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Metal-organic frameworks of cobalt and nickel centers with carboxylate and pyridine functionality linkers: Thermal and physical properties; precursors for metal oxide nanoparticle preparation

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Abstract

This article provides an overview on preparation, design, crystal structure and properties of some metal-organic frameworks of carboxylate coordination polymers mixed with pyridine-functionality linkers prepared in our laboratory. The article covers coordination polymers in two- and three-dimensional supramolecular architectures. The reported coordination polymers exhibit interesting structural features for cobalt and nickel centers. They also show various physical properties together with high thermal stabilities, which candidate them for a wide range of applications. Moreover, one of the frameworks was used as a precursor for preparation of metal oxide nanoparticles with sizes of about 35-45 nm.

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1. Introduction

Crystal engineering of metal complexes, especially coordination polymers or metal-organic frameworks (MOFs) has been greatly developed in the past decade [1-3]. Self-assembly of coordination polymers from metal ions as nodes, together with organic ligands as linkers construct these supramolecular architectures. They exhibit a wide range of infinite one- (1D), two- (2D) or three-dimensional (3D) frameworks with various interesting structural features [4-6]. The intense interest in this field arises not only because of their diverse and beautiful structures, but also for their wide potential applications as luminescence,

electrochemical, nanoparticle precursors, magnetic and gas storage properties [7-13].

Aromatic carboxylic acids and heterocyclic nitrogen-donor ligands simply coordinate with inorganic moieties and have great propensity to form metal-organic frameworks. Poly-carboxylates are widely used in assembly of supramolecular architectures because of their diverse coordination modes and bridging abilities. Dicarboxylates are the best studied till now [14-16]. On the other hand, heterocyclic N-donor ligands such as pyrazine, piperazine and other related molecules are good donor ligands due to the presence of at least one nitrogen ring atom and rigid backbones of aromatic rings which help the controlled and predictable synthesis of open frameworks. Compared with N-donor ligands, carboxylate groups are more complex and less predictable for the framework formation, because of their flexible binding behavior from monodentate and chelating to multi-bridging fashions (Scheme 1) [17]. Moreover, carboxylate-based polymers have neutral frameworks which obviating the need of counter ion within the cavities. Since N-donor ligands and carboxylic acids have their own separate features, predictability from N-donors and flexibility from carboxylates, combining their advantages and utilize them to construct more diverse MOFs could be an attractive strategy. Concerning to mixed N, O-donor systems, pyridine carboxylic acid family can be also a particularly good candidate for transition metal coordination. They have great propensity to form neutral frameworks.
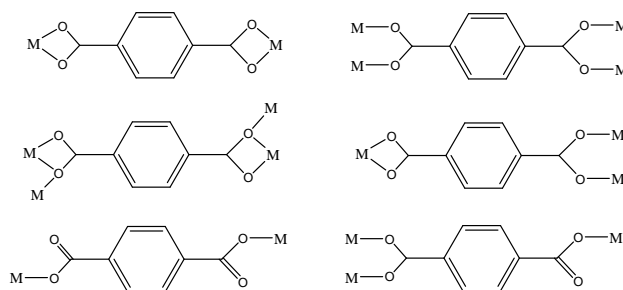
Scheme 1. Some coordination modes of dicarboxylate groups

In this review, our goal was to explore the crystal engineering and the chemistry behind construction of MOFs from mixed carboxylate and pyridine functionalities, and investigate their thermal and physical properties, together with their decomposition to metal oxide nanoparticles.

2. Molecular architectures assembled via coordination bonds

In order to design the targets with different structural features and potential functions, selection of node plays an important role in final structure architecture. Different metal ions could exhibit different coordination geometries, resulting in different framework topologies. Motifs of two- or three-coordinated, with linear or T-shaped fashions can be found in Ag(I) and Cu(I) complexes as it is reported a large number of these supramolecular architectures [18]. Square-planar and tetrahedral coordination motifs, are usually found in four-coordinated metal complexes [19]. Octahedral coordination spheres will results in coordination

polymers with higher dimensionalities [20, 21]. In this review, we report Co and Ni metal centers as nodes in metal-organic frameworks, which often select octahedral geometry.

