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Cu(II) AND Cd(II) COORDINATION POLYMERS DERIVED FROM PYRAZINE-2,3-DICARBOXYLATO AND 1-VINYLIMIDAZOLE LIGANDS: SYNTHESIS, CHARACTERIZATION AND HYDROGEN STORAGE CAPACITIES

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In this study, two new coordination polymers of Cu(II) and Cd(II) ions with pyrazine-2,3-dicarboxylic acid and 1-vinylimidazole were synthesized. The structures of these coordination polymers were characterized with elemental analysis, infrared spectroscopy, thermal analysis, powder X-ray diffraction, and magnetic susceptibility techniques. According to the results of the thermal analysis, the coordination polymers that contained water molecules decomposed below 100 °C, and the final products for both coordination polymers were the related metal oxides in an oxygen atmosphere. Powder X-ray diffraction analysis revealed that the coordination polymers were in the crystalline form. The hydrogen storage capacities and surface areas of the coordination polymers were also determined. The highest hydrogen storage capacities were measured as 296 ml/g for the Cu(II) coordination polymer and 330 ml/g for the Cd(II) coordination polymer at approximately 75 bar and 75 K.

Keywords: pyrazine-2,3-dicarboxylato; 1-vinylimidazole; coordination polymer; hydrogen storage; bridging ligand

КООРДИНАЦИСКИ КОМПЛЕКСИ НА Cu(II) И Cd(II) ИЗВЕДЕНИ ОД ЛИГАНДИ НА ПИРАЗИН-2,3-ДИКАРБОКСИЛАТО И 1-ВИНИЛИМИДАЗОЛ: СИНТЕЗА, КАРАКТЕРИЗАЦИЈА И КАПАЦИТЕТ ЗА СКЛАДИРАЊЕ ВОДОРОД

Во ова истражување се синтетизирани два нови координациски полимери на јони на Cu(II) и Cd(II) со пиразин-2,3-дикарбоксилна киселина и 1-винилимидазол. Карактеризацијата на овие координациски комплекси е извршена со помош на елементна анализа, инфрацрвена спектроскопија, термичка анализа, рендгенска дифракција од прашок, како и техники на магнетен сусцептибилитет. Според резултатите на термичката анализа, координациските комплекси што содржат вода се разложуваат под 100 °C и конечните продукти за двата координациски комплекса се поврзани со металните оксиди во атмосфера на кислород. Рендгенската дифракција на прашок откри дека координациските полимери имаат кристална форма. Беа определени капацитетот за складирање на водород и површината на координациските полимери. Најголем капацитет за складирање на водород изнесуваше 296 ml/g за координацискиот полимер на Cu(II) и 330 ml/g за координацискиот полимер на Cd(II) на приближен притисок од 75 bar и 75 K.

Клучни зборови: пиразин-2,3-дикарбоксилато; 1-винилимидазол; координациски полимер; складирање на водород; премостен лиганд

1. INTRODUCTION

Owing to their fascinating varied architectures, intriguing topologies, and desired functions, coordination polymers (CPs) have been extensively studied [1, 2] and used in many applications, such as gas storage [3], catalysis [4], luminescence [5], magnetism [6], and drug delivery [7]. In recent years, the gas storage properties of CPs have been extensively investigated, and the number of related studies is increasing day by day [8]. The design and synthesis of CPs are closely related to the ligands, metal ions, solvents, and reaction conditions [9]. Particularly, the choice of ligands due to their features such as flexibility, electron pair donation, and functional groups plays a key role in designing of CPs [10]. Recently, the syntheses of CPs with mixed-ligands containing O– and N– donor groups have attracted the particular interest of researchers [11–13]. Different combinations of organic ligands around the metal centers provide diversity in the structures of CPs [14, 15]. Currently, ligands based on carboxylic acid and imidazole are widely used as mixed ligands for the building of CPs, and many studies including these ligands have been reported in the literature [16, 17].

Due to their donor atoms, lengths and geometries, carboxylic acid ligands have been extensively used in the syntheses of CPs [18, 19]. Pyrazine-2,3-dicarboxylic acid (H_2pzdc; Fig. 1A), which contains two neighboring carboxyl groups and two nitrogen atoms in the ring, is an important bridging ligand candidate for the design of CPs [20, 21]. H_2pzdc has six donor atoms with four oxygen atoms and two nitrogen atoms in its structure and can form different polymeric complexes with various structural properties [22, 23]. H_2pzdc can coordinate with metal ions through the oxygen atoms of the carboxyl groups and the nitrogen atoms of the pyrazine ring [24]. Due to its multifunctional coordination modes, H_2pzdc can give one or two protons to generate Hpzdc$^–$ and pzdc$^{2–}$ anions at different pH values [25, 26]. CPs containing H_2pzdc are usually multi-centered because H_2pzdc generally prefers to behave as a bridge ligand between metal atoms [27, 28]. There are several known complexes of H_2pzdc that act as mono-, di-, or multidentates. For these reasons, H_2pzdc is an important bridging ligand that is used to design CPs [29–34].

Imidazole derivatives with different lengths, flexibilities and donor atoms have been frequently used as second ligands together with carboxylate ligands in the design of CPs [35, 36]. In the present study, we selected 1-vinylimidazole (vim; Fig. 1B), which contains a vinyl group and two nitrogen atoms, as the second ligand because CPs based on H_2pzdc and vim have rarely been studied. Additionally, Cu(II) and Cd(II) coordination polymers containing these ligands have not been investigated in the literature. Vim has important properties for polymerization and reactivity [37, 38] and can coordinate to metal ions via the ring nitrogen atom [39, 40]. The polymeric complexes of Co(II), Ni(II), Cu(II), Zn(II), and Cd(II) ions containing vim were studied in our previous works [41–44].

