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Adsorption of Water Vapour on the Microstructure and Stability of Cu-Zn Bimetallic Coordination Polymer

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Abstract

A current challenge in the design of synthesis lies in the incorporation of two or more transition metals into a coordination polymer. The most widely used approach has been to incorporate a second metal as a generally innocent (coordinatively saturated) part of a linear linker as in the case of multifunctional carboxylated porphyrins (MCPs). The empirical method has been used to obtain many other types of MCPs; however, the selective, direct replacement of one transition metal within a monometallic coordination polymer via controlled stoichiometry has not generally led to maintained structural fidelity. In this present work, three pyromellitic acid complexes were synthesized at room temperature and characterized by Elemental analysis, Powder X-ray diffraction, Fourier transform infrared spectroscopy, Scanning electron microscopy, N_2 adsorption-desorption Isotherm, and Thermal analysis. The reaction in water-methanol between pyromellitic acid and copper ions by ambient precipitation method formed $[CuH_2B4C]\cdot 5H_2O$. When zinc is combined with copper and the ligand, $[Cu_2Zn(B4C)_{1.5}(H_2O)_{4.5}]\cdot 9H_2O$ is formed. A repeat of this step under solvothermal condition produced Solvo-$[Cu_2Zn(B4C)_{1.5}(H_2O)_5]\cdot 2H_2O$. The N_2-adsorption isotherm of these compounds showed them to be Type III according to the IUPAC classification, with small pores only capable of small molecule sorption.

Keywords: Coordination, microporous, polymer, pyromellitic, sorption.

Introduction

Coordination polymers, also known as coordination networks or porous coordination polymers have appeared in the literature. In recent years, there has been a rapid development in the construction of these coordination polymeric complexes because of their astounding and interesting molecular topologies and usage as functional materials (Rzqczykska et al. 2006, Wang et al. 2011). Quite a number of coordination polymers with interesting physical, chemical, and structural properties have been obtained with aromatic carboxylic acid (Chu et al. 2001, Gurunatha and Maji 2009, Dikio and Farah 2013, Yang et al. 2018). A synthetic method widely used in this area is by coordination of polydentate ligands acting as connectors to metal ions (Yang et al. 2018).

Reports have shown that benzene polycarboxylic acids such as 1,2,4,5-benzenetetracarboxylic acid (H_4B4C), 1,3,5-benzenetricarboxylic acid (BTC) and 1,4-benzenedicarboxylic acid (BDC) are suitable candidates as ligands for the synthesis of complexes (Ward and Luehrs 1983, Karanović et al. 1999, Yang et al. 2003, Zhang et al. 2011, Sanda et al. 2014, Zhao et al. 2015). They consist of four carboxyl groups capable of undergoing partial or complete deprotonation which produces a rich coordination node. Depending on the number of deprotonations, they can form 1, 2, or 3-dimensional framework structures with metal centres being coordinated by two-four carboxylato groups (Rochon and Massarweh 2000, Cao et al. 2002). There has been deep research on materials with large cavities and channels, because of their intriguing structural diversity and their potential applications in molecular adsorption, catalysis, ion-exchange, etc. (Fletcher et al. 2004, Férey 2008). Although the mixed-metal complexes have been in existence since 1907, the most studied are the monometals. Studies on bimetallic polymers involve either two different metals in similar oxidation states (Chun et al. 2005) or different oxidation states (Dong et al. 2000) states or same metals in two different oxidation states.