2.1 Coordination polymers of benzene-dicarboxylates and pyrazine

The assembly of six coordinate cobalt and nickel metal ions with dicarboxylate bridging ligand, in this case 1,4-benzene dicarboxylic acid (terephthalic acid) in the presence of pyrazine furnishes two three-dimensional coordination polymers [22, 23].

The hydrothermal reaction of $Co(NO_3)_2.6H_2O$ with terephthalic acid and pyrazine yielded $[Co(\mu_3-tp)(\mu_2-pyz)]_n$ (**1**), where tp = terephthalic acid and pyz = pyrazine. In this structure, the equivalent

Co(II) centers are surrounded by four carboxylate oxygen atoms from three tp ligands and two nitrogen atoms from two pyrazine ligands in equatorial and axial positions, respectively [22]. This coordination gives a distorted octahedral geometry (Figure 1). Each two Co(II) centers are linked by two tp ligands from the bridging ends, to form a $[Co_2C_2O_4]$ eight-membered rings as secondary building units (SBUs). Connecting these rings by terephthalic linkers makes two dimensional sheets of Co-terephthalates in *bc* plane (Figure 2). The parallel sheets are pillared via the axial pyrazine ligands, forming an interpenetrated 3D network, which is arranged as an ABAB interconnected pattern (Figure 3).
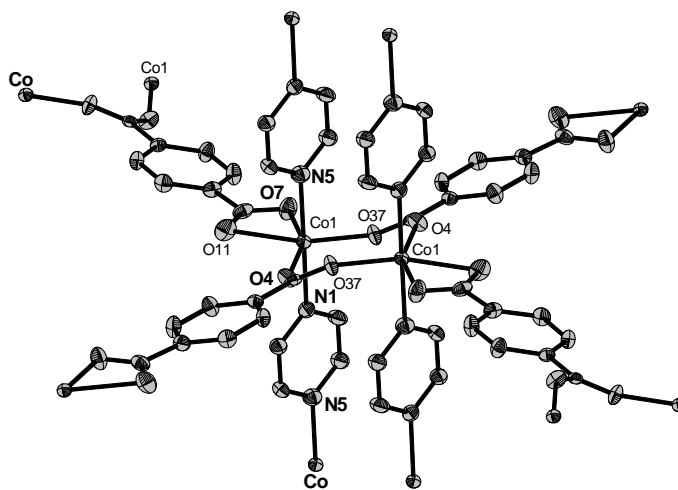

Fig. 1. Perspective view of the coordination environment of the dicobalt centers in **1**

$Ni(NO_3)_2.6H_2O$ metal salt was also used in the synthesis of the isomorphous 3-D coordination polymer, $[Ni(\mu_3-tp)(\mu_2-pyz)]_n$ (**2**). Interestingly, **2** is exactly isostructural with **1**, in which Ni(II) centers select distorted octahedral geometry from four

oxygen atoms and two nitrogen atoms in equatorial and axial sites, respectively [23].

Moreover, isophthalic acid was selected to investigate the effect of dicarboxylate component in the final synthesized MOF [24]. The assembly of $Ni(NO_3)_2.6H_2O$ with isophthalic acid and pyrazine

resulted in $[Ni_2(ip)_2(pyz)_2]_n$, (**3**) coordination polymer, in which ip = isophthalic acid. In this structure, each Ni(II) atom is in a distorted octahedral geometry, coordinated by four oxygen atoms in the equatorial plane, two from bridging carboxylate and two from the chelating carboxylate, and also two pyz molecules at the axial positions. Two equivalent Ni(II) centers are linked by ip ligands to form a $[Ni_2C_2O_4]$ eight-membered ring. The dinuclear metal units are bridged by ip linkers to form infinite 1D chains along the crystallographic *a*-axis (Figure 4).
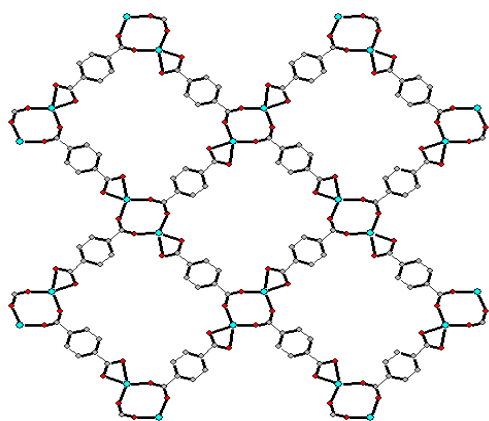