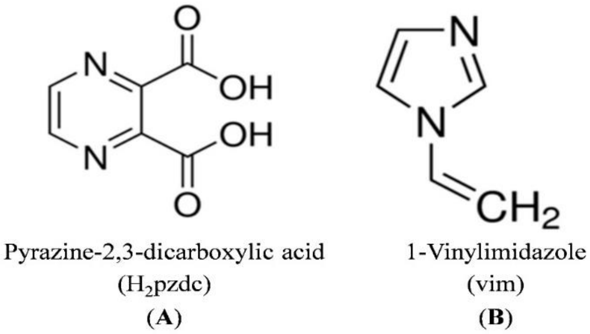

Fig. 1. The chemical structures of H_2pzdc **(A)** and vim **(B)**

In the current study, Cu(II) and Cd(II) coordination polymers derived from pyrazine-2,3-dicarboxylato and 1-vinylimidazole ligands were synthesized and characterized using several techniques, and the hydrogen storage capacities of these coordination polymers were investigated.

2. EXPERIMENTAL SECTION

2.1. *Materials and measurements*

We used basic copper(II) carbonate {$CuCO_3 \cdot Cu(OH)_2$} and cadmium(II) carbonate ($CdCO_3$) as the metal ion sources to obtain coordination polymers without complementary ions. We used pyrazine-2,3-dicarboxylic acid (H_2pzdc) and 1-vinylimidazole (vim) as ligands and used distilled water, ethanol and diethyl ether as solvents. All chemicals and solvents used in the syntheses were supplied from the Sigma-Aldrich Company and were used without further purification.

The elemental analysis measurements for C, H, and N were performed on a CHNS-932 (LECO) instrument. A Bruker Vertex 80 V spectrophotometer was used for the IR spectra, and the measurements were performed using thin KBr pellets in the range of 4000–400 cm$^{–1}$. Simultaneous thermogravimetry (TG), derivative thermogravimetry (DTG) and differential scanning calorimetry (DSC) analyses were performed in an oxygen atmosphere on a TA Instruments SDT Q600 thermal analyzer (heating rate: 10 ºC/min, temperature range: 25–1000 ºC). Powder X-ray diffraction (PXRD) analyses were performed using a PANalytical X'pert Pro MPD model multi-purpose X-ray powder diffractometer. Magnetic susceptibility studies were performed with the Evans magnetic balance method, which is an improved version of the Gouy method, on an MX I Model Sherwood Scientific device. A STOE IPDS II type diffractometer equipped with a graphite-monochromatic (λ = 0.71073 Å) device was used to collect the single-crystal X-ray diffraction data at 293±2 K. Surface area measurements were performed on a Quantachrome Instruments Nova 4200e Surface area and Pore Size Analyzer. The hydrogen storage studies were completed using a VTI HPVA 100 high-pressure adsorption analyzer.

2.2. *Preparation of the coordination polymers*

The coordination polymers in the study were synthesized according to the procedure given in our previous works [43, 44]. As the only difference, basic copper(II) carbonate (0.211 g, 1.0 mmol) and cadmium(II) carbonate (0.345 g, 2.0 mmol) were used for syntheses of the Cu(II) coordination polymer and Cd(II) coordination polymer, respectively.

Cu(II) coordination polymer: Light blue crystals were obtained with a yield of 90% (0.615 g). The crystals were not suitable for single-crystal X-ray analysis because they exhibited polycrystalline structure. Therefore, this analysis could not be performed. Anal. calcd. for $\{Cu(pzdc)(vim)(H_2O)\}_n$ ($C_{11}H_{10}CuN_4O_5$, M_W: 341.7 g/mol): C 38.65, H 2.93, and N 16.40; found: C 38.45, H 3.01, and N 15.92 %. The selected IR peaks (KBr disk/cm^{-1}) were as follows: 3456 (w, br) υ(O–H); 3150–3010 (w, mt) υ(C–H); 1681 (s, sh) υ(C=O); 1582 (w, sh) υ(C=N); and 1449 (w, sh) υ(C=C).

Cd(II) coordination polymer: Light brown crystals were obtained with a yield of 50 % (0.681 g), and the crystal data were collected for this compound. The solving of the crystal structure was very difficult because the single crystal was slightly problematic, and the structure was quite disordered. The major problems in the structure were not completely eliminated; therefore, the solving of the structure could not be fully realized. However, it is thought that the possible structure of the Cd(II) coordination polymer without the solvate groups is similar to the structure provided in Fig. 2 according to the results of all characterization techniques with the collected raw data from the single-crystal X-ray analysis. Anal. calcd. for $\{[Cd_2(pzdc)_2(vim)_6]\cdot 2vim\cdot 3H_2O\}$ ($C_{52}H_{58}N_{20}O_{11}Cd_2$, M_W:1363.8 g/mol): C 45.79, H 4.26, and N 20.55; found: C 45.83, H 4.32, and N 20.44%. The selected IR peaks (KBr disk/cm^{-1}) were as follows: 3378 (m, br) υ(O–H); 3112–3001 (m, mt) υ(C–H); 1649 (s, sh) υ(C=O); 1499 (s, sh) υ(C=N); and 1449 (m, sh) υ(C=C).

