static air atmosphere with a heating rate of 10 °C per minute in the range of 30 to 1000 °C using platinum crucibles (Fig. S4).

2.2. Single crystal X-ray diffraction (SC-XRD) analysis

Suitable crystals of 1–2 were selected for data collection which was performed on a D8-QUEST diffractometer equipped with a graphite-monochromatic $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073$ Å) at 293 K. The structures were solved by direct methods using SHELXS-2013 [66] and refined by full-matrix least-squares methods on F^2 using SHELXL-2013 [67]. In 2, the H atoms of water molecule were in a difference map and refined freely. The other H atoms were located from different maps and then treated as riding atoms with C–H distances of 0.93–0.97 Å. The following procedures were implemented in our analysis: data collection: Bruker APEX3 [68]; program used for molecular graphics were as follow: MERCURY programs [69]; GUI for other software related to structure solution: WinGX [70]. Details of data collection and crystal structure determinations are given in Table 1.



Scheme 1. Synthesis methods of compounds 1 and 2.

2.3. General synthesis methods

A solution of 4 mmol of 1-meim (0.328 g) or 1-etim (0.385 g) in 15 mL of ethanol was added dropwise to the stirring solution of 1 mmol Cd (CH_3COO) $_2 \cdot 2\text{H}_2\text{O}$ (0.266 g) dissolved in 20 mL of water. After stirring for 15 min, the clear white solution formed was added dropwise to 1 mmol $\text{K}_3[\text{Co}(\text{CN})_6]$ (0.332 g) in dissolved in 20 mL of water. The solutions were stirred for 50 °C for 4 h in a temperature-controlled bath. The obtained solutions were filtered and kept for crystallization at room temperature. $\{[\text{Cd}(\text{1-meim})_3\text{Cd}_{0.5}(\text{1-meim})\text{Co}(\mu\text{-CN})_4(\text{CN})_2]\}_n$ (**1**) and $\{[\text{Cd}(\text{1-etim})_3\text{Cd}_{0.5}(\text{1-etim})_2\text{Co}(\mu\text{-CN})_3(\text{CN})_3] \cdot \text{H}_2\text{O}\}_n$ (**2**) single crystals were obtained by slow evaporation after two weeks. Colorless crystals of the compounds were obtained in (0.094 g) 48.26 % yield for compound **1** and (0.085 g) 57.20 % yield for **2** (based on $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$). Anal. Calcd. for $\text{C}_{44}\text{H}_{48}\text{Cd}_3\text{Co}_2\text{N}_{28}$ (**1**) (MW = 1424.16 g mol^{-1}): C 37.11, H 3.40, N 27.54 %; found C 37.03, H 3.08, N 26.85 %. Anal. Calcd. for $\text{C}_{62}\text{H}_{84}\text{Cd}_3\text{Co}_2\text{N}_{32}\text{O}_2$ (**2**) (MW = 1764.67 g mol^{-1}): C 43.08, H 4.66, N 25.93 %; found C 42.97, H 4.28, N 25.62 % (see Scheme 1).

2.4. Hydrogen production tests

Metal complexes were used for hydrogen production via NaBH_4 methanolysis and its catalytic activity was evaluated. The experimental setup consisted of a sealed glass flask, a gas burette, and a water bath. The volume of hydrogen gas generated during the methanolysis reaction was determined by measuring the volume of water displaced in a 500 mL gas burette. Furthermore, the effects of varying amounts of catalysts and NaBH_4 and different temperature conditions on the hydrogen production rate were investigated. This investigation to identify the optimal reaction conditions that would yield the catalyst's maximum hydrogen generation rate. Finally, the hydrogen generation rate of the catalyst under its respective optimum conditions was determined.

2.5. Thymol oxidation

Catalytic oxidation of Thymol experiments was conducted in a sealed glass tube with a magnetic stirrer under specified conditions. In a typical experimental procedure, the required amounts of reactants were calculated. Then, first the catalyst and then the substrate (Thymol) were added to the solvent and the reaction temperature was reached by stirring. Finally, the reaction was started by adding the oxidant. At the end of 24 h, the reaction was stopped, and the Gas Chromatography (HP-

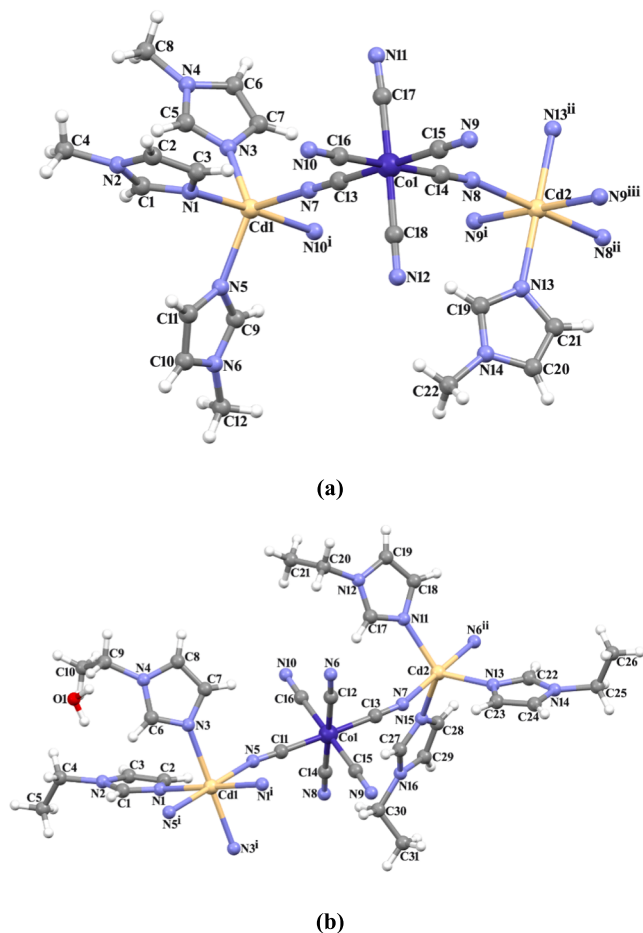


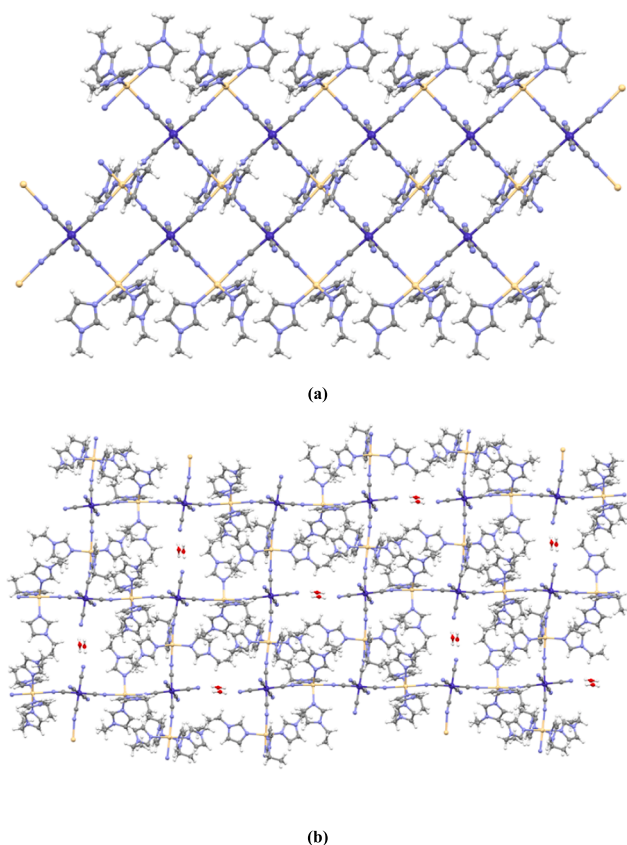
Fig. 1. The molecular structures of **1** (a) and **2** (b) showing the atom numbering schemes. [(i) $x-1, y, z$; (ii) $-x, -y+1, -z$; (iii) $-x+1, -y+1, -z$ for **1**; (i) $-x+1, -y+1, -z+1$; (ii) $-x+1, y-1/2, -z+3/2$ for **2**].

5 quartz capillary column 30 m x 0.32 mm x 0.25 μm equipped with an FID detector) method was used for the analysis of the reaction components.

Table 2
Selected bond distances for compounds 1–2 (Å, °).