Fig.2. Two dimensional sheets in **1** and **2**

Pillaring the adjacent chains by pyrazine molecules resulted in formation of infinite 2D layers along the crystallographic *ab*-plane (Figure 5). The π-π stacking interactions which exist between the ip and pyz aromatic rings connect the adjacent layers and extend the 2D network into a 3D framework.

2.2 Coordination polymers of pyridine-3,5-dicarboxylic acid

As it was noted, pyridine-carboxylates can be a good candidate for investigating the frameworks containing mixed N-, O- donor linkers. The hydrothermal reaction of pyridine-3,5-dicarboxylic acid (H_2PDB) with $Co(NO_3)_2.6H_2O$ and $Ni(NO_3)_2.6H_2O$ in the presence of pyrazine results in two coordination polymers of formula $[Co(PDB)(H_2O)_2]_n$ (**4**) and $[Ni(PDB)(H_2O)]_n$ (**5**) [25].

Cobalt atoms have a distorted trigonal bipyramidal geometry in **4**. The three equatorial positions are occupied by two oxygen atoms and one nitrogen atom from three equivalent PDB groups. Two water molecules occupy two axial positions. The PDB linkers act as tri-dentate ligand, by two carboxylate groups with chelate modes and one nitrogen atom, which finally bridges three equivalent cobalt atoms (Figure 6). A two-dimensional layer of $\{Co(pydc)\}_n$ is thus constructed in the *ab*-plane with openings along *c*-direction, which is finally extended as an hexagonal arrangement (Figure 7).
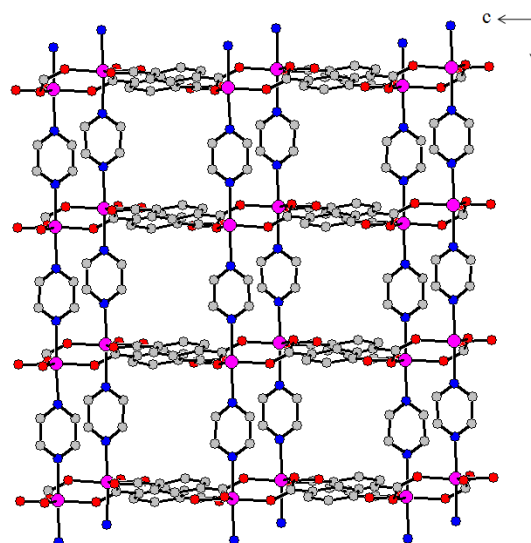