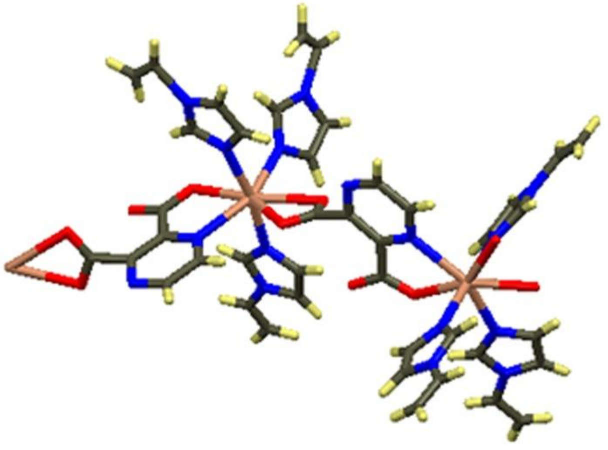

Fig. 2. The possible structure of the Cd(II) coordination polymer without the solvate groups

3. RESULTS AND DISCUSSION

3.1. *IR spectroscopy*

In the IR spectra of the coordination polymers (Fig. 3), the ν(O–H) stretch vibrations were observed at 3456 cm^{-1} for the Cu(II) coordination polymer and 3378 cm^{-1} for the Cd(II) coordination polymer. The IR spectrum of H_2pzdc displays a broad band at approximately 2500 cm^{-1} [43, 44]. The disappearance of this broad band in the IR spectra of the coordination polymers demonstrated that H_2pzdc lost two hydrogens with coordination polymer formation and coordinates to the metal ions via the deprotonated oxygen atoms of the carboxylate groups [31, 43–45]. The peaks of the ν(C=O) and ν(C=N) stretch vibrations belonging to H_2pzdc appeared at lower energetic frequencies in the IR spectra of the coordination polymers. This result suggests that the metal ions were coordinated by the O and N atoms of H_2pzdc.

In our previous studies, the structures of synthesized complexes containing the pzdc ligand were determined with the single-crystal X-ray technique [43, 44]. From the crystal structures of these complexes, we understand that the pzdc ligand exhibits various binding modes. Based on our previous studies and the possible structure of the

Cd(II) coordination polymer (Fig. 2), we believe that the pzdc ligands coordinate to Cd(II) ions via the O atoms of the carboxylate groups in the structure. Examination of the IR spectrum of the Cd(II) coordination polymer (Fig. 3) revealed that there are three different ν(C=O) stretch vibrations in the range of 1649–1590 cm^{-1} that depend on the binding modes of the carboxyl oxygen atoms. Similarly, two peaks in the range of 1681–1644 cm^{-1} were observed in the IR spectrum of the Cu(II) coordination polymer. This finding also demonstrates that the Cu(II) coordination polymer has two different ν(C=O) stretch vibrations that depend on the binding modes of the carboxyl oxygen atoms (Fig. 3).

The peaks belonging to the ν(C=N) and ν(C=C) stretch vibrations of the vim ligand appear from 1650 cm^{-1} to 1500 cm^{-1} [43, 44]. There are also similar peaks in the structure of the pzdc ligand. For this reason, it was difficult to determine whether these peaks belong to the vim or pzdc ligands in the IR spectra of the coordination polymers. Finally, the ν(C–H) stretch vibrations belonging to the pzdc and vim ligands were observed in the range of 3150–3000 cm^{-1}.

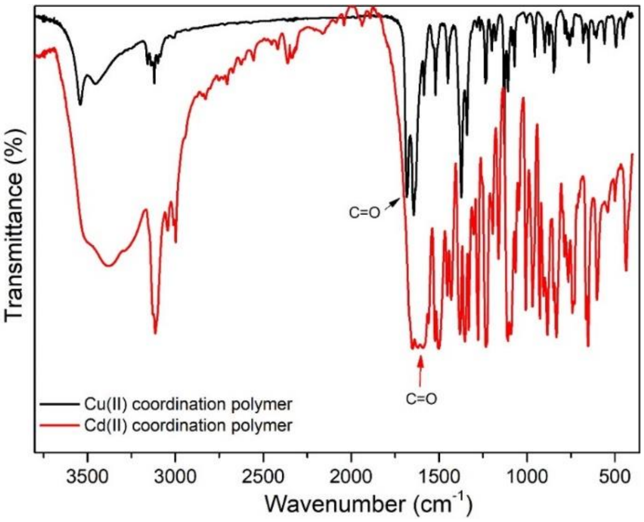

Fig. 3. The IR spectra of the Cu(II) coordination polymer and the Cd(II) coordination polymer

3.2. *Thermal analysis*

The thermal analysis curves of the Cu(II) coordination polymer are given in Fig. 4A. According to these curves, the Cu(II) coordination polymer exhibits two main decomposition steps. Initially, 1 mol of water molecules per molecular unit is separated from the structure at 30–81 °C (found: 5.1%; theoretical: 5.3 %). The endothermic peak at DSC$_{max.}$: 72 °C supports the separation of the water molecule from the structure (DTG$_{max.}$: 68 °C). A stable anhydrous intermediate product forms between 81 °C and 285 °C. After this temperature, the vim and pzdc ligands are removed from the structure (DTG$_{max.}$: 346 °C). The excessive exothermic peak at DSC$_{max.}$: 351 °C indicates that the remaining organic residue severely decomposes. CuO remains as the final product at the end of the decomposition process (found: 23.9 %; theoretical: 23.3 %).

The thermal analysis curves of the Cd(II) coordination polymer demonstrate that the thermal decomposition occurs in five main steps (Fig. 4B). Initially, 3 mol of crystal water per molecular unit are removed from the structure at 29–79 °C (found: 4.2 %; theoretical: 4.0 %). The endothermic peak at DSC$_{max.}$: 51 °C supports the separation of the crystal water from the structure. After 79 °C, the anhydrous structure constantly decomposes, and the fixed weight plateaus do not form. In other words, the decomposition reactions overlap; before the one of the decomposition reaction ends, another reaction begins. The DTG curve shows the overlapping reactions in greater detail. With the overlapping reactions, the solvate vim groups and vim and pzdc ligands are removed from the structure, respectively. The excessive exothermic peak at DSC$_{max.}$: 478 °C (DTG$_{max.}$: 480 °C) indicates that the remaining organic residue severely decomposes. The final product at the end of the decomposition process is considered to be CdO (found: 19.5%; theoretical: 18.8 %).