Pioneering studies have shown that mixed metal-metal, and Metal-Organic Frameworks (MOFs) exhibit properties that are superior to their parent MOFs and, in some cases, new temperature functionalities can be induced because of the introduction of the second metal ions. Improved selective adsorption of CO_2 over CH_4 and CO (Shi et al. 2013) and increasing the capacity of selective H_2 sorption (Yue et al. 2005) has been achieved by this method. Creating multifunctional MOFs has been one of the recent directions in MOF research (Zhou et al. 2016). Zhou et al. (2016) reported a novel bimetallic MIL-101 (Cr, Mg) by doping Mg during solvothermal synthesis of MIl-101 (Cr); a BDC-Cr complex. They observed that the addition of Mg results into a MIL-101 (Cr, Mg) with a higher surface area than its monometal and creates a new and strong adsorptive site for CO_2. In another report by Botas et al. (2010), the doping of MOF-5 with different numbers of Co^{2+} ions were incorporated through solvothermal crystallization into the Zn-based MOF-5 (IRMOF-1) framework to form Co8-MOF-5, and Co21-MOF-5. They observed an increase in the uptake of H_2, CH_4 and CO_2 with increasing Co content particularly at high pressure. Since reports have shown the strengths and weaknesses of the Zn and Cu monometal coordination polymers, the goal of this study was to use the power of one to improve on the weakness of the other. In this work, the experimental investigation of the synthesis, properties and applications of the monometal and bimetallic complexes of Zn(II) and Cu(II) using H_4B4C are presented. The aim was to produce bimetallic complexes with better stability (than their corresponding monometal complexes) when exposed to saturated water vapour at room temperature.

Materials and Methods

All the chemical reagents were purchased from Sigma Aldrich and used without further purification. The analar grade reagents used were zinc acetate dihydrate; $Zn(CH_3COO)_2{\cdot}2H_2O$), cupric nitrate trihydrate; $Cu(NO_3)_2{\cdot}3H_2O$ (with 99% purity), and the methanol (HPLC grade). CHNS analyses were performed on an Elementar Analysensysteme varioMICRO V1.6.2 GmbH analysis system. The percentage of the metals (zinc and copper) were determined using a Perkin-Elmer Analyst200 Atomic Absorption Spectrophotometer with copper and zinc hollow cathode lamps at wavelengths 324 nm and 213 nm, respectively. The FT-IR spectra were obtained using a Perkin-Elmer Spectrum 100FT-IR with ATR attachment in the range of 4000–650 cm^{-1}. The XRPD patterns of the synthesized compounds were recorded on a Bruker D8 Discover X-ray powder diffractometer equipped with a proportional counter, using Cu-Kα radiation (λ = 1.5405 Å, Nickel filter). The collection of data was in the range 2θ = 5–65°, scanning at 0.5° min^{-1}. The thermal decomposition and stability of all the complexes were determined using a Perkin-Elmer TG-4000 (Pyris Version 4.01 software), at a temperature range of 25–700 °C under nitrogen gas and gas flow of 19.8 mL min^{-1} under nitrogen gas. Surface area and pore characteristics of compounds synthesized were measured on a Micromeritics ASAP

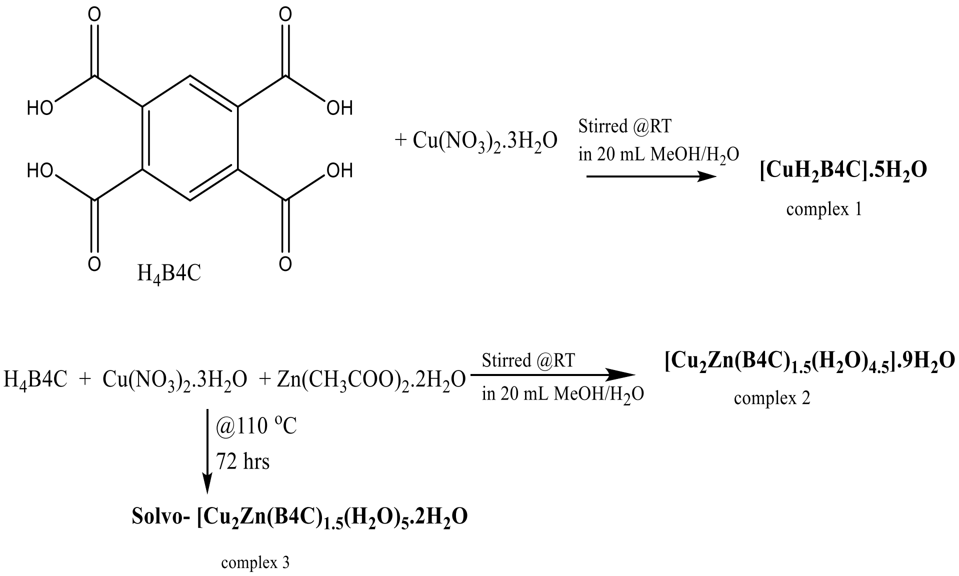
2020 HD analyzer (Accelerated Surface Area and Porosimetry System) using N2, and the Brunauer, Emmett and Teller (BET) surface areas were obtained from the linear region of the N2 isotherms. Prior to the measurement, degassing was carried at 90 °C for four days.