Compound 1			
Cd1-N1	2.328(2)	Cd1-N3	2.243(2)
Cd1-N5	2.256(2)	Cd1-N7	2.253(2)
Cd1-N10 ⁱ	2.338(2)	Cd2-N8	2.362(2)
Cd2-N9 ⁱ	2.392(2)	Cd2-N13	2.309(2)
Co1-C13	1.900(2)	Co1-C14	1.901(2)
Co1-C15	1.907(2)	Co1-C16	1.892(2)
Co1-C17	1.903(3)	Co1-C18	1.906(3)
Compound 2			
Cd1-N1	2.331(3)	Cd1-N3	2.349(3)
Cd1-N5	2.366(3)	Cd2-N11	2.234(3)
Cd2-N13	2.246(3)	Cd2-N15	2.249(3)
Cd2-N6 ⁱⁱ	2.347(2)	Cd2-N7	2.348(2)
Co1-C11	1.892(3)	Co1-C12	1.894(3)
Co1-C13	1.893(3)	Co1-C14	1.901(3)
Co1-C15	1.909(3)	Co1-C16	1.913(3)

Symmetry codes: (i) x-1, y, z for 1; (ii) -x + 1, y-1/2, -z + 3/2 for 2.

**Fig. 2.** An infinite 2D supramolecular network in 1 (a), 2 (b).

3. Results and discussion

3.1. Structural analysis of the compounds

The single crystal X-ray study shows that the heterometallic compound **1** has one-dimensional CP, while the heterometallic compound **2** has two-dimensional CP. The compound **1** has $P2_1/n$ space group, while the compound **2** is $Pbca$. The asymmetric unit of **1** consists of one and a half Cd(II) ions, one Co(III) ion, six cyanide ligands and four 1-meim ligands, while the asymmetric unit of **2** consists of one and a half Cd(II) ions, one Co(III) ion, six cyanide ligands, five 1-etim ligands and one water molecule (Fig. 1). In 1–2, the Cd(II) ion [Cd1 in **1** and Cd2 in **2**] is

Table 3
Hydrogen-bond parameters for compounds 1–2 (Å, °).

D-H...A	D-H	H...A	D...A	D-H...A
Compound 1				
C1-H1...N11 ^v	0.93	2.31	3.213(3)	163
C12-H12A...N12 ^{vi}	0.96	2.60	3.378(5)	139
Compound 2				
O1-H1B...N8 ⁱ	0.86(2)	2.07(3)	2.914(7)	168
O1-H1A...N8 ^{iv}	0.86(2)	2.16(3)	3.002(7)	167

Symmetry codes: (v) x-1/2, -y + 3/2, z + 1/2; (vi) -x, -y + 1, -z + 1 for **1**; (i) -x + 1, -y + 1, -z + 1; (iv) x, y + 1, z for **2**.**Table 4**
C—H... π and π ... π interactions parameters for 1–2 (Å, °).

D-H...Cg	D-H	H...Cg	D...Cg	D-H...Cg
Compound 2				
C25-H25A...Cg(5) ⁱ	0.97	2.72	3.6510 (4)	161
Cg(I)	Cg(J)	Cg-Cg	Perpendicular distance	
Compound 1				
Cg(3)	Cg(3) ⁱ	3.7768 (2)	3.4352	

Symmetry codes: (i) 1-x, -y, -z; Cg(3) = N5/N6/C9/C10/C11 for **1**, (i) x-1/2, y, 1/2-z; Cg(5) = N15/N16/C27/C28/C29 for **2**.

coordinated by three nitrogen atoms from ligands [1-meim in **1** and 1-etim in **2**] and two nitrogen atoms from cyanide ligands (Table 2), thus showing a trigonal bipyramidal coordination geometry. The geometry of these Cd(II) ions can be evaluated by the Addison distortion index τ [$\tau = (\beta - \alpha)/60$, where α and β are the two largest coordinated angles in the complex]. In a five-coordinate geometry, $\tau = 0$ for a square pyramidal geometry and $\tau = 1$ for a trigonal bipyramidal geometry. The τ values are 0.87 for **1** and 0.90 for **2**. In **1**, the Cd2 atom is coordinated by two nitrogen atoms from 1-meim ligands and four nitrogen atoms from cyanide ligands, while in **2**, the Cd1 atom is coordinated by four nitrogen atoms from 1-etim ligands and two nitrogen atoms from cyanide ligands (Table 2). Thus, the Cd(II) ions [Cd2 in **1** and Cd1 in **2**] have an octahedral coordination geometry. In 1–2, each Co(III) ion is coordinated by six carbon atoms from cyanide ligands, thus showing an octahedral coordination geometry. The metal ions are bridged by cyanide ligands to form [Cd₂Co₂(CN)₄] in **1** and [Cd₆Co₆(CN)₁₂] units in **2**. The Cd...Co separations are 5.378 and 5.438 Å in **1** and 5.254, 5.298 and 5.305 Å in **2**. In **1**, the combination of [Cd₂Co₂(CN)₄] units produces a one-dimensional CP running parallel to the [100] direction (Fig. 2a), while in **2**, the combination of [Cd₆Co₆(CN)₁₂] units produces a two-dimensional CP running parallel to the bc plane (Fig. 2b). In **1**, two-dimensional molecular packing is achieved by C—H...N hydrogen bonds (Table 3) and π ... π interactions (Table 4), while in **2**, three-dimensional molecular packing (Fig. 3) is achieved by O—H...N hydrogen bonds and C—H... π interactions.

3.2. Spectral (FT-IR and Raman) analysis

Vibrational spectra, as observed by infrared absorption and Raman scattering, are direct manifestations of these forces. Interatomic forces can be expressed as force constants (or compliance constants, which may be more appropriate in some cases) which determine the vibrational frequencies of the system [71]. The FT-IR and Raman spectra of the compounds **1** and **2** can be seen in Figs. S1 and S2, respectively, and are listed in Table S1. The presence of bands belonging to the ligands in the FT-IR and Raman spectra of the compounds indicates the presence of 1-meim and 1-etim in the compounds. Vibrational wavenumbers and vibrational assignments for 1-meim and 1-etim are taken from studies in the literature and are given in Table S1 [72,73]. The vibrational

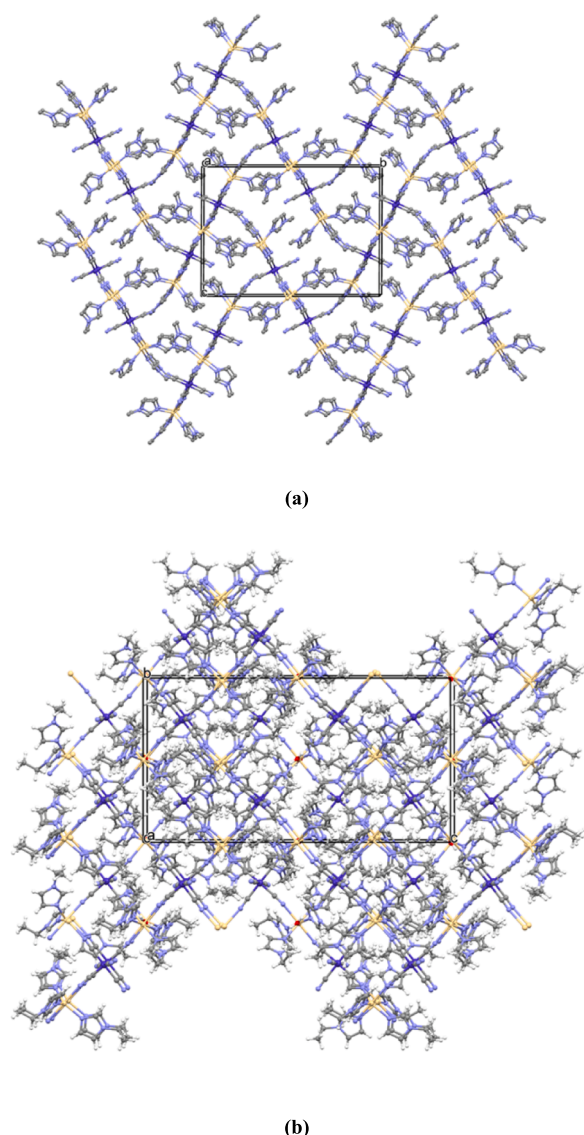


Fig. 3. An infinite 3D supramolecular network in 1 (a) and 2 (b).

absorption bands for compound 2, observed between 3500 and 3250 cm^{-1} , are assigned to the symmetric and asymmetric $\nu(\text{OH})$ stretching vibrations of water molecules. Additionally, the presence of water molecules is indicated by two vibrational bands at 1525 and 1414 cm^{-1} , corresponding to $\delta(\text{OH})$ deformation vibrations. Elemental, thermal, and XRD analyses further confirm the presence of water in compound 2.