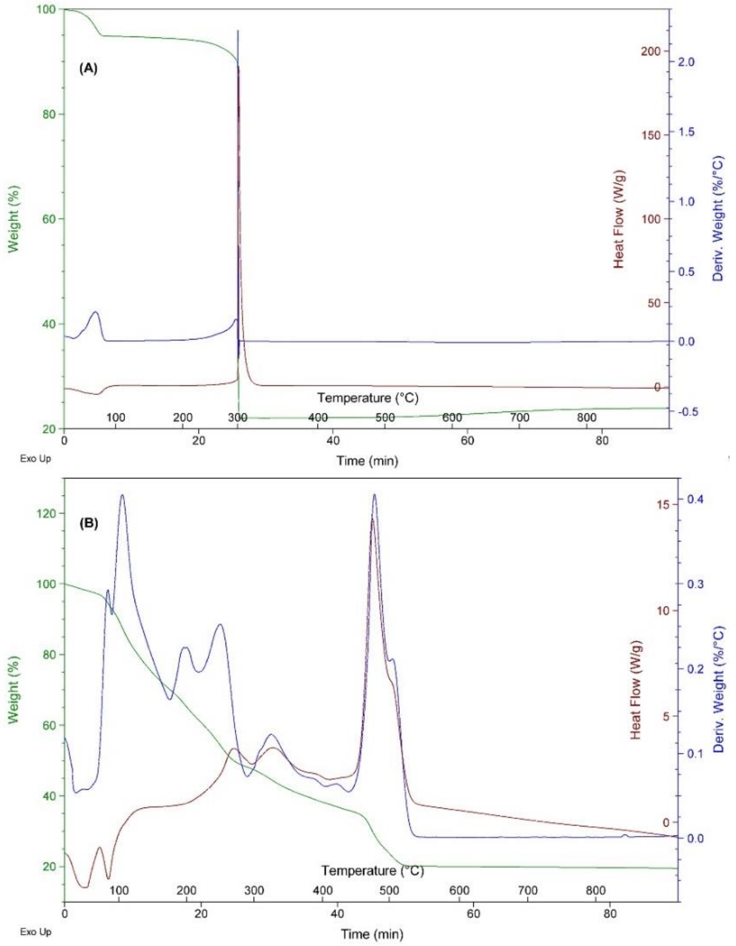

Fig. 4. Thermal analysis curves of the Cu(II) coordination polymer **(A)** and Cd(II) coordination polymer **(B)**

3.3. *Powder X-ray diffraction and magnetic susceptibility*

The synthesized coordination polymers are in crystalline form according to the PXRD patterns (Fig. 5). To illustrate the phase purity of the Cd(II) coordination polymer, the theoretical pattern obtained from the single-crystal X-ray data for the Cd(II) coordination polymer was compared with the experimental pattern. The results revealed that the two patterns matched each other despite the use of the collected raw data (Fig. 5B).

The Cu(II) and Cd(II) coordination polymers are in polymeric structures. Therefore, the magnetic properties per unit metal were considered, while the calculations were performed. The calculated magnetic moment values are only spin-based and do not contain orbital contribution. For this reason, some differences can be observed between the calculated and experimental magnetic moment values. The Cu(II) coordination polymer (d^9 electron configuration) with one unpaired electron is paramagnetic.

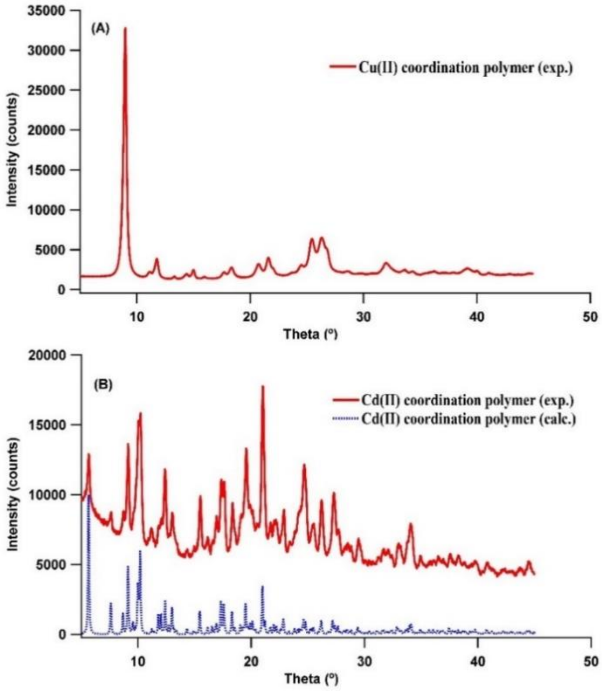

Fig. 5. PXRD patterns of the Cu(II) coordination polymer **(A)** and Cd(II) coordination polymer **(B)**

The calculated and experimental magnetic moment values of the Cu(II) coordination polymer are 1.73 and 1.79 BM, respectively. The Cd(II) coordination polymer with the d^{10} electron configuration is also diamagnetic as expected.

3.4. *Surface area studies*

To determine the BET surface areas of the coordination polymers, the standard volumetric method with nitrogen gas adsorption was used. The method was applied at liquid nitrogen temperature (77 K) and certain relative pressures. The degassing process was performed before the surface area measurements were made. This process was performed under vacuum for half an hour at room temperature. Then, the BET surface area plots of the coordination polymers were obtained (Fig. 6). We determined the surface areas from these plots as 12.9 $m^2 g^{-1}$ for the Cu(II) coordination polymer and 1.3 $m^2 g^{-1}$ for the Cd(II) coordination polymer (Table 1).