Fig.3. Representation of the 3D network in **1** and **2**

There are also hydrogen bonds between the coordinated water molecules and the carboxylate oxygen atoms of adjacent 2D layers. These interactions could be responsible for further stabilizing the structure.
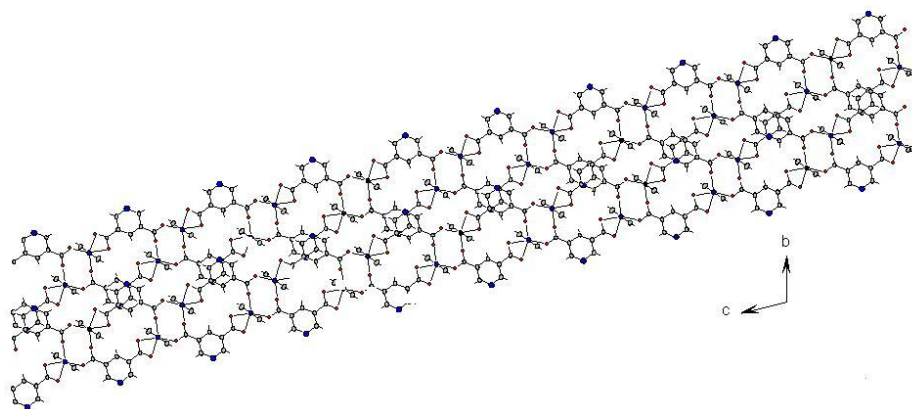
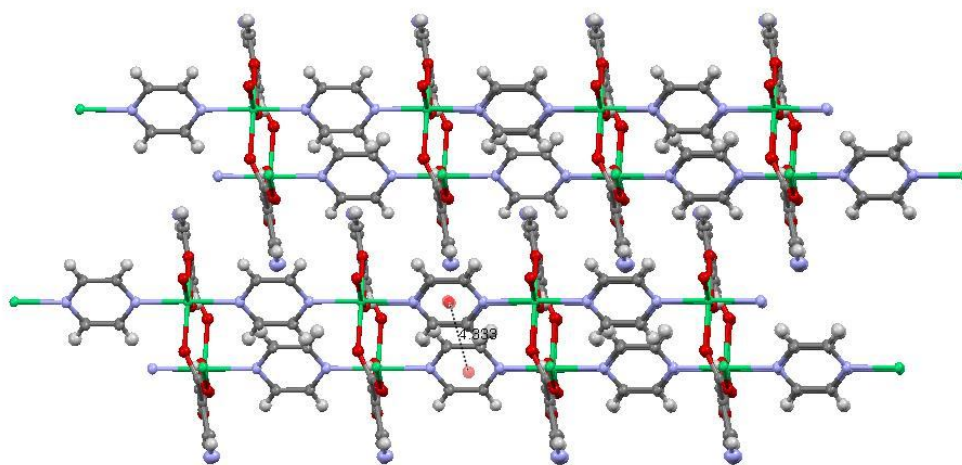**Fig. 4.** A view of one-dimensional chain in $[Ni_2(ip)_2(pyz)_2]_n$

Fig. 5. View of **3** along the c-axis, showing pillaring of 1D chain by pyrazine ligands

Using nickel metal salt rather than the cobalt one results in completely different structure in this case. The corresponded nickel structure, (**5**), has a three-dimensional framework in comparison with two-dimensional network of **4**. Nickel centers in **5**, adopt a distorted octahedral coordination geometry achieved by four 3,5-pydc and one water molecule. The equatorial plane is consisted of three carboxylate oxygen atoms and one nitrogen atom. The other carboxyl oxygen atom and the oxygen atom from a coordinated water molecule occupy the axial positions. The main difference between **4** and **5** are in PDB coordination modes, in a way that in **4** acts as a tridentate ligand, whereas in **5**, it is tetra-dentate. The coordination modes of PDB in these two frameworks are summarized in Scheme 2.
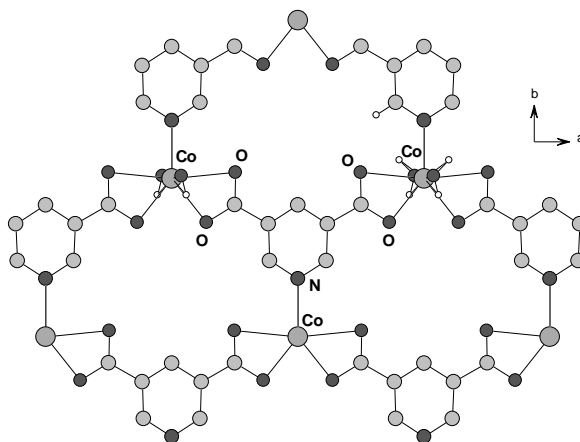
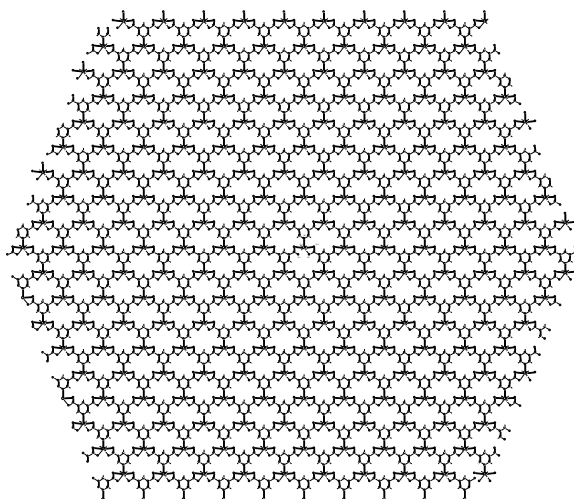**Fig.6.** The coordination environments of the Co(II) ions in $[Co(PDB)(H_2O)_2]_n$