As can be seen from Table S1, the vibrational spectral analyses for 1-meim and 1-etim ligands are performed based on $\nu(\text{CH})$, $\nu(\text{CH}_3)$, ν_{ring} , $\nu(\text{N}-\text{CH}_3)$, $\delta(\text{CH}_3)$, $\gamma(\text{CH})$ and δ_{ring} vibrations. The bands observed in the FT-IR spectra of 1-meim and 1-etim ligands in the range of 3100–3000 cm^{-1} belong to $\nu(\text{CH})$ vibrational bands [72,73]. The $\nu(\text{CH})$ stretching vibrations originating from the imidazole ring of 1-meim and 1-etim ligands are assigned as 3136 cm^{-1} , 3102 cm^{-1} and 3027 cm^{-1} for compound 1 and 3132 cm^{-1} and 3117 cm^{-1} for compound 2 in the FT-IR spectra. The $\nu(\text{CH})$ stretching vibrations in the Raman spectra are assigned as 3183 cm^{-1} , 3109 cm^{-1} and 3045 cm^{-1} for compound 1. The absorption bands of $\nu(\text{CH}_3)$ and $\nu(\text{CH})$ groups in the complexes are observed at 3130–2930 cm^{-1} range and shift towards lower or higher frequencies according to the ligands. It was found that these vibrations correspond to the vibrations of C1-H1 and C12-H12 bonds for compound 1, and from crystallographic data, these bond lengths are 0.93 Å and

0.96 Å, respectively. The $\nu(\text{C}-\text{H})$ bands seen in the FT-IR spectrum of compound 1 are observed as [3132 cm^{-1} , 3106 cm^{-1} and 3025 cm^{-1} for C1-H1 and 2987 cm^{-1} and 2952 cm^{-1} for C12-H12]. The $\nu(\text{OH})$ bands seen in the FT-IR spectrum of compound 2 are at wavenumbers [3503 cm^{-1} for O1-H1 and 3259 cm^{-1} for O1-H2]. It was found from crystal data that the bond lengths corresponding to these vibrations were 0.86 (2) Å. $\delta(\text{CH}_3)$ vibration bands in ligands occur between 1558 and 1028 cm^{-1} in FT-IR, spectra. When aromatic ring nitrogen is involved in complex formation, certain ring modes, especially at 1229 cm^{-1} and 1228 cm^{-1} , increase in value both due to coupling by M–N (ligand) bond vibrations and due to changes in the ring force field. These shifts can be explained as the coupling of the internal modes of 1-meim and 1-etim molecules with M–N (1-meim and 1-etim) vibrations. Similar shifts have been observed in the vibrational spectra of other metal-coordinated imidazole complexes [53,74,75].

The most important point of the FT-IR and Raman spectra of the compounds include the characteristic vibrations of the cyanide groups between 2200 cm^{-1} and 2000 cm^{-1} [76]. The number and positions of $\nu(\text{C}\equiv\text{N})$ absorptions reveal bridging or terminal cyanides in the compounds. $\nu(\text{C}\equiv\text{N})$ vibrations are observed in two regions, 2148 cm^{-1} , 2126 cm^{-1} for compound 1 and 2135 cm^{-1} and 2120 cm^{-1} for compound 2. The strong and sharp absorption band observed at 2148 cm^{-1} for 1 and 2135 cm^{-1} for compound 2 is the stretching vibration of bridging cyanide groups, the other band observed at 2126 cm^{-1} for compound 1 and 2120 cm^{-1} for compound 2 is the terminal cyanide originating from groups. A_{1g} and B_{1g} modes in the Raman spectrum of the $\text{K}_3[\text{Co}(\text{CN})_6]$ were observed in 2150 cm^{-1} and 2137 cm^{-1} , respectively. These modes were observed in 2260 cm^{-1} and 2234 cm^{-1} (for 1), 2255 cm^{-1} (for 2) in the Raman spectra of the compounds. According to these spectral values, A_{1g} and B_{1g} modes were shifted to the high frequency range in the compounds. Terminal cyanide frequencies $\nu(\text{CN})$ in cyanide-bridged compounds are generally observed at lower frequencies than the $\nu(\text{CN})$ frequencies of bridging cyanides [77,78]. Bridge cyanide frequencies in cyanide-bridged compounds are observed at higher frequencies due to kinematic coupling [79,80].

When the FT-IR and Raman spectral data of the compounds were compared with the single crystal X-ray data, it was seen that the results were compatible with each other. Accordingly, the bond lengths of $\text{C14}\equiv\text{N8}$ and $\text{C13}\equiv\text{N7}$ for compound 1 were found to be 1.146(3) Å. Cd–N bond lengths in compound 1 are $\text{Cd1-N1} = 2.328(2)$ Å, $\text{Cd1-N3} = 2.243(2)$, $\text{Cd1-N5} = 2.256(2)$, $\text{Cd1-N7} = 2.253(2)$, $\text{Cd1-N10} = 2.337(2)$, $\text{Cd2-N8} = 2.362$, $\text{Cd2-N9} = 2.392$ and $\text{Cd2-N13} = 2.309$ Å. The stretching bands seen in the FT-IR spectrum of compound 1 [2148 cm^{-1} for $\text{C14}\equiv\text{N8}$ and 2126 cm^{-1} for $\text{C13}\equiv\text{N7}$]. For compound 2, the $\text{C13}\equiv\text{N7}$ and $\text{C11}\equiv\text{N5}$ bond lengths were found to be 1.148(4) and 1.142(4) Å, respectively. Cd–N bond lengths in compound 2 are $\text{Cd1-N1} = 2.331$ Å, $\text{Cd1-N3} = 2.349$, $\text{Cd1-N5} = 2.336$, $\text{Cd2-N7} = 2.348(2)$, $\text{Cd2-N11} = 2.234(3)$, $\text{Cd2-N13} = 2.246(3)$ and $\text{Cd2-N15} = 2.249$ Å. Stretching bands seen in the FT-IR spectrum of compound 2 [2135 cm^{-1} for $\text{C13}\equiv\text{N7}$ and 2120 cm^{-1} for $\text{C13}\equiv\text{N7}$].

3.3. Thermal analysis

To determine the thermal behaviour of the compounds, the thermal analysis curves of the compounds were recorded in the temperature range of 30–1000 °C under a dry air atmosphere (Fig. S4). The thermal decomposition of compounds 1 and 2 proceeded in three steps. In its first step, 1 loses three 1-meim ligands in the temperature range of 202–303 °C [found (calculated)(%) = 33.80 (34.56)]; In 2, one water molecules remove from the structure in the temperature range of 110–200 °C [found (calculated)(%) = 2.04 (2.00)]. In the second step, 1 loses one 1-meim ligand in the temperature range of 303–415 °C [found (calculated)(%) = 29.36 (28.75)]; For 2, it loses five 1-etim ligands in the temperature range of 200–378 °C [found (calculated)(%) = 53.60 (54.47)]. In the last step, six cyanide ligands the released with strong exothermic peak for 1 in the temperature range of 415–477 °C [found