Experimental

Synthesis of the complexes

A brief of the procedures undertakings to obtain the complexes described in this work is shown in Scheme 1. A mixture of 2.0 mmol of $Cu(NO_3)_2{\cdot}3H_2O$ (0.4832 g) and H_4B4C (0.2542 g, 1.0 mmol) were dissolved in 20 mL of $MeOH/H_2O$ (1:1 v/v) solution in a beaker. The solution was stirred for 30 minutes at ambient temperature, allowed to stand for 12 hrs, filtered, washed with methanol, and air-dried at a dust-free atmosphere to obtain a sky-blue microcrystalline powder of complex 1. For complex 2, 0.2215 g (1.0 mmol) of $Zn(CH_3COO)_2$ salt, 0.4832 g of $Cu(NO_3)_2{\cdot}3H_2O$ and 0.2542 g H_4B4C were all dissolved in 20 mL of $H_2O/MeOH$ mixture.

The resulting solution was treated in the same manner as complex 1 to produce complex 2. When the same reactants in 2 were transferred into a reaction Pyrex glass, sealed, placed in the oven, and heated at 110 °C for 72 hrs, greenish blue microcrystalline complex 3 was obtained.



Scheme 1: Synthetic path of the complexes.

Results and Discussion

The confirmation of the products **1**, **2** and **3** (Table 1) was achieved by elemental analysis and authenticated by the thermal analysis study. The elemental compositions of the complexes were obtained from the AAS and CHNS analyzer and were found to be in good agreement with the calculated values.

Table 1: Microanalytical data % found (calculated)

Sample ID	1	2	3
Molecular Formular	$[CuH_2B4C]{\cdot}5H_2O$	$[Cu_2Zn(B4C)_{1.5}(H_2O)_{4.5}]{\cdot}9H_2O$	Solvo-$[Cu_2Zn(B4C)_{1.5}(H_2O)_5]{\cdot}2H_2O$
Mol. Mass (g mol^{-1}	405.76	810.88	693.78
C	29.12 (29.59)	22.23 (22.22)	25.86 (25.97)
H	3.53 (2.98)	3.63 (3.73)	2.47 (2.58
Cu	15.88 (15.65)	15.25 (15.67)	18.31 (18.09)
Zn	-	7.65 (8.06)	18.31 (18.09)

X-ray diffraction patterns

The XRD patterns and SEM images of the complexes synthesized are as shown in Figure 1 and Figure 2, respectively. The X-ray diffraction pattern of **1** showed a poor crystallinity and its surface morphology, a non-regular order arrangement with no distinct shape (SEM image in Figure 2). This is an indication that some of the functional groups are stacked upon one another. Hence no metal-ligand arrangement in a long-range periodic order. In the case of the bimetallic complexes **2** and **3,** a high degree of crystallinity was observed between 2θ = 5° and 65° with their highly intense X-ray diffraction patterns. Their SEM images revealed complexes **2** and **3** as tetragonal. The calculated inter-planar d-spacing have been calculated using the Bragg‘s equation: $n\lambda = 2d\sin\theta$, together with relative intensities for the most intense peak.