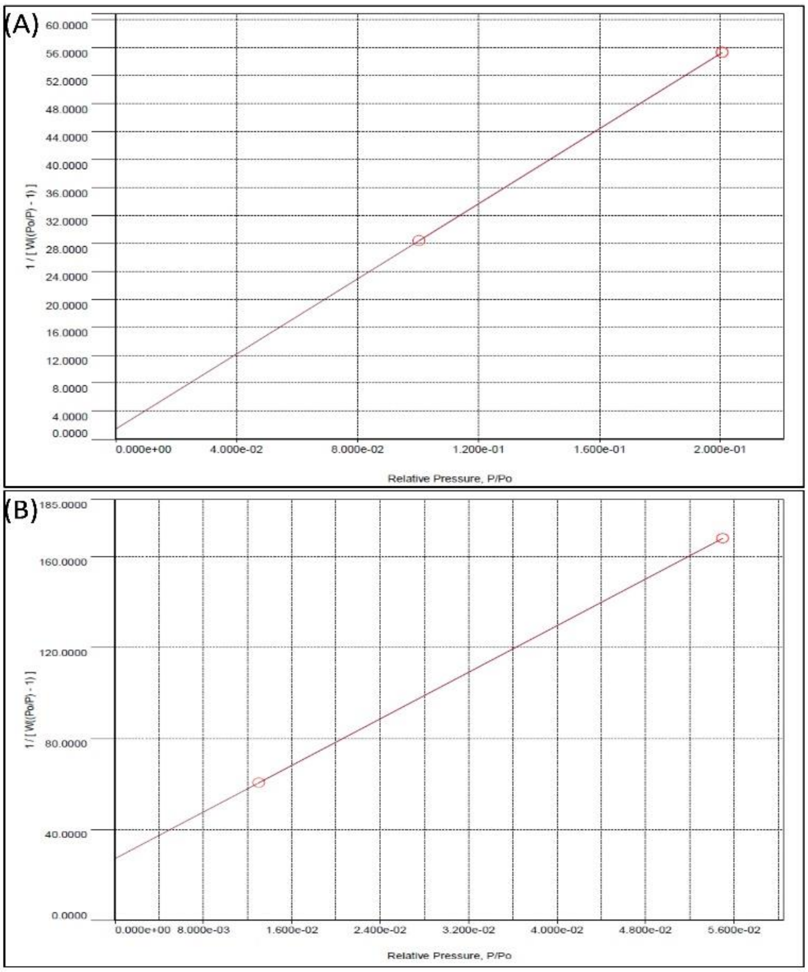

Fig. 6. BET surface area plots for the Cu(II) coordination polymer **(A)** and Cd(II) coordination polymer **(B)**

3.5. *Hydrogen storage capacities*

Hydrogen storage measurements were performed on a VTI/HPVA 100 high-pressure analyzer. The static volumetric method under high-pressure was used for the adsorption isotherms of hydrogen gas. The degassing operation was performed for 6 hours immediately before the measurements were made. For the measurements, various increasing pressure values were used at 75 K, and the hydrogen adsorption isotherms of the coordination polymers were then obtained (Fig. 7). The maximum hydrogen storage amounts for the Cu(II) and Cd(II) coordination polymers are 296 and 330 ml/g, respectively, at approximately 75 bar and 75 K (Table 1). The obtained values are relatively low compared with those of related studies in the literature [46, 47]. However, the Cu(II) and Cd(II) coordination polymers have some potential to store hydrogen gas.

Table 1

BET surface areas and hydrogen storage capacities of the coordination polymers

Coordination polymer	**BET surface area ($m^2\ g^{-1}$)**	**Hydrogen storage capacities (ml/g)**
Cu(II) coordination polymer	12.9	296
Cd(II) coordination polymer	1.3	330

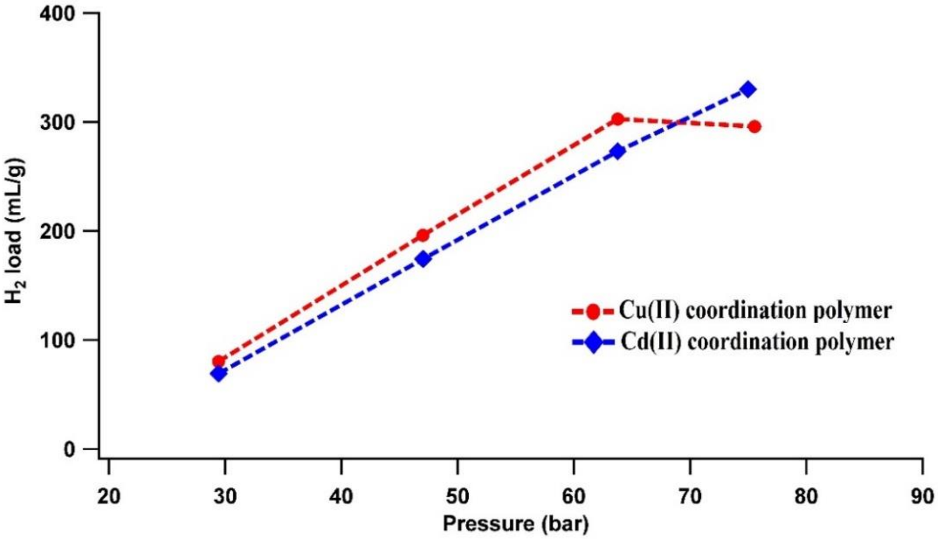

Fig. 7 Hydrogen storage isotherms of the coordination polymers

4. CONCLUSIONS

In this study, Cu(II) and Cd(II) coordination polymers constructed from pyrazine-2,3-dicarboxylato and 1-vinylimidazole ligands were synthesized and characterized using various methods. The coordination polymers contain water molecules; thus, they have ν(O–H) stretch vibrations in the IR spectra, and they decompose under an oxygen atmosphere at low temperatures with respect to the thermal analysis curves. CuO and CdO remain as the final products. The Cu(II) and Cd(II) coordination polymers are in crystalline form according to the powder X-ray diffraction data and are paramagnetic and diamagnetic, respectively. The surface areas and hydrogen storage capacities of the coordination polymers were also determined. The surface areas were found to be lower than the values in the literature. Despite the low surface areas, the Cu(II) and Cd(II) coordination polymers have moderate hydrogen storage capacities.