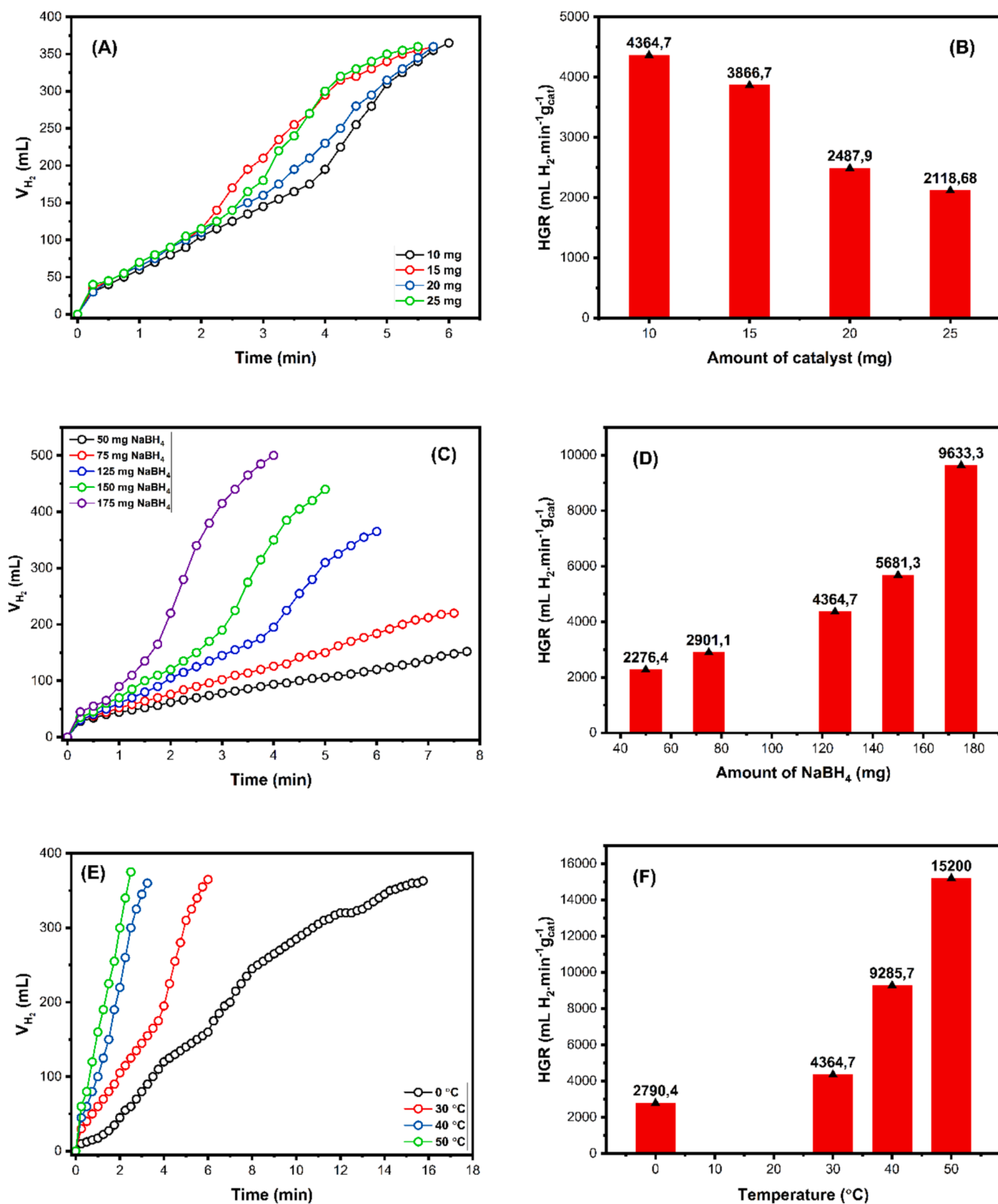


Fig. 4. Effects of compound 1 amounts (a), NaBH_4 amounts (c), and temperature (f) on hydrogen generation of compound 1 and the calculated HGR values for compound 1 (b), NaBH_4 amounts (d), and temperature (f), respectively.

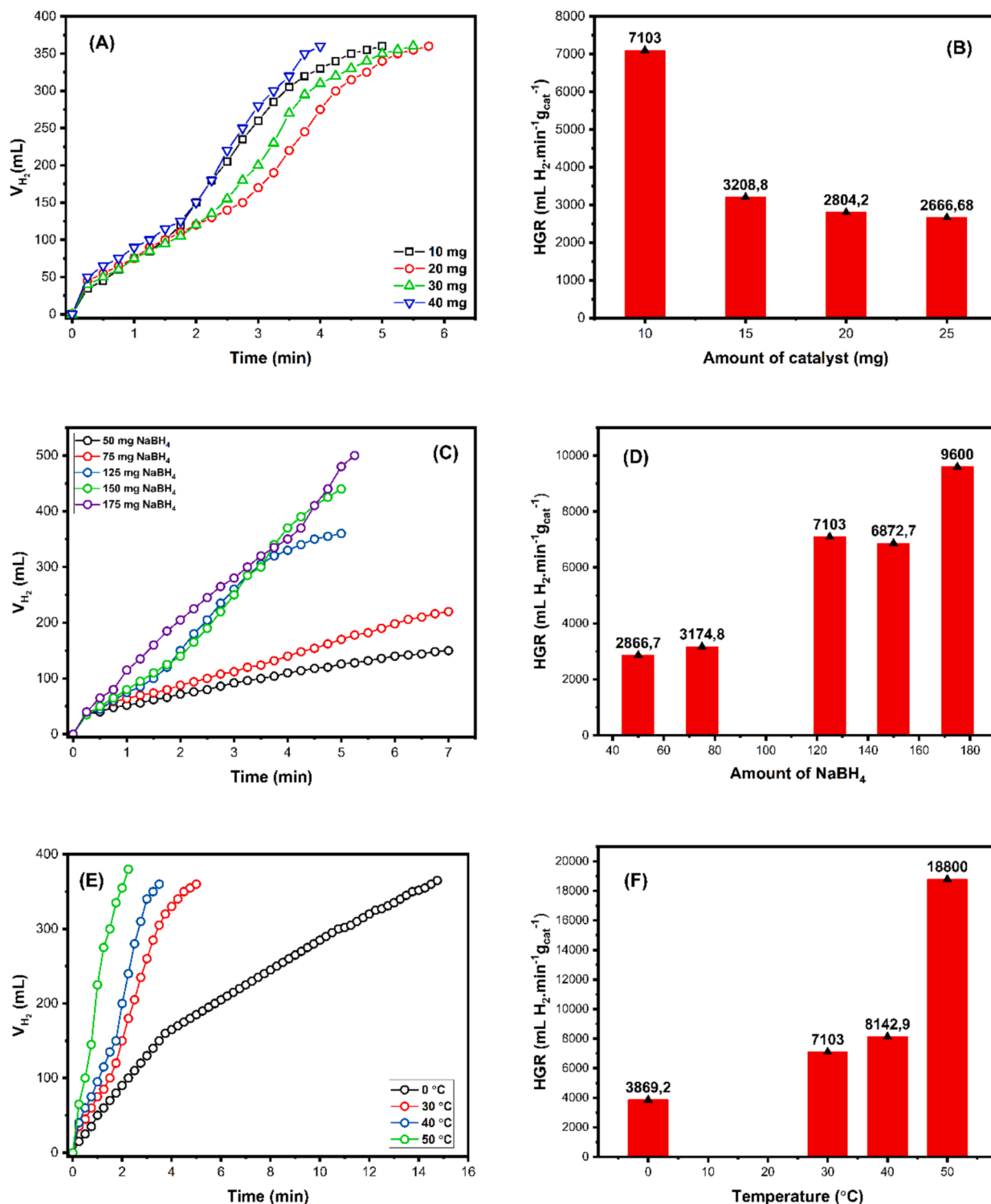


Fig. 5. Effects of compound 2 amounts (a), NaBH_4 amounts (c), and temperature (e) on hydrogen generation of compound 2 and the calculated HGR values for compound 1 (b), NaBH_4 amounts (d), and temperature (f), respectively.

(calculated)(%) = 20.98 (21.92)] and for 2 in the temperature range of 378–474 °C [found (calculated)(%) = 30.73 (31.26)]. ($\text{DTA}_{\text{max.}} = 448$ °C for 1 and 435 °C for 2). After these stages, the solid products of thermal decomposition are $\text{CdO} + \text{Co}_3\text{O}_4$ for 1 and 2. The decomposition product, Co_3O_4 , converted into CoO above 905 °C.

3.4. Hydrogen production results

In this study, to reveal the catalytic effects of compounds 1 and 2 were used to produce hydrogen from NaBH_4 methanolysis. For this purpose, the effects of catalysts (10–25 mg) and NaBH_4 amounts (50–175 mg) and various temperature (0–50 °C) on hydrogen generation were investigated. HGR (hydrogen generation rate) data were calculated based on half the theoretical hydrogen volume.

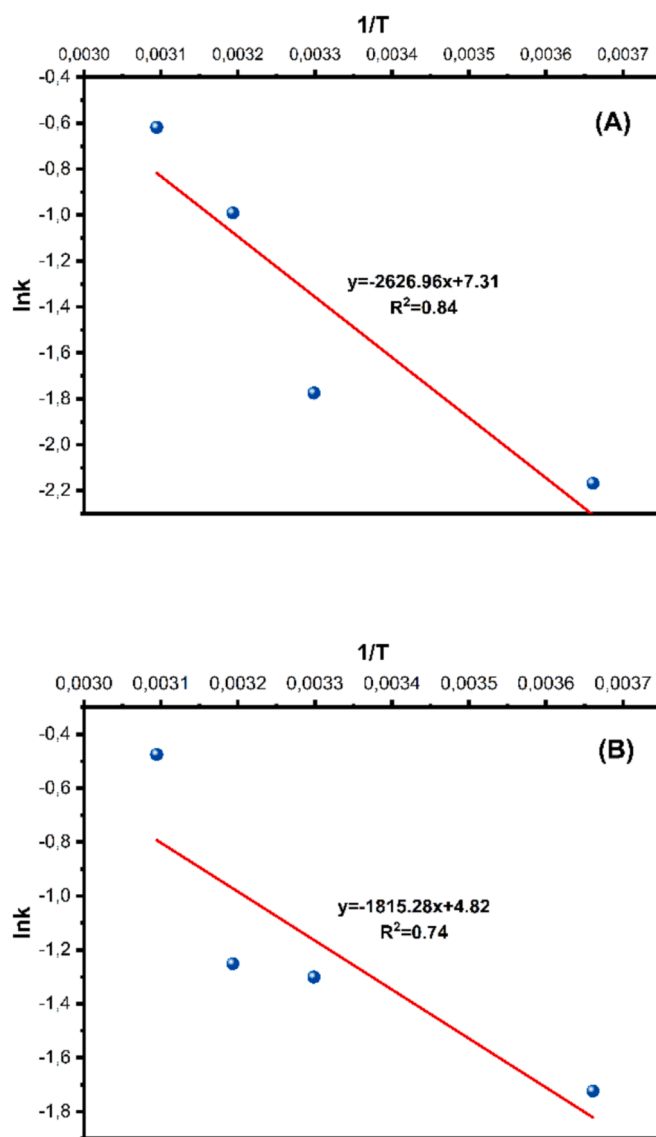


Fig. 6. Arrhenius plots of catalysts; compound 1 (A), and compound 2 (B).