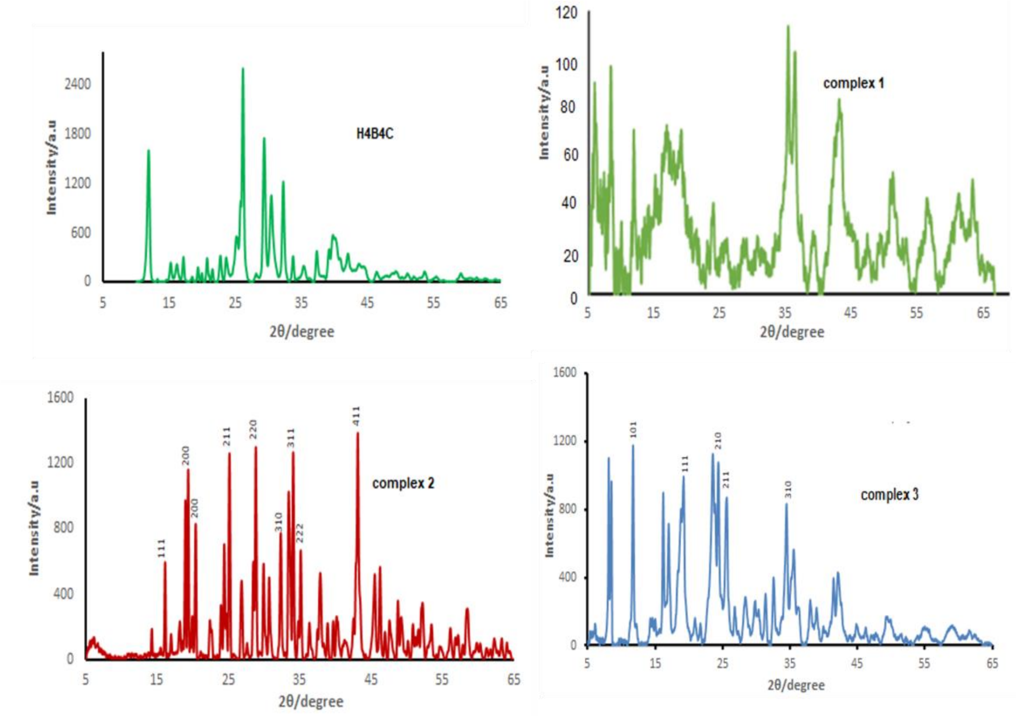


Figure 1: X-ray powder diffraction patterns of the complexes.

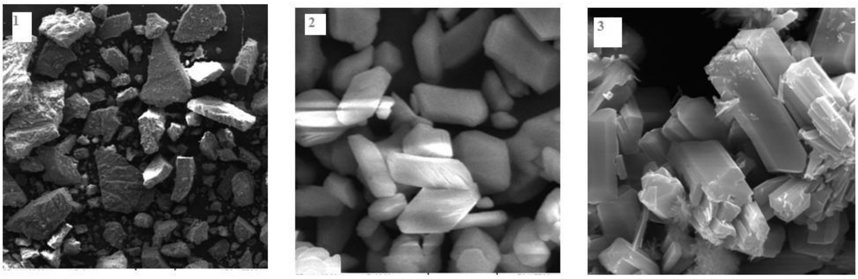


Figure 2: SEM images of complexes.

The unit cell calculations for cubic symmetry from the all-essential peaks yielding h k l (Miller indices) unit cell parameter values were carried out using PAnalytical Xpert HighScore 3.0 Software (Degen et al. 2014).