Fig. 7. The perspective view of hexagonal arrangement of **4**

The carboxyl groups of chelate mode and nitrogen atoms connect Ni(II) centers to form parallel layers of $\{Ni\text{-}(pydc)\}_n$ in *ab*-plane (Figure 8). The carboxylic groups of bridging mode link these layers along the *c*-axis to shape a three-dimensional framework with one-dimensional channels of about $3.3 \times 12.5 \ \mathring{A}^2$ (Figure 9). The coordinated water molecules fill the one-dimensional channels. An efficient magnetic interaction between the nickel centers can be developed between parallel layers, through $Ni(OCO)_2Ni$ dimmers formed by bridging carboxyl modes between layers. The hydrogen bonding between the water molecules and carboxylic oxygen atoms between the layers further stabilize the framework.
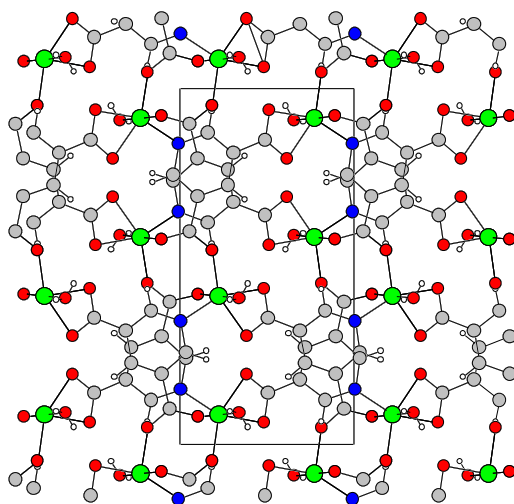
Fig. 8. 2D network of [Ni(PDB)(H$_2$O)]$_n$ (**5**), along *c*-axis. Hydrogen atoms are omitted for clarity
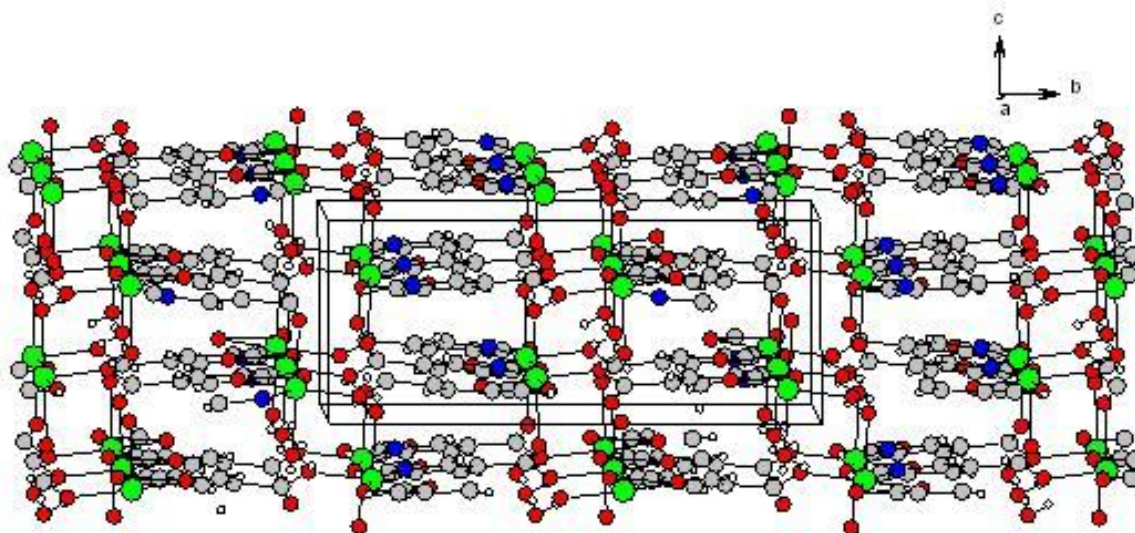