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REFERENCES

[1] S. R. Batten, S. M. Neville, D. R. Turner, *Coordination Polymers: Design, Analysis and Application*, Royal Society of Chemistry, Cambridge, 2008.

[2] M.-C. Hong, L. Chen, *Design and Construction of Coordination Polymers*, John Wiley & Sons, The United States of America, 2009.

[3] J. L. Rowsell, A. R. Millward, K. S. Park, O. M. Yaghi, Hydrogen sorption in functionalized metal−organic frameworks, *J. Am. Chem. Soc.* **126**, 5666–5667 (2004). DOI: https://doi.org/10.1021/ja049408c

[4] S. Hasegawa, S. Horike, R. Matsuda, S. Furukawa, K. Mochizuki, Y. Kinoshita, S. Kitagawa, Three-dimensional porous coordination polymer functionalized with amide groups based on tridentate ligand: selective sorption and catalysis, *J. Am. Chem. Soc.* **129**, 2607–2614 (2007). DOI: https://doi.org/10.1021/ja067374y

[5] R. Decadt, K. Van Hecke, D. Depla, K. Leus, D. Weinberger, I. Van Driessche, P. Van Der Voort, R. Van Deun, Synthesis, crystal structures, and luminescence properties of carboxylate based rare-earth coordination polymers, *Inorg. Chem.* **51**, 11623–11634 (2012). DOI: https://doi.org/10.1021/ic301544q

[6] H.-L. Sun, Z.-M. Wang, S. Gao, Synthesis, crystal structures, and magnetism of cobalt coordination polymers based on dicyanamide and pyrazine-dioxide derivatives, *Inorg. Chem.* **44**, 2169–2176 (2005). DOI: https://doi.org/10.1021/ic048342j

[7] L. Wang, M. Zheng, Z. Xie, Nanoscale metal–organic frameworks for drug delivery: a conventional platform with new promise, *J. Mater. Chem. B* **6**, 707–717 (2018). DOI: https://doi.org/10.1039/C7TB02970E

[8] J. Duan, W. Jin, S. Kitagawa, Water-resistant porous coordination polymers for gas separation, *Coord. Chem. Rev.* **332**, 48–74 (2017). DOI: https://doi.org/10.1016/j.ccr.2016.11.004

[9] M. Du, C.-P. Li, C.-S. Liu, S.-M. Fang, Design and construction of coordination polymers with mixed-ligand synthetic strategy, *Coord. Chem. Rev.* **257**, 1282–1305 (2013). DOI: https://doi.org/10.1016/j.ccr.2012.10.002

[10] M. Zhang, Y.-P. Chen, H.-C. Zhou, Structural design of porous coordination networks from tetrahedral building units, *CrystEngComm*. **15**, 9544–9552 (2013). DOI: https://doi.org/10.1039/C3CE41105B

[11] H.-Y. Lin, J. Luan, X.-L. Wang, J.-W. Zhang, G.-C. Liu, A.-X. Tian, Construction and properties of cobalt(II)/copper(II) coordination polymers based on N-donor ligands and polycarboxylates mixed ligands, *RSC Adv.* **4**, 62430–62445 (2014). DOI: https://doi.org/10.1039/C4RA12367K

[12] H. Deng, S. Grunder, K. Cordova, C. Valente, H. Furukawa, M. Hmadeh, F. Gándara, A.C. Whalley, Z. Liu, S. Asahina, H. Kazumori, M. O'Keeffe, O. Terasaki, J. F. Stoddart, O. M. Yaghi, Large-pore apertures in a series of metal-organic frameworks, *Science* **336**, 1018–1023 (2012). DOI: https://doi.org/10.1126/science.1220131

[13] M. Ž. Mijajlović, M. V. Nikolić, V. V. Jevtić, Z. R. Ratković, J. Milovanović, A. Arsenijević, B. Stojanović, S. B. Novaković, G. A. Bogdanović, S. R. Trifunović, G. P. Radić, Cytotoxicity of platinum(IV) and palladium(II) complexes with meso-1,2-diphenyl-ethylenediamine-N,N'-di-3-propanoic acid. Crystal structure of [Pd(1,2-dpheddp)] complex, *Maced. J. Chem. Chem. Eng.* **35**, 79–86 (2016). DOI: http://dx.doi.org/10.20450/mjcce.2016.729

[14] S. L. James, Metal-organic frameworks, *Chem. Soc. Rev.* **32**, 276–288 (2003). DOI: https://doi.org/10.1039/B200393G

[15] W. Lu, Z. Wei, Z.-Y. Gu, T.-F. Liu, J. Park, J. Tian, M. Zhang, Q. Zhang, T. Gentle III, Tuning the structure and function of metal–organic frameworks via linker design, *Chem. Soc. Rev.* **43**, 5561–5593 (2014). DOI: https://doi.org/10.1039/C4CS00003J

[16] B.-H. Ye, M.-L. Tong, X.-M. Chen, Metal-organic molecular architectures with 2,2′-bipyridyl-like and carboxylate ligands, *Coord. Chem. Rev.* **249**, 545–565 (2005). DOI: https://doi.org/10.1016/j.ccr.2004.07.006

[17] Y.-P. Gao, L. Guo, Y.-H. Lv, W. Dong, M. Jia, F. Chang, A series of 1-D, 2-D and 3-D coordination polymers self-assembled from a flexible dicarboxylate and mixed N-donor ligands: syntheses, structural diversity, and luminescent properties, *J. Coord. Chem.* **69**, 3745–3761 (2016). DOI: https://doi.org/10.1080/00958972.2016.1239087