FT-IR analysis

Figure 3 shows the FTIR spectra of the ligand and all the complexes. The number of absorption bands of all the complexes is less when compared with that obtained for the ligand. This is an indication that the complexes have good symmetry (Yang et al. 2018). The first IR band of interest of these compounds is the νO-H which appears between 3007–2871 cm^{-1} in the ligand and is sensitive to hydrogen bonding (intra and inter) showed by the broadness of the band. In all the complexes, this band appeared at a higher wavenumber (frequency region) 3420, 3122 and 3240 cm^{-1} in the complexes **1**, **2** and **3**, respectively and shows that water (loosely bound to the metal ions through hydrogen) is associated with the structures. At the carbonyl region, the type of coordination existing between the metal and the carboxylic acid group of the ligand is shown. There is a shift of asymmetry carbonyl stretch (ν_{as}COO) from higher wavenumber 1694 cm^{-1} (in the free ligand) to lower wavenumbers 1568, 1574 and 1575 cm^{-1} in all the complexes **1**, **2** and **3**, respectively. The symmetry stretching frequency (ν_{sy}COO) shifted from lower 1264 cm–1 to higher wavenumber of 1378, 1365, and 1388 cm^{-1} in **1**, **2** and **3** (Lyszczek 2008) suggesting coordination of the carbonyl oxygen to a heavier atom' the metal (Deacon and Phillips 1980). The splitting difference Δν, between the asymmetric and symmetric stretch in these complexes, were: 190 cm^{-1} in **1**, 209 cm^{-1} in **2,** and 187 cm^{-1} in **3**. These values are larger than the corresponding value in Na_4B4C (95 cm^{-1}), showing that the carboxylate groups behave as monodentate ligands in these complexes (Nara et al. 1996).

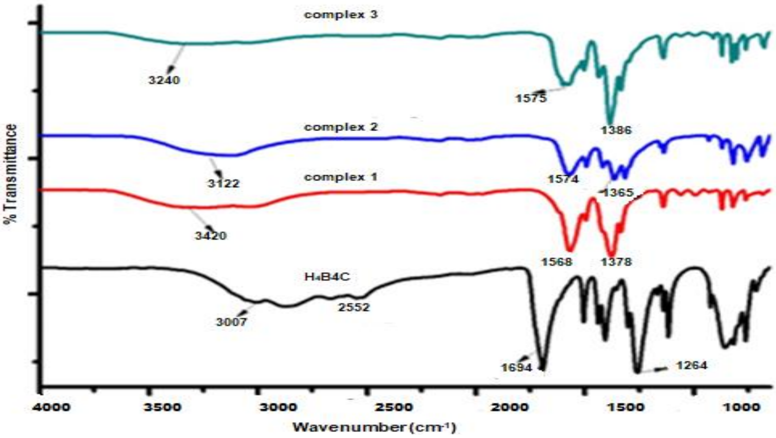


Figure 3: FT-IR vibrational spectra of ligands and complexes.

Thermogravimetry analysis

A better understanding of the coordination structures of all these complexes can be achieved via their thermal decomposition study (Figure 4). The behaviour of each of the complexes reflects the bond strength that makes up the molecule. The complexes can be said to vary from moderate to very stable. In the monometal compounds, the loss of guest water molecules in the monometal complex **1**. In the monometal compounds, the loss of guest water molecules in the monometal complex 1 occurred at a lower temperature of 38 °C, the decomposition temperature at 237 °C. The HSAB theory is demonstrated in this context as copper being a soft acid forms a weak hydrogen bond with the hard donor base and therefore lost its lattice water more efficiently at a lower temperature of 38 °C, the decomposition temperature at 237 °C. The HSAB theory is demonstrated in this context as copper being a soft acid forms a weak hydrogen bond with the hard donor base and therefore lost its lattice water more efficiently.