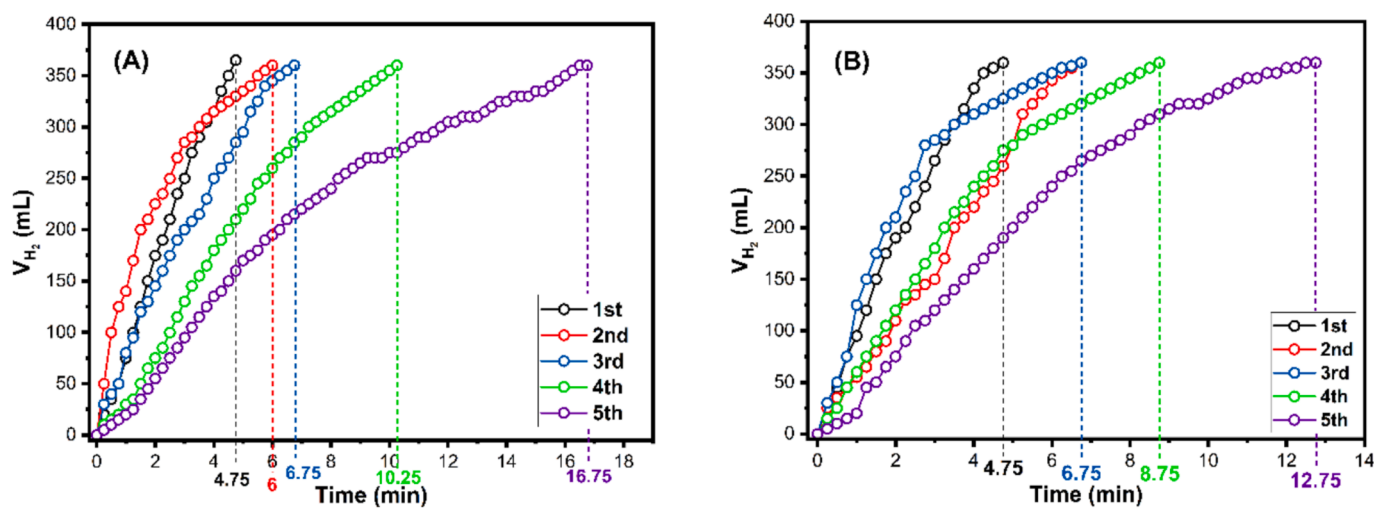


Fig. 7. Reusability of catalysts; compound 1 (A), and compound 2 (B).

The amount of catalyst is a quite important parameter for the economy of the process. While a high catalyst amount is uneconomical, a low amount results in an insufficient catalytic effect. Experiments were conducted with varying amounts (10, 15, 20, and 25 mg) of catalysts. During the experiments, 10 mL MeOH, 125 mg NaBH₄, 30 °C temperature, and 700 rpm stirring speed were kept constant. The results of compounds **1** and **2** were depicted in Fig. 4 (A and B) and 5 (A and B), respectively. According to the results, 10, 15, 20, and 25 mg of compound **1** produced the theoretical hydrogen volume in 6, 5.75, 5.75, and 5.5 mins, respectively. In terms of compound **2**, the hydrogen generation times were 5, 5.5, 5.75, and 4 mins, respectively. It was clearly understood that the increase in the amount of catalyst positively affected hydrogen production. For 10, 15, 20, and 25 mg compound **1** amounts, HGR values were calculated 4364.7, 3866.7, 2487.9, and 2118.7 mL H₂.min⁻¹g_{cat}⁻¹, and 7103, 3208.8, 2804.2, and 2666.7 mL H₂.min⁻¹g_{cat}⁻¹ for compound **2**, respectively. It was observed that the HGR values for both compounds decreased depending on the increase in the amount of catalyst. At the same time, the HGR value obtained for compound **2** was 1.63 times higher than that of compound **1**. Similarly, hydrogen production was faster with compound **2**. Since the highest HGR value for both compounds were obtained at 10 mg catalyst, subsequent studies were continued with this amount of catalyst. See Fig. 5.

Sodium borohydride amounts of 50, 75, 125, 150, and 175 mg were used for both compounds to determine the effect of NaBH₄ amount on hydrogen production. Other conditions were kept constant: 10 mg catalyst, 10 mL MeOH and 30 °C. The results were shown in Fig. 4 (C and D), and 5 (C and D), respectively. As expected, the amount of hydrogen increased with increasing amount of NaBH₄. According to the results, the theoretical hydrogen volume for 50, 75, 125, 150, and 175 mg NaBH₄ were produced 7.75, 7.5, 6, 5, and 4 mins for compound **1**, and 7, 7, 5, 5, and 5.25 mins for compound **2**, respectively. The HGR values were 2276.4, 2901.1, 4364.7, 5681.3, and 9633.3 mL H₂.min⁻¹g_{cat}⁻¹ for compound **1** and 2866.7, 3174.8, 7103, 6872.7, and 9600 mL H₂.min⁻¹g_{cat}⁻¹ for compound **2**, respectively. It was clearly understood that the increase in the amount of NaBH₄ positively affected hydrogen production. As with the catalyst amount, better high results were obtained with compound **2** in NaBH₄ studies. Although the highest HGR value was reached at 175 mg NaBH₄ for both compounds, subsequent experiments were continued with 125 mg NaBH₄ for comparison with the literature.

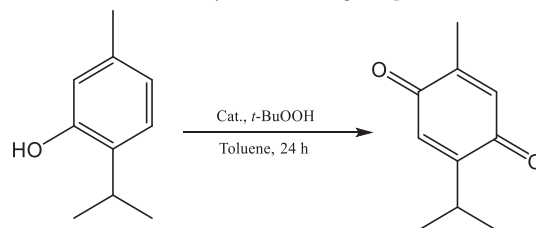
Kinetic studies of hydrogen production were carried out at 0, 30, 40, and 50 °C temperatures for compounds **1** and **2**. The experiments were performed in the presence of 10 mg g catalyst, 125 mg NaBH₄ and 10 mL MeOH. The results were presented in Fig. 4 (E and F), and 5 (E and F), respectively. As can be seen, the rate of hydrogen production increased as the temperature increased and the reaction completion time decreased. For 0, 30, 40, and 50 °C temperatures, the reaction was completed in 15.75, 6, 3.25, and 2.5 mins for compound **1** and 14.75, 5, 3.5, and 2.25 mins for compound **2**, respectively. The HGR values were 2790.4, 4364.7, 9285.7, and 15200 mL H₂.min⁻¹g_{cat}⁻¹ for compound **1** and 3869.2, 7103, 8142.9, and 18800 mL H₂.min⁻¹g_{cat}⁻¹ for compound **2**, respectively.

Since activation energy (E_a) is very important in hydrogen production, activation energy was calculated with temperature data. Activation energies were calculated according to the Arrhenius equation given in Eqs. (1) and (2):

$$k = A \cdot e^{-E_a/RT} \quad (1)$$

$$\ln k = \ln A - E_a/RT \quad (2)$$

In the equation, k is the reaction rate constant, A is the Arrhenius constant, R is the ideal gas constant, T is the temperature and E_a is the activation energy. Fig. 6 showed the 1/T graph plotted against lnk. The activation energy was calculated from the slope of this graph. Accordingly, the activation energy for compound **1** and **2** was calculated as 21.84, and 15.09 kJ.mol⁻¹, respectively. When both compounds were

Table 5Catalytic oxidation results of Thymol with using compound **1**^a

Entry	Solvent	T(°C)	sub/cat	Oxidant	Yield (%)
1	EtOH	60	100	<i>t</i> -BuOOH (1 mL)	35.4
2	CH ₃ CN	60	100	<i>t</i> -BuOOH (1 mL)	33.2
3	Toluene	60	100	<i>t</i> -BuOOH (1 mL)	37.6
4	Toluene	30	100	<i>t</i> -BuOOH (1 mL)	30.5
5	Toluene	40	100	<i>t</i> -BuOOH (1 mL)	33.2
6	Toluene	60	100	<i>t</i> -BuOOH (1 mL)	37.6
7	Toluene	100	100	<i>t</i> -BuOOH (1 mL)	54.2
8	Toluene	100	100	H ₂ O ₂ (1 mL)	3.3
9	Toluene	100	100	<i>t</i> -BuOOH (2 mL)	83.6
10	Toluene	100	200	<i>t</i> -BuOOH (1 mL)	48.3
11	Toluene	100	50	<i>t</i> -BuOOH (1 mL)	97.8
12 ^b	Toluene	100	100	<i>t</i> -BuOOH (1 mL)	8.6
13 ^c	Toluene	100	100	<i>t</i> -BuOOH (1 mL)	47.6

^a Reaction conditions: n_{cat}: 4.8x10⁻⁶ mol, V_{solv.} = 4 mL, t = 24 h.