Fig. 9. Molecular packing of **5**, showing the three-dimensional network

Consequently, the difference between the structures **4** and **5** could be arises from the different preferency of Co^{2+} and Ni^{2+} ions in their coordination modes. As we know, Co^{2+} can adopt various geometries in coordination to weak field ligands such as H$_2$O, while Ni^{2+} has a stronger preference for octahedral geometry.
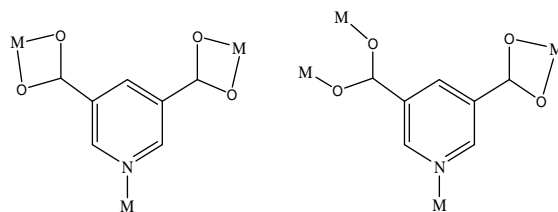
Scheme 2. Coordination modes of the PDB ligand in compounds (a) **4** and (b) **5**

3. Thermal, physical properties and potential applications

Structures **1** and **2** were investigated for thermal and physical properties. Thermogrvimetric investigations show interestingly high thermal stability up to 410 °C for both polymers (Figure 10). This high thermal stability could be assigned to the lack of any co-crystallized or solvent-coordinated in two frameworks. Both MOFs exhibit blue fluorescence emissions in solid state with acceptable intensity (Figure 11).
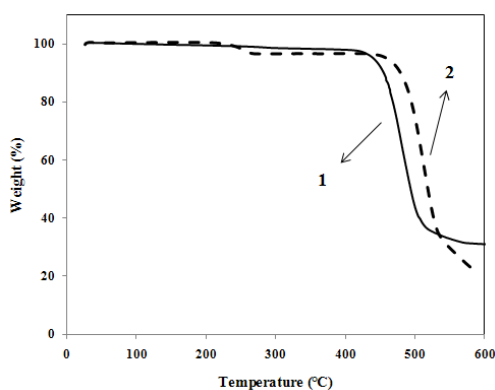
The intense blue-emission, together with high thermal stability and solvent resistance property of **1** and **2** make them a suitable candidate for thermally stable blue-light materials. Moreover, **1** shows a reasonable electrochemical activity within a carbon paste electrode, involving quasi-reversible redox behavior which is pH-dependent (Figure 12). The corresponded electrode shows acceptable stability during consecutive scan cycles. Based on these observations, **1** could have potential application as catalyst in electron transfer processes, via its redox ability and active cobalt sites, which can act as electron transfer centers. Compounds **4** and **5** show magnetic properties (Fig. 13).

Fig. 10. TGA of **1** and **2**, showing high thermal stability for both structures
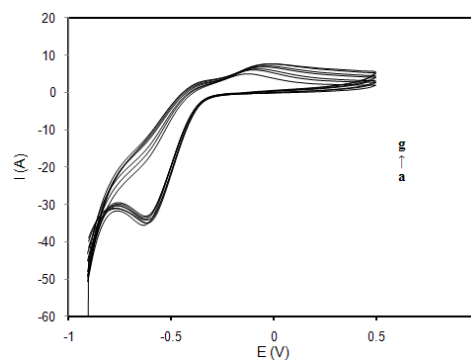
Fig. 12. Electrochemical behavior of **1**-CPE in pH 2

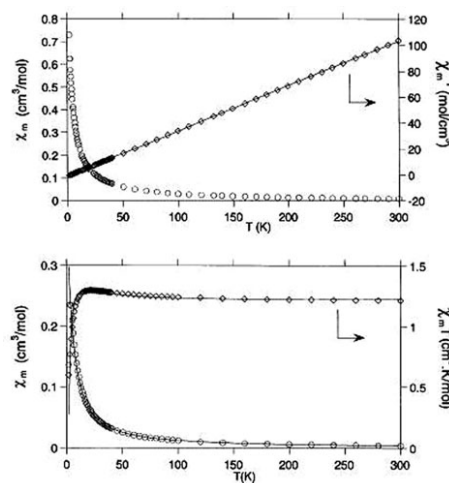**Fig. 11.** Photoluminescence emissions of **1** and **2** in solid state