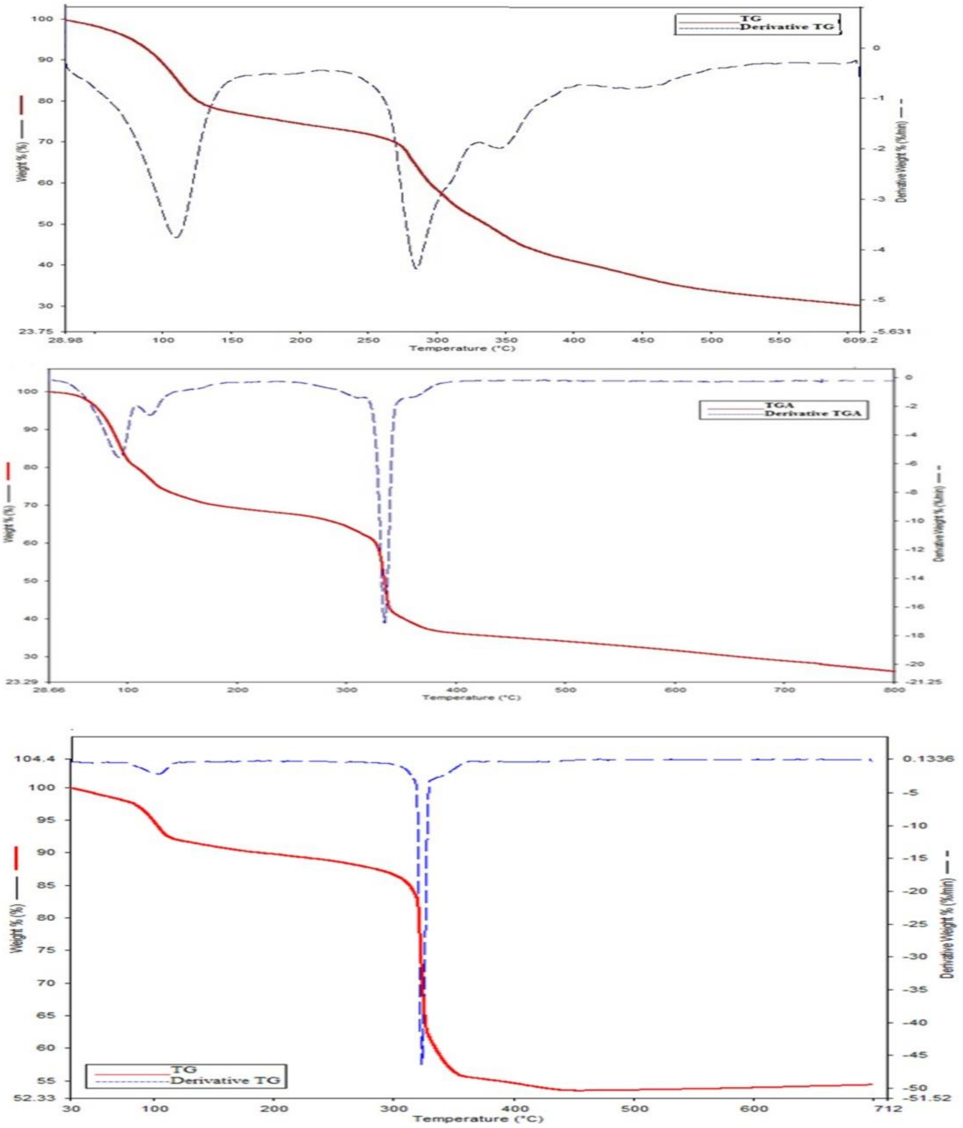


Figure 4: TGA/derivative TGA curves for complexes **1**, **2** and **3**.

In the case of the bimetallics, the dehydration temperatures were 41 °C and 32 °C for complexes **2** and **3** while the decomposition temperatures were 256 °C and 279 °C, respectively. This shows that the stability of all the complexes follows this order, **3** > **2** > **1**. The monometal being the least stable while the bimetallic complex obtained via solvothermal method was the most stable.