^b Without catalyst.

^c With using compound **2**.

compared, it was clearly seen that compound **2** had lower E_a value than compound **1**. This result supports that compound **2** showed higher performance in catalyst and NaBH₄ amounts and temperature experiments. The compound showed faster catalytic effect due to lower activation energy. This made compound **2** a much more effective catalyst.

3.5. Reusability of compounds **1** and **2**

It is quite significant to show the usability of the catalyst from an industrial perspective. Therefore, reusability studies were carried out in this study to show the economics of compound **1**, and **2**. Reusability studies were carried out by using the same sample five times. After each use, it was waited for 45 min and then next use was started. During the experiments, 10 mg catalyst, 125 mg NaBH₄ and 30 °C were kept constant. The results obtained for compounds **1** and **2** are presented in Fig. 7 (A and B). Accordingly, the required amount of hydrogen was produced in all five uses. This result showed that compounds **1** and **2** have serious potential in hydrogen production by methanolysis of NaBH₄. However, the hydrogen production period was extended after each use. It was thought that the main reason for this was the accumulation of Na and/or tetramethoxyborate residues on the catalyst surfaces in each use. Kaya [81] obtained similar results during the reusability studies of activated carbons produced from defatted spent coffee ground. It was stated that this situation was caused by tetramethoxyborate residues accumulated on the surface of activated carbons and the increase in solution viscosity.

3.6. Catalytic oxidation results

In catalytic activity studies, both compound **1** and compound **2** were compared under the same conditions and it was determined that compound **1** was more active (Entries 7 and 13). Therefore, the studies were continued with compound **1**. It was tested for the oxidation of Thymol to Thymoquinone under several experimental conditions. As a result of the test carried out in the absence of catalyst, the product formation found to be below 10 % (Entry 12). In solvent effect experiments carried out at 60 °C, the highest product conversion was achieved with toluene (37.6

%), followed by ethanol (35.4 %) and acetonitrile (33.2 %) solvents, respectively (Entries 1–3). As a result, catalytic studies were continued with toluene, which is the most suitable solvent. In temperature effect experiments, 30, 40, 60 and 100 °C were studied, respectively (Entries 4–7). As expected, an increase in product yield was observed with increasing reaction temperature. 54.2 % thymoquinone formation was reached at 100 °C (Entry 7). When a different oxidant (H₂O₂) was used under the same conditions, no significant product formation was detected (3.3 %, Entry 8). In the ongoing studies, when the oxidant amount (*t*-BuOOH) was doubled, 83.6 % thymoquinone was detected (Entry 9). In terms of the substrate/catalyst ratio, when *s/c* = 200 was used, almost half the conversion was obtained (48.3 %, Entry 10), while at *s/c* = 50, it was observed that almost all of the substrate was converted to desired product (97.8 %, Entry 11) (Table 5).

4. Conclusions

In this study, two new heteronuclear Cd(II)/Co(III) compounds were synthesized using imidazole-derived ligands and characterized using different techniques. The single crystal X-ray study shows that compound **1** has one-dimensional CP, while compound **2** has two-dimensional CP. Compound **1** is in the space group *P2₁/n*, whereas compound **2** is in the space group *Pbca*. When the 1-meim ligand was replaced by the 1-etim ligand, 2D layer network was obtained, which is extended into a 3D supramolecular framework by O—H...N hydrogen bonds and C—H... π interactions. In the complexes, each Co(III) ion is coordinated by six carbon atoms from cyanide ligands, thus showing an octahedral coordination geometry. As a result of this study, the compounds were characterized by different techniques and at the same time the catalytic activities of the compounds were investigated and it was shown that they could be alternatives to existing catalysts.

Funding

This work has been financially supported by Eskişehir Osmangazi University, Scientific research Unit (Grant No: 2022–2561).

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

Acknowledgement

The authors acknowledge to Scientific and Technological Research Application and Research Center, Sinop University, Turkey, for the use of the Bruker D8 QUEST diffractometer. The authors would like to thank the editor for considering the manuscript for review and the esteemed reviewers for reviewing and giving valuable suggestions for modifications of the manuscript.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ica.2024.122400>.

References

- [1] M.C. Hong, L. Chen, *Design and construction of coordination polymers*, John Wiley & Sons, 2009.
- [2] X.J. Hong, M.F. Wang, H.G. Jin, Q.G. Zhan, Y.T. Liu, H.Y. Jia, X. Liu, Y.P. Cai, Single-crystal to single-crystal transformation from a 1-D chain-like structure to a 2-D coordination polymer on heating, *CrystEngComm* 15 (2013) 5606–5611.
- [3] B.M. Ji, D.S. Deng, L.F. Ma, H.L. Li, X.S. Fan, G.R. Qu, L. Cao, L. Zhou, Cobalt (II), nickel (II), manganese (II) and zinc (II) metal–organic frameworks constructed with the newly designed 2-(pyridin-4-yl)-4, 6-pyrimidine dicarboxylic acid ligand: syntheses, crystal structures and properties, *CrystEngComm* 15 (2013) 4107–4116.
- [4] B. Li, Z. Ju, M. Zhou, K. Su, D. Yuan, A reusable MOF-supported single-site zinc(II) catalyst for efficient intramolecular hydroamination of *o*-alkynylanilines, *Angew. Chem. Int. Ed.* 58 (2019) 7687–7691.
- [5] Y.-C. He, J. Wang, C.-S. Geng, H.-L. Yu, X.-F. Ren, Y.-K. Sun, Z.-H. Zhao, T. Lu, F.-H. Zhao, Three new alkaline earth-based metal-organic frameworks based on two tricarboxylic acid ligands: Structural diversity, stability study and luminescent properties, *J. Mol. Struct.* 1301 (2024) 137363.
- [6] Y.-C. He, H.-L. Yu, K.-Y. Zhao, Y. Wang, C.-S. Geng, S. Wu, H.-K. Yang, F.-H. Zhao, Three new Zn(II) coordination polymers for highly selective and sensitive detection of Fe³⁺, *CrystEngComm* 25 (2023) 328–336.
- [7] X. Deng, Y. Li, Y.-C. He, A new 8-connected Cd(II)-MOF as luminescent sensor for Fe³⁺, *Inorg. Chem. Commun.* 155 (2023) 111108.
- [8] Y.-C. He, X.-H. Li, Y.-M. Ruan, Q. Xu, S.-X. Li, H.-X. Mao, F.-H. Zhao, M.-T. Li, Syntheses, structures and luminescent properties of five new Ag(I)-based coordination polymers, *Inorg. Chim. Acta* 557 (2023) 121710.
- [9] C. Janiak, Engineering coordination polymers towards applications, *Dalton Trans.* 2781–2804 (2003).
- [10] V.M. Hiiuk, S.I. Shylin, D.D. Barakhtii, D.M. Korytko, V.O. Kotsyubynsky, A. Rotaru, S. Shova, I.Y.A. Gural'skiy, Two-Step Spin Crossover in Hofmann-Type Coordination Polymers [Fe(2-phenylpyrazine)₂][M(CN)₂]₂ (M = Ag, Au), *Inorg. Chem.* 61 (2022) 2093–2104.
- [11] M. Magott, B. Gaweł, M. Sarewicz, M. Reczyński, K. Ogorzały, W. Makowski, D. Pinkowicz, Large breathing effect induced by water sorption in a remarkably stable nonporous cyanide-bridged coordination polymer, *Chem. Sci.* 12 (2021) 9176–9188.
- [12] Y.-L. Qin, H. Sun, Y. Jing, X.-P. Jiang, G.-F. Wang, J.-F. Qin, A novel three-dimensional copper(I) cyanide coordination polymer constructed from various bridging ligands: synthesis, crystal structure and characterization, *Acta Crystallogr. Sect. c: Struct. Chem.* 75 (2019) 1517–1523.
- [13] K. Sasaki, H. Yoshino, Y. Shimoda, M. Saigo, K. Miyata, K. Onda, K. Sugimoto, H. Yamate, H. Miura, B. Le Ouay, Guest-tunable excited states in a cyanide-bridged luminescent coordination polymer, *Inorg. Chem.* 60 (2021) 6140–6146.
- [14] M.B.Z. Hegazy, F. Hassan, M. Hu, Small, Hofmann-Type Cyanide Bridged Coordination Polymers for Advanced Functional Nanomaterials, *Small* 20 (11) (2024) 2306709.
- [15] M. Gorra, F.N. Watchou, M.A. Palacios, J. Long, S. Sene, G. Félix, N. Tanchoux, F. Quignard, J. Larionova, Y. Guari, Composites based on nitroprusside cyanide-bridged coordination polymer particles and chitosan for NO delivery, *New J. Chem.* 47 (2023) 3207–3214.
- [16] A. Şenocak, A. Karadağ, M.S. Soylu, Ö. Andaç, Two novel cyanide-bridged polymeric complexes with suspension bridge type connections and a series of related complex salts: crystallographic and thermal characterizations, *New J. Chem.* 39 (2015) 3675–3686.
- [17] Z. Smekal, I. Čisarová, J. Mroziński, Cyano-bridged bimetallic complexes of copper (II) with tetracyanonickelate(II). Crystal structure of [Cu(dpt)Ni(CN)₄], *Polyhedron* 20 (2001) 3301–3306.
- [18] F.B. Stocker, M.A. Troester, D. Britton, Crystal structures of a family of new copper (I) cyanide complexes of thiourea and substituted thioureas, *Inorg. Chem.* 35 (1996) 3145–3153.
- [19] Z. Travnický, R. Zboril, M. Matikova-Malarova, B. Drahos, J. Cernak, Thermal decomposition of [Co(en)₃][Fe(CN)₆]•2H₂O: Topotactic dehydration process, valence and spin exchange mechanism elucidation, *Chem. Cent. J.* 7 (2013) 1–18.
- [20] S.R. Batten, S.M. Neville, D.R. Turner, Coordination polymers: design, analysis and application, *Coordination polymers: design, analysis and application*, Royal Society, 2009.
- [21] S.L. Huang, L. Zhang, Y.J. Lin, G.X. Jin, Discrepant gas adsorption in isostructural heterometallic coordination polymers: strong dependence of metal identity, *CrystEngComm* 15 (2013) 78–85.
- [22] T. Iwamoto, Past, present and future of the clathrate inclusion compounds built of cyanometallate hosts, *J. Inclusion Phenom. Mol. Recognit. Chem.* 24 (1996) 61–132.
- [23] Y. Avila, P. Acevedo-Pena, L. Reguera, E. Reguera, Recent progress in transition metal hexacyanometallates: From structure to properties and functionality, *Coord. Chem. Rev.* 453 (2022) 214274.
- [24] I.I. Lungu, A.M. Grumezescu, C. Fleaca, Unexpected ferromagnetism-A review, *Appl. Sci.* 11 (2021) 6707.
- [25] G. Penche, M.P. González-Marcos, J.R. González-Velasco, Transition metal hexacyanoferrate(II) complexes as catalysts in the ring-opening copolymerization of CO₂ and propylene oxide, *Top. Catal.* 65 (2022) 1541–1555.
- [26] L. Li, Y.-T. Yu, Y. Hua, X.-N. Li, H. Zhang, Recent progress in polyoxometalate-viologen photochromic hybrids: structural design, photochromic mechanism, and applications, *Inorg. Chem. Front.* 10 (2023) 1965–1985.
- [27] E.G. Neiva, A.J. Zarbin, Nickel hexacyanoferrate/graphene thin film: a candidate for the cathode in aqueous metal-ion batteries, *New J. Chem.* 46 (2022) 11118–11127.
- [28] X. Zhao, Z. Xing, C. Huang, Investigation of high-entropy Prussian blue analog as cathode material for aqueous sodium-ion batteries, *J. Mater. Chem. A* 11 (2023) 22835–22844.