Fig. 13. Magnetic properties of **4** and **5**, adapted from ref [25]

4. Preparation of metal oxide nanoparticles

Nano-structured metal oxides have attracted great interest in both fundamental as well as applied research areas due to their outstanding physical and chemical properties together with very interesting applications [26, 27]. Among the various techniques for synthesis of metal oxide nanoparticles, direct thermal decomposition of complexes becomes increasingly important mainly due to its simple process, the low cost and easiness to obtain high purity materials [28]. Direct calcinations of bulk powder of **2** produced regularly spherical-shaped NiO nanoparticles with a diameter of about 35-45 nm. Nanoparticles were characterized using SEM/EDAX characterization techniques (Fig. 14).
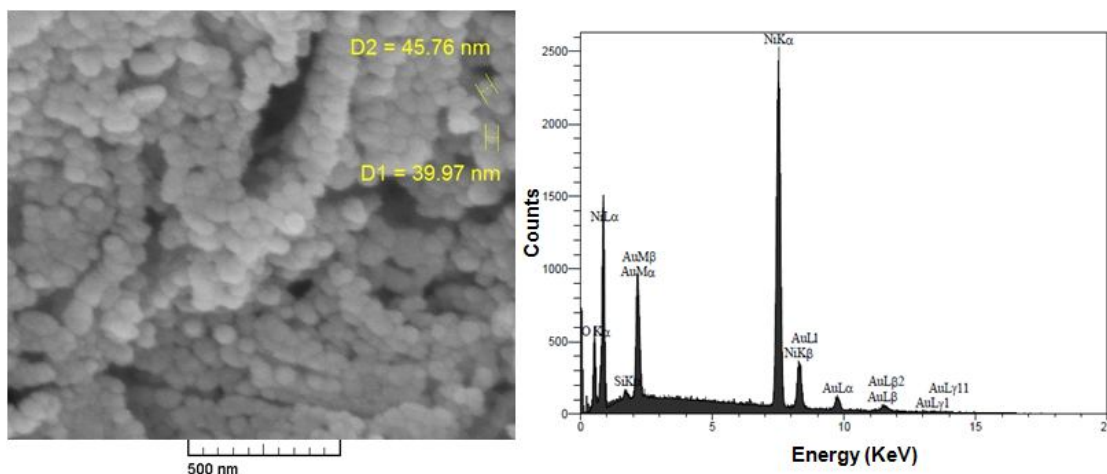

Fig. 14. SEM images of NiO nanoparticles, showing the chemical composition (EDAX) and the morphologies of nanoparticle sample

5. Conclusions

Coordination polymers of mixed carboxylate and pyridine-like ligands exhibit a diverse range of interesting structural motifs. The presence of water coordinated ligands lowers the tendency of metal complexes to form high-dimensional frameworks. The previous reports show that in the presence of N-donor ligands, dimensionality of the polymers can be increased in most cases, via preventing the solvent coordination. Rational combinations of the bridging carboxylates, N-donor ligands and metal ions could allow for generation of interesting coordination molecular architectures based on coordination bonding and supramolecular interactions, as noted by the ABAB interconnected pattern, hexagonal arrangements and other architectures.

Although the synthesis of such coordination architectures with certain useful properties is not exactly predictable, a number of coordination architectures summarized in this paper exhibited interesting physical properties including electrochemical and photoluminescent properties, together with high thermal stabilities. Moreover, a synthesized MOF was used as precursor for preparation of NiO nanoparticles.

In conclusion, mixed N-, O- donor ligands, separately in two ligands or pyridine-carboxylates, offer a wide range of possibilities for MOF

formation and may lead to supramolecular interactions of hydrogen bonding and π-π stacking types. We may expect that with a rational design, more unusual coordination architectures such as new mixed-ligand systems will be possible that can also possess properties and potential applications. The results of such designed syntheses will be likely to have great importance in crystal engineering and supramolecular chemistry.

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