Nitrogen gas sorption properties

Gas adsorptions on these complexes were studied to find the surface area and pore volume. Their isotherms (Figure 5) revealed them to be typical Type III mesoporous complexed as defined by the IUPAC classification scheme. The mesoporous material is typical of pore size 2–50 nm which are due to only surface adsorption, suggesting that N_2 molecules cannot diffuse into the pores at a low temperature (IUPAC 1985). Among these complexes, complexes **1** and **3** showed the characteristic hysteresis of adsorption and desorption, with only bimetallic **2** showing no hysteresis, corresponding to a reversible type III isotherm which is convex to the x-axis over its entire range, which is an indication of weak adsorbent-adsorbate interactions. The pore sizes and pore volume vary from 0.003 nm (9.12 $cm^3 g^{-1}$) in **1**; 0.012 nm (18.05 $cm^3 g^{-1}$) in **2** and 0.017 nm (14.80 $cm^3 g^{-1}$) in **3**, respectively.

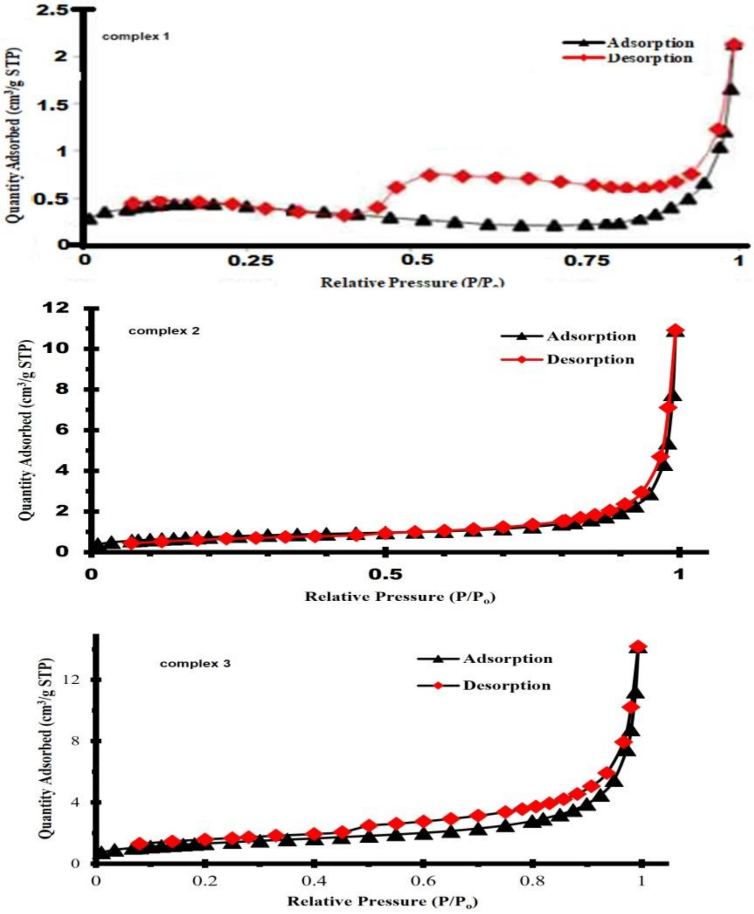


Figure 5: Nitrogen adsorption isotherms of complexes.