- [29] G. Penche, J.R. González-Velasco, M.P. González-Marcos, Porous hexacyanometallate (III) complexes as catalysts in the ring-opening copolymerization of CO₂ and propylene oxide, *Catalysts* 11 (2021) 1450.
- [30] E.J. Canto-Aguilar, M.A. Oliver-Tolentino, G. Ramos-Sánchez, I. González, Effect of the external metal on the electrochemical behavior of M₃[Co(CN)₆]₂ (M: Co, Ni, Cu, Zn), towards their use as anodes in potassium ion batteries, *Electrochim. Acta* 371 (2021) 137828.
- [31] S.S. Wong, R. Shu, J. Zhang, H. Liu, N. Yan, Downstream processing of lignin derived feedstock into end products, *Chem. Soc. Rev.* 49 (2020) 5510–5560.
- [32] K.M. Lee, Electrochemical Properties of Metal Hexacyanoferrate Complexes and Cobalt Oxide Thin Films and Their Application to Electrochromic Devices, PhD Thesis (2014).
- [33] J. Sîma, R. Sîpos, Insight into coordination, Applied photochemistry of iron(III) compounds, *Bioinorg. Appl. Inorg. Chem.* (2009) 306–365.
- [34] M. Ciabocco, P. Cancemi, M.L. Saladino, E. Caponetti, R. Alduina, M. Berrettoni, Synthesis and antibacterial activity of iron-hexacyanocobaltate nanoparticles, *J. Biol. Inorg. Chem.* 23 (2018) 385–398.
- [35] R. Mojica, A. Torres, Y. Avila, E. Reguera, Electronic structure that gives rise to the optical properties of zinc, cadmium and silver hexacyanocobaltates(III), *Chem. Inorg. Mater.* 1 (2023) 100021.
- [36] O. Mikhailov, T. Tatarintseva, N. Naumkina, Complexation in binary Cd2[Fe(CN)6]–M(II) systems (M = Mn Co, Ni, Cu, Zn) in gelatin-immobilized cadmium(II) hexacyanoferrates(II), *Koord. Khim.* 29 (2003) 327–334.
- [37] X. Li, N. Yang, X. Cen, S. Li, L. Zhang, Z.-H. Lu, Exceptional activity of hollow porphyrin frameworks-confined Ni nanoparticles for hydrogen production from NaBH₄ methanolysis, *Fuel* 354 (2023) 129332.
- [38] N. Sahiner, S.B. Sengel, Various amine functionalized halloysite nanotube as efficient metal free catalysts for H₂ generation from sodium borohydride methanolysis, *Appl. Clay Sci.* 146 (2017) 517–525.
- [39] L. Semiz, Hydrogen generation from sodium borohydride by sulfonated polymers, *J. Phys. Chem. Solids* 143 (2020) 109498.
- [40] C. Saka, A. Balbay, Oxygen and nitrogen-functionalized porous carbon particles derived from hazelnut shells for the efficient catalytic hydrogen production reaction, *Biomass Bioenergy* 149 (2021) 106072.
- [41] J. Liao, Y. Shao, Y. Feng, J. Zhang, C. Song, W. Zeng, J. Tang, H. Dong, Q. Liu, H. Li, Interfacial charge transfer induced dual-active-sites of heterostructured Cu_{0.8}Ni_{0.2}WO₄ nanoparticles in ammonia borane methanolysis for fast hydrogen production, *Appl. Catal., B: Environmental* 320 (2023) 121973.
- [42] N. Sahiner, A.O. Yasar, N. Aktas, Metal-free pyridinium-based polymeric ionic liquids as catalyst for H₂ generation from NaBH₄, *Renew. Energy* 101 (2017) 1005–1012.
- [43] D. Alpaslan, T. Ersen Dudu, N. Aktas, Synthesis of poly (ginger oil) organo particles as a metal free catalysts and their use in hydrogen production from sodium borohydride methanolysis, *J. Polym. Environ.* 31 (2023) 1191–1201.
- [44] M.F. Nagoor Meeran, H. Javed, H. Al Taei, S. Azimullah, S.K. Ojha, Pharmacological properties and molecular mechanisms of thymol: prospects for its therapeutic potential and pharmaceutical development, *Front. Pharmacol.* 8 (2017) 380.
- [45] L.A. Sampaio, L.T.S. Pina, M.R. Serafini, D.D.S. Tavares, A.G. Guimaraes, Antitumor effects of carvacrol and thymol: a systematic review, *Front. Pharmacol.* 12 (2021) 702487.
- [46] H. Xu, B.-Y. Zhou, K. Yu, Z.-H. Su, B.-B. Zhou, Z.-M. Su, Copper cyanide polymers with controllable dimensions modulated by rigid and flexible bis-(imidazole) ligands: synthesis, crystal structure and fluorescence properties, *CrystEngComm* 21 (2019) 1242–1249.
- [47] A.M. Abu-Dief, L.H. Abdel-Rahman, A.A. Abdelhamid, A.A. Marzouk, M. R. Shehata, M.A. Bakheet, O.A. Almaghrabi, A. Nafady, Synthesis and characterization of new Cr(III), Fe(III) and Cu(II) complexes incorporating multi-substituted aryl imidazole ligand: Structural, DFT, DNA binding, and biological implications, *Spectrochim. Acta, Part a: Mol. Biomol. Spect.* 228 (2020) 117700.
- [48] M. Ismael, A. Abdou, A.M. Abdel-Mawgoud, Synthesis, CHARACTERIZATION, MODELING, AND ANTIMICROBIAL ACTIVITY of Fe(III), Co(II), Ni(II), Cu(II), and Zn(II) complexes based on tri-substituted imidazole ligand, *Z. Anorg. Allg. Chem.* 644 (2018) 1203–1214.
- [49] J. Huo, H. Li, D. Yu, N. Arulsamy, Three new metal complexes with imidazole-containing tripodal ligands as fluorophores for nitroaromatics-and ion-selective sensing, *Inorg. Chim. Acta* 502 (2020) 119310.
- [50] B. An, F. Yin, N.J. de Voogd, X. Chen, W. Cheng, W. Lin, Chagosendines A-C, New Metal Complexes of Imidazole Alkaloids from the Calcareous Sponge Leucetta chagosensis, *Chem. Biodiver.* 15 (2018) e1700481.
- [51] G.S. Kırkkıoğlu, E. Sayın, T. Yavuz, O. Şahin, One-dimensional heteronuclear complexes with cyanide and 2-ethylimidazole ligands, *Spectrosc. Lett.* 54 (2021) 1–13.
- [52] D. Karaağaç, G.S. Kırkkıoğlu, Syntheses and characterizations of the cyanide-bridged heteronuclear polymeric complexes with 2-ethylimidazole, *Bull. Chem. Soc. Eth.* 30 (2016) 263–272.
- [53] G.S. Kırkkıoğlu, O.Z. Yeşilel, I. Kavlak, S. Kurtaran, O. Büyükgüngör, Synthesis, Characterization and Crystal Structure of a Novel Three-Dimensional Supramolecular Framework Containing Ni---π Interaction Heteronuclear Complex: {[Cu(4(5)-Meim)4][Ni(CN)4]·H2O}_n, *J. Inorg. Organomet. Poly. Mater.* 19 (2009) 314–321.