[18] X. Feng, W. Chen, B. Xiang, Syntheses, crystal structures and luminescent properties of two new Zn(II) coordination polymers based on a dicarboxylate and different imidazole-containing ligands, *J. Coord. Chem.* **69**, 1551–1558 (2016). DOI: https://doi.org/10.1080/00958972.2016.1179289

[19] C.-S. Liu, J.-J. Wang, L.-F. Yan, Z. Chang, X.-H. Bu, E.C. Sañudo, J. Ribas, Copper(II), cobalt(II), and nickel(II) complexes with a bulky anthracene-based carboxylic ligand: syntheses, crystal structures, and magnetic properties, *Inorg. Chem.* **46**, 6299–6310 (2007). DOI: https://doi.org/10.1021/ic070086y

[20] S. Taşcıoğlu, A. Aydın, B. Yalçın, E. Kakı, Ö. Andaç, O. Büyükgüngör, B. Koşar, Synthesis and characterization of Cu(II) complexes of pyrazine-2,3-dicarboxylicacid, *Polyhedron*, **30**, 2171–2180 (2011). DOI: https://doi.org/10.1016/j.poly.2011.05.018

[21] R. Kitaura, K. Fujimoto, S.-I. Noro, M. Kondo, S. Kitagawa, A Pillared-Layer Coordination Polymer Network Displaying Hysteretic Sorption: $[Cu_2(pzdc)_2(dpyg)]_n$ (pzdc= Pyrazine-2,3-dicarboxylate; dpyg= 1,2-Di (4-pyridyl)glycol), *Angew. Chem. Int. Ed.* **41**, 133–135 (2002). DOI: https://doi.org/10.1002/1521-3757(20020104)114:1<141::AID-ANGE141>3.0.CO;2-D

[22] G. Günay, O. Z. Yeşilel, C. Darcan, S. Keskin, O. Büyükgüngör, Synthesis, crystal structures, molecular simulations for hydrogen gas adsorption, fluorescent and antimicrobial properties of pyrazine-2,3-dicarboxylate complexes, *Inorg. Chim. Acta*. **399**, 19–35 (2013). DOI: https://doi.org/10.1016/j.ica.2012.12.036

[23] J.-W. Zhang, Y. Man, Y.-N. Ren, W.-H. Liu, B.-Q. Liu, Y.-P. Dong, Syntheses, structures, photoluminescent and magnetic properties of pyrazine-2,3-dicarboxylate-based cadmium-lanthanide/lanthanide coordination polymers tuned by Cd^{II}, *Inorg. Chim. Acta*. **488**, 41–48 (2019). DOI: https://doi.org/10.1016/j.ica.2019.01.004

[24] X.-H. Li, Q. Shi, M.-L. Hu, H.-P. Xiao, A crossing double chain $\{[Cu(PZDC_2]\cdot 3(H_2O)\cdot 2(IDZC)\}_n$ (H_2PZDC= 2,3-pyrazinedicarboxylic acid, IDZC= imidazole cation), *Inorg. Chem. Commun.* **7**, 912–914 (2004). DOI: https://doi.org/10.1016/j.inoche.2004.05.017

[25] F. Takusagawa, A. Shimada, The crystal structure of pyrazine-2,3-dicarboxylic acid dihydrate, *Chem. Lett.* **2**, 1121–1122 (1973). DOI: https://doi.org/10.1246/cl.1973.1121

[26] T. Okubo, M. Kondo, S. Kitagawa, Synthesis, structure, and magnetic properties of one-dimensional copper(II) coordination polymer, $[Cu(pyrazine\text{-}2,3\text{-}dicarboxylate)(H_2O)_2]\cdot 2H_2O_n$, *Synth. Met.* **85**, 1661–1662 (1997). DOI: https://doi.org/10.1016/S0379-6779(97)80386-4

[27] M. Gryz, W. Starosta, J. Leciejewicz, Doubly bridged molecular ribbons in the structure of an ionic complex, hydronium zinc(II) pyrazine-2,3-dicarboxylate, *J. Coord. Chem.* **58**, 931–935 (2005). DOI: https://doi.org/10.1080/00958970500055492

[28] J. W. Zhang, Y. N. Ren, J. X. Li, B. Q. Liu, Y. P. Dong, Syntheses, structures and magnetic properties of two series of 3d–4f heterometallic coordination polymers derived from pyrazine-2,3-dicarboxylic acid, *Eur. J. Inorg. Chem.* **2018**, 1099–1106 (2018). DOI: https://doi.org/10.1002/ejic.201701394

[29] Y. Kubota, M. Takata, R. Matsuda, R. Kitaura, S. Kitagawa, K. Kato, M. Sakata, T. C. Kobayashi, Direct observation of hydrogen molecules adsorbed onto a microporous coordination polymer, *Angew. Chem. Int. Ed.* **44**, 920–923 (2005). DOI: https://doi.org/10.1002/ange.200461895

[30] H. Zhang, H. Li, P. Chen, P. Yan, Syntheses, structures, and photoluminescence properties of a series of 3D zn-ln heterometallic complexes with 2,3-pyrazine dicarboxylic acid as a bridging ligand, *Z. Anorg. Allg. Chem.* **644**, 346–352 (2018). DOI: https://doi.org/10.1002/zaac.201700392

[31] O. Z. Yeşilel, A. Mutlu, C. Darcan, O. Büyükgüngör, Syntheses, structural characterization and antimicrobial activities of novel cobalt-pyrazine-2,3-dicarboxylate complexes with N-donor ligands, *J. Mol. Struct.* **964**, 39–46 (2010). DOI: https://doi.org/10.1016/j.molstruc.2009.10.048