Solvation and desolvation studies

There is a vast amount of documentation in the literature noting that, coordination polymers containing a large number of water molecules can be transformed into the porous materials to serve as hosts for a variety of guest molecules. Figure 6 shows the effects of the exposure of all the synthesized compounds were observed to contain water as a guest. An essential factor in the study of the functions of porous coordination polymers is structural stability, maintenance, or reversible collapse of the framework upon removal of the guest molecules. The structural stability was investigated using X-ray Powder Diffraction analysis. All the synthesized compounds were exposed to saturated water vapour at room temperature. The monometal complex **1** showed promise for small molecule adsorption but formed a new structure with definite structural pattern (showed by the distinct crystalline peaks). When bimetallic $[Cu_2Zn(B4C)_{1.5}(H_2O)_{4.5}]\cdot 9H_2O$ (2), was exposed to saturated water vapour in two cycles, the XRPD patterns of the rehydrated samples showed a 100% reproducibility of patterns for the first and second rehydration after the complete collapse of the structure as a result of dehydration. A new framework structure was formed with enhanced solvation properties. This showed promise for sorption in two-cycles and its original structure was maintained as shown in the peak-peak match of the XRD patterns. In the case of the complex 3; Solvo-$\{[Cu_2Zn(B4C)_{1.5}(H_2O)_5]\cdot 2H_2O\}$, structural fidelity is observed upon dehydration and rehydration in two-cycles, with a slight re-arrangement of bonds upon rehydration which can be observed with the emergence of new peak at $2\theta = 7.3°$. The loss of water molecules (anhydrous) without change of structure allows obtaining a material with an open channel. This material was suitable for multiple dehydration/rehydration cycles. A critical condition for the practical application of these complexes under consideration as sorbents is the reversibility of the change in the crystal structure during adsorption/desorption processes. The loss of adsorbed water molecules from these complexes without changes of structures gives room for them to be used as the material of desired properties: porous with open channels which are capable of small molecules adsorption. A possible use for zinc/copper mixed metal salts is as precursors for methanol synthesis catalysts. Table 2 shows the percent mass gained and the calculated enthalpy changes for dehydrated complexes after exposure to saturated water.

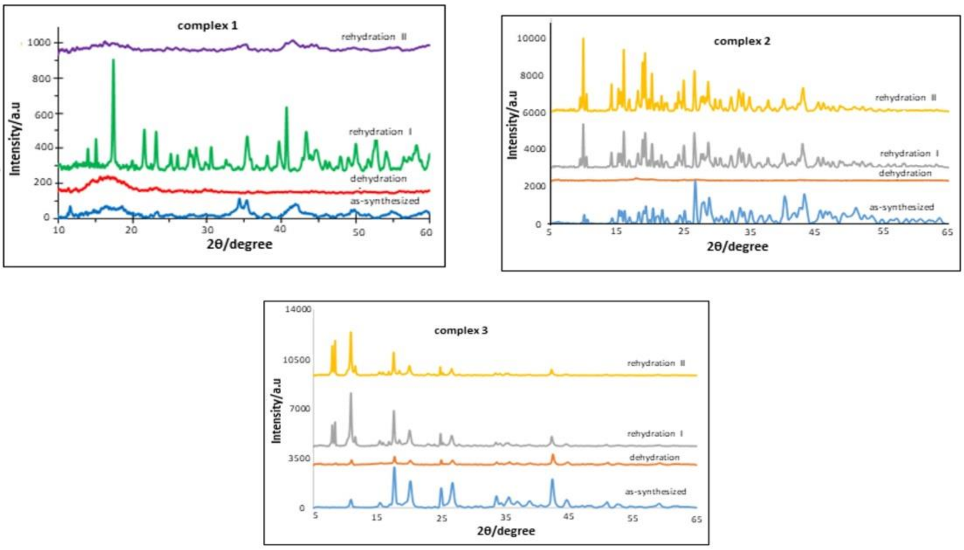


Figure 6: Powder X-ray diffraction patterns of complexes upon rehydration.

Table 2: Percent mass gained and the calculated enthalpy changes for dehydrated complexes after exposure to saturated water

Complex ID	%Mass gained	No. of guests	ΔHJg^{-1} (kJ mol^{-1})
1	21.50	5	503 (204)
2	19.99	9	435 (352)
3	7.79	3	183 (129)

Conclusion

In this study, the stated aims of the formation of the bimetallic complex with enhanced properties were achieved. The addition of Zn(II) to the monometal complex of Cu(II) has led to a new framework structure with enhanced solvation properties. The study has also proven that the incorporation of zinc to copper polymer has an impact on the crystallinity and adsorption properties of the bimetallic complex.

Acknowledgement

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