- [54] G.S. Kırkkıoğlu, O.Z. Yeşilel, İ. Çaylı, O. Büyükgüngör, One- and two-dimensional cadmium(II) tetracyanonickelate(II) coordination polymers with imidazole and 2-methylimidazole ligands, *J. Inorg. Organomet. Poly. Mater.* 21 (2011) 306–315.
- [55] G.S. Kırkkıoğlu, K. Gör, O. Büyükgüngör, New cyano bridged heteropolynuclear Cu(II) and Cd(II)-tetracyanopalladate(II) polymeric complexes with 2-methylimidazole ligand, *Spectrochim. Acta Part a: Mol. Biomol. Spec.* 124 (2014) 588–594.
- [56] T. Mwanza, G.S. Kırkkıoğlu, H. Ünver, O. Şahin, O.Z. Yeşilel, Synthesis, spectroscopic, structural characterizations, and catalytic properties of cyanide-bridged heteronuclear metal organic frameworks with imidazole, *J. Solid State Chem.* 314 (2022) 123344.
- [57] H. Tchouka, A. Meetsma, G. Molnár, L. Rechignat, W.R. Browne, Solution and single crystal spectroscopic characterization of (PPH₄)₂[Fe(CN)₅(imidazole)]·2H₂O, *J. Mol. Struct.* 999 (1–3) (2011) 39–48.
- [58] A. Al Abbas, B. Heinrich, M. L'Her, E. Couzigné, R. Welter, L. Douce, Bolaamphiphilic liquid crystals based on bis-imidazolium cations, *New J. Chem.* 41 (2017) 2604–2613.
- [59] İ. Çaylı, G.S. Kırkkıoğlu, O.Z. Yeşilel, O. Şahin, O. Büyükgüngör, C-H...Pd interactions and cyano-bridged heteronuclear polymeric complexes, *Polyhedron* 31 (2012) 386–394.
- [60] F. Çetinkaya, G.S. Kırkkıoğlu, O.Z. Yeşilel, O. Büyükgüngör, Two dimensional heteropolynuclear Zn(II) and Cd(II)-tetracyanopalladate(II) complexes with the 1-ethylimidazole ligand exhibiting C-H... Pd interactions, *Polyhedron* 55 (2013) 10–17.
- [61] F. Çetinkaya, G.S. Kırkkıoğlu, O.Z. Yeşilel, T. Hökelek, H. Dal, One-dimensional cyano-bridged heterometallic (Cu/Ni and Cu/Pd) complexes with 1-ethylimidazole, *Polyhedron* 47 (2012) 126–133.
- [62] F. Çetinkaya, G.S. Kırkkıoğlu, O.Z. Yeşilel, T. Hökelek, Y. Süzen, Syntheses, crystal structures and spectral properties of 1D tetracyanonickelate(II) complexes with 1-ethylimidazole, *J. Mol. Struct.* 1048 (2013) 252–260.
- [63] G.S. Kırkkıoğlu, F.Ç. Kiraz, E. Sayın, Vibrational spectra, powder X-ray diffractions and physical properties of cyanide complexes with 1-ethylimidazole, *Spectrochim. Acta Part a: Mol. Biomol. Spect.* 149 (2015) 8–16.
- [64] G.S. Kırkkıoğlu, O.Z. Yeşilel, İ. Kavlak, O. Büyükgüngör, Hetero-Metallic Coordination Polymers: Syntheses, Vibrational Spectra, Thermal Analyses and Crystal Structures of trans-[M(N-Meim)₂Ni(μ-CN)₄]_n (M = Cu(II), Zn(II) and Cd (II)), *J. Inorg. Organomet. Poly. Mater.* 19 (2009) 539–548.
- [65] E. Sayın, G.S. Kırkkıoğlu, O.Z. Yeşilel, T. Hökelek, Synthesis, crystal structure and spectroscopic properties of one-dimensional zinc(II)-cyanide complex with 1-methylimidazole, [Zn(μ-CN)(CN)(1-meim)]_n, Z. Kristallogr. -Crystalline Mater. 230 (2015) 421–426.
- [66] G.M. Sheldrick, A short history of SHELX, *Acta Cryst. Sect. a: Found. Crystallogr.* 64 (2008) 112–122.
- [67] G.M. Sheldrick, SHELXT-Integrated space-group and crystal-structure determination, *Acta Cryst. Sect. C, Struct. Chem.* 71 (2015) 3–8.
- [68] Bruker, Bruker AXS Inc. Madison, Wisconsin, USA, 2013.
- [69] C.F. Macrae, I. Sovago, S.J. Cottrell, P.T. Galek, P. McCabe, E. Pidcock, M. Platings, G.P. Shields, J.S. Stevens, M. Towler, Mercury 4.0: From visualization to analysis, design and prediction, *J. Appl. Crystallogr.* 53 (2020) 226–235.
- [70] L.J. Farrugia, WinGX and ORTEP for Windows: an update, *J. Appl. Crystallogr.* 45 (2012) 849–854.
- [71] L.H. Jones, B.I. Swanson, Interpretation of potential constants: Application to study of bonding forces in metal cyanide complexes and metal carbonyls, *Accounts Chem. Res.* 9 (1976) 128–134.
- [72] H. Baranska, J. Kuduk-Jaworska, K. Waszkiewicz, Vibrational study of cytotoxic bis (1-ethylimidazole)₂(-)-malatoplatinum(II), *J. Mol. Struct.* 550 (2000) 307–317.
- [73] V. Sheinker, D.Y. Movshovich, O.A. Osipov, Investigation and structure of properties of heterocyclic compounds and their complexes. IV. Calculation and interpretation of the vibrational spectra of N-methylimidazole, *Zh. Obshch. Khim* 43 (1973) 2725.
- [74] J.B. Hodgson, G.C. Percy, D.A. Thornton, The infrared spectra of imidazole complexes of first transition series metal(ii) nitrates and perchlorates, *J. Mol. Struct.* 66 (1980) 81–92.
- [75] Y. Tufan, N. Karacan, J.E.D. Davies, Vibrational spectroscopic investigations of M (Imidazole)₂Ni(CN)₄·2C₆H₁₂ clathrates, *Vib. Spectrosc.* 23 (2000) 51–55.
- [76] A. Karadağ, İ. Önal, A. Şenocak, İ. Uçar, A. Bulut, O. Büyükgüngör, Syntheses, IR spectra, thermal properties and crystal structures of novel cyano-bridged polymeric complexes of zinc(II) and cadmium(II) with tetracyanopalladate(II), *Polyhedron* 27 (2008) 223–231.
- [77] S. Zhan, X. Chen, A. Vij, D. Guo, Q. Meng, Synthesis, studies and molecular structure of trinuclear cyanide-bridged copper-iron complexes, *Inorg. Chim. Acta* 292 (1999) 157–162.
- [78] K. Nakamoto, Infrared and Raman spectra of inorganic and coordination compounds, part B: applications in coordination, organometallic, and bioinorganic chemistry, John Wiley & Sons, 2009.
- [79] D.M. Gil, M. Avila, E. Reguera, S. Pagola, M.I. Gómez, R.E. Carbonio, Lead hexacyanoferrate(II) tetrahydrate: Crystal structure, FTIR spectroscopy and thermal decomposition studies, *Polyhedron* 33 (2012) 450–455.
- [80] K.F. Purcell, sigma- and pi-Bonding effects in the coordination of the cyano group, *J. Am. Chem. Soc.* 89 (1967) 6139–6143.
- [81] M. Kaya, Production of metal-free catalyst from defatted spent coffee ground for hydrogen generation by sodium borohydride methanolysis, *Int. J. Hydrogen Energy* 45 (2020) 12731–12742.