[32] G. Świderski, A. Z. Wilczewska, R. Świsłocka, K. H. Markiewicz, W. Lewandowski, Thermal and spectroscopic study of zinc, manganese, copper, cobalt and nickel 2,3-pyrazinedicarboxylate, *Polyhedron*, **162**, 293–302 (2019). DOI: https://doi.org/10.1016/j.poly.2019.01.071

[33] R. R. Arrieta-Pérez, J. N. Primera-Pedrozo, J. Exley, A. J. Hernández-Maldonado, Synthesis and characterization of a $Cu_2(pzdc)_2(bix)$ [pzdc:2,3-pyrazinedicarboxylate; bix:1,3-bis(imidazol-1-yl)benzene] porous coordination pillared-layer network, *Cryst. Growth Des.* **18**, 1676–1685 (2018). DOI: https://doi.org/10.1021/acs.cgd.7b01616

[34] S. E. H. Etaiw, M. M. El-bendary, Cd(II) supramolecular coordination polymer incorporating pyrazine-2-carboxylic acid: Crystal structure, spectral characteristics and catalytic activity, *J. Lumin.* **199**, 232–239 (2018). DOI: https://doi.org/10.1016/j.jlumin.2018.03.041

[35] R. A. Agarwal, N. K. Gupta, CO_2 sorption behavior of imidazole, benzimidazole and benzoic acid based coordination polymers, *Coord. Chem. Rev.* **332**, 100–121 (2017). DOI: https://doi.org/10.1016/j.ccr.2016.11.002

[36] L. Liu, J. Ding, M. Li, X. Lv, J. Wu, H. Hou, Y. Fan, Structural variability, topological analysis and photocatalytic properties of neoteric Cd(II) coordination polymers based on semirigid bis(thiazolyl-benzimidazole) and different types of carboxylic acid linkers, *Dalton Trans.* **43**, 12790–12799 (2014). DOI: https://doi.org/10.1039/c4dt01080a

[37] S. Vasnin, R. Geanangel, Adducts of tin(II) chloride with imidazole and methylimidazoles, *Inorg. Chim. Acta*. **160**, 167–170 (1989). DOI: https://doi.org/10.1016/S0020-1693(00)80581-2

[38] P. De Vaal, F. Hulsbergen, R. De Graaff, Structure of tetrakis(1-vinylimidazole) cobalt(II) dichloride, $[Co(C_5H_6N_2)_4]Cl_2$, *Acta Crystallogr. Sect. C: Cryst. Struct. Commun.* **39**, 1543–1544 (1983). DOI: https://doi.org/10.1107/S0108270183009191

[39] S. Ghosh, F. Ahmed, G. G. Hossain, D. T. Haworth, S. E. Kabir, Reactivity of $[Re_2(CO)_8(MeCN)_2]$ with 1-vinylimidazole: X-ray structures of $[Re_2(CO)_8\{\eta^{1\text{-}}NC_3H_3N(CH{=}CH_2)\}_2]$ and $[ReCl_2(CO)_2\{\eta^{1\text{-}}NC_3H_3N(CH{=}CH_2)\}_2]$, *J. Chem. Crystallogr.* **39**, 702–707 (2009). DOI: https://doi.org/10.1007/s10870-009-9536-x

[40] K. Kurdziel, T. Głowiak, J. Jezierska, Complexes of some transition metal ions with 2-methyl-1-vinylimidazole in aqueous solution and the solid state, *J. Chem. Soc., Dalton Trans.*, 1095–1100 (2000). DOI: https://doi.org/10.1039/A908718D

[41] H. Yilmaz, O. Andac, S. Gorduk, Synthesis, characterization, and hydrogen storage capacities of polymeric squaric acid complexes containing 1-vinylimidazole, *Polyhedron*. **133**, 16–23 (2017). DOI: https://doi.org/10.1016/j.poly.2017.05.014

[42] H. Yilmaz, S. Gorduk, O. Andac, Polymeric Ni(II) and Cu(II) complexes based on squaric acid and 1-vinylimidazole: Structural studies and hydrogen adsorption properties, *Inorg. Chim. Acta*. **469**, 154–163 (2018). DOI: https://doi.org/10.1016/j.ica.2017.09.026

[43] O. Andac, S. Gorduk, H. Yilmaz, Synthesis, characterization and H_2 adsorption performances of polymeric Co(II) and Ni(II) complexes of pyrazine-2,3-dicarboxylic acid and 1-vinylimidazole, *J. Iran. Chem. Soc*. **15**, 1699–1708 (2018). DOI: https://doi.org/10.1007/s13738-018-1367-2

[44] H. Yilmaz, O. Andac, A novel zinc(II) complex containing square pyramidal, octahedral and tetrahedral geometries on the same polymeric chain constructed from pyrazine-2,3-dicarboxylic acid and 1-vinylimidazole, *J. Chem. Sci.* **130**, 32 (2018). DOI: https://doi.org/10.1007/s12039-018-1436-1

[45] O. Z. Yeşilel, A. Mutlu, O. Büyükgüngör, Novel dinuclear and polynuclear copper(II)-pyrazine-2,3-dicarboxylate supramolecular complexes with 1,3-propanediamine, N,N,N′,N′-tetramethylethylenediamine and 2,2′-bipyridine, *Polyhedron*, **28**, 437–444 (2009). DOI: https://doi.org/10.1016/j.poly.2008.11.044

[46] H. W. Langmi, J. Ren, B. North, M. Mathe, D. Bessarabov, Hydrogen storage in metal-organic frameworks: A review, *Electrochim. Acta.* **128**, 368–392 (2014). DOI: https://doi.org/10.1016/j.electacta.2013.10.190

[47] M. P. Suh, H. J. Park, T. K. Prasad, D.-W. Lim, Hydrogen storage in metal–organic frameworks, *Chem. Rev.* **112**, 782–835 (2011). DOI: https://doi.org/10.1021/cr200274s