Synthesis, Properties and Environmentally Important Nanostructured and Antimicrobial Supramolecular Coordination Polymers Containing 5-(3-Pyridyl)-1,3,4-Oxadiazole-2-Thiol and Benzimidazole

Aref AM Aly*, Mahmoud A Ghandour, Bahaa M Abu-Zied and Maged S Al-Fakeh

Department of Chemistry, Faculty of Science, Assiut University, Assiut Egypt

Abstract

A new series of coordination polymers of Co(II), Ni(II), Cu(II), Cd(II) and UO$_2$(II), 5-(3-pyridyl)-1,3,4-oxadiazole-2-thiol (POZT) and benzimidazole (BIMZ) has been prepared and characterized. The compounds have been characterized based on elemental analysis, FT-IR and electronic spectral studies, thermal analysis and X-ray powder diffraction. Thermogravimetry (TG), derivative thermogravimetry (DTG) and differential thermal analysis (DTA) have been used to study the thermal decomposition steps and to calculate the thermodynamic parameters of the nano-sized metal coordination polymers. The kinetic parameters have been calculated making use of the Coats-Redfern and Horowitz-Metzger equations. The scanning electron microscope SEM photographs and particle size calculations from the powder XRD data indicate the nano-sized nature of the prepared supramolecular coordination polymers (average size 17-28 nm). The antimicrobial activity of the synthesized compounds was tested against six fungal and five bacterial strains. The majority of compounds were effective against the tested microbes. The bacteria and fungi strains are common contaminants of the environment in Egypt. In this article the studied strains are frequently reported from contaminated soil, water and food.

Keywords: Coordination polymers; X-ray powder diffraction, Thermal studies and biological activity.

Introduction

In recent decades, metal-organic frameworks (MOFs) are extensively developed as a new type of functional crystalline materials for a wide range of promising applications in separation, storage, exchange, and heterogeneous catalysis due to their high stability and structural diversity [1-4]. In general, the final coordination polymers significantly depend on the metal and ligand precursors [5]. Recently, a variety of pyridyl connectors have been extensively applied in this facet [6]. It should be noted that organosulfur compounds, which play an important role in chemical or biological processes are well documented [7]. Heterocyclic thiones are known in the field of coordination chemistry because of their potential multifunctional donor sites, viz either exocyclic sulfur or endocyclic nitrogen [8]. The pyridyl oxadiazoles are suitable bridging ligands for the synthesis of coordination polymers and several papers were published on using cyclized pyridyl 1,3,4-oxadiazoles for the preparation of metal complexes [9-11]. By changing the steric and electronic properties of ancillary organic ligands such as the heterocycle N-donor molecules, (e.g. benzimidazole), it was possible to modulate the construction and the dimension of the polymeric coordination network [12]. Also benzimidazole belongs to a class of compounds which are of interest because of their pharmaceutical, analytical, most common binding sites in various metalloenzymes and industrial applications [13]. The chemistry of uranium is the most developed, due to the low radioactivity of one of its isotopes and its wide use at industrial and laboratory scales [14]. Uranium (VI) tends to form linear cation with two oxygen atoms UO$_2$\(^2+\) which can be further surrounded by a number of anions commonly lying in one plane, which is perpendicular to O–U–O structure [15]. In this work, we synthesized and characterized new coordination polymers derived from the bridging ligand 5-(3-pyridyl)-1,3,4-oxadiazole-2-thiol, benzimidazole and Co(II), Ni(II), Cu(II), Cd(II) and UO$_2$(II).

Material and Methods

High purity 5-(3-pyridyl)-1,3,4-oxadiazole-2-thiole and benzimidazole were supplied from Sigma Aldrich and Merck. All other chemicals were of AR grade. Figure 1 shows the structure of the ligands.

Physical measurements

Elemental analysis (carbon, hydrogen, nitrogen and sulphur) were performed using a Thermo Flash EA 1112 elemental analyzer. FT-IR spectra were recorded on a Bruker Tensor 27 spectrometer in the range 4000-400 cm\(^{-1}\). The electronic spectra were recorded on Shimadzu UV-1800 spectrophotometer in the range 200-800 nm. Thermal analysis was performed using a simultaneous TG-DTA Perkin Elmer Diamond apparatus in the range 30-800°C at a heating rate of 10°C min\(^{-1}\) in air atmosphere.

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performed using Analytischer Funktionstest Vario El Fab-Nr.11982027 elemental analyzer. Infrared spectra were recorded as KBr disks (400–4000 cm⁻¹) with a FT-IR spectrophotometer model (Thermo-Nicolet-6700 FTIR) and the electronic spectra were obtained using a Shimadzu UV-2101 PC spectrophotometer. Magnetic susceptibility measurements were done on a magnetic susceptibility balance of the type MEGAMAG. The conductance was measured using a conductivity Meter model 4310 JENWAY. Thermal studies were carried out in dynamic air on a Shimadzu DTA/DSC-60 H thermal analyzer at a heating rate 10 °C/min. XRD Model PW 1710 control unit Philips, Anode material Cu 40 K. V 30 M.A Optics: Automatic divergence slit. Scanning electron microscope (JEOL JFC-1100E ION SPUTTERING DEVICE, JEOL JSM-5400LV SEM), SEM specimens were coated with gold to increase the conductivity. For the biological activity all microbial strains were kindly provided by the Assiut University Mycological Centre (AUMC), Egypt. These strains are common contaminants of the environment in Egypt and some of which are involved in human and animal diseases (Candida albicans, Geotrichum candidum, Scopulariopsis brevicaulis, Aspergillus flavus, Staphylococcus aureus), plant diseases (Fusarium oxysporum) or frequently reported from contaminated soil, water and food substances (Escherichia coli, Bacillus cereus, Pseudomonas aeruginosa and Serratia marcescens). To prepare inocula for bioassay, bacterial strains were individually cultured for 48 h in 100 ml conical flasks containing 30 ml nutrient broth medium. Fungi were grown for 7 days in 100 ml conical containers containing 30 ml Sabouraud’s dextrose broth. Bioassay was done in 10 cm sterile plastic Petri plates in which microbial suspension (1 ml/plate) and 15 ml appropriate agar medium (15 ml/plate) were poured. Nutrient agar and Sabouraud’s dextrose agar were respectively used for bacteria and fungi. After solidification of the media, 5 mm diameter cavities were cut in the solidified agar (4 cavities/plate) using sterile cork borer. The chemical compounds dissolved in dimethyl sulfoxide (DMSO) at 2%w/v (=20 mg/ml) were pipetted in the cavities (20 μl /cavity). Cultures were then incubated at 28°C for 48 h in case of bacteria and up to 7 days in case of fungi. Results were read as the diameter (in mm) of inhibition zone around cavities [16].

Synthesis of the coordination polymers

[Co(POZT)(BIMZ)Cl(H₂O)]ₙ (1): A methanolic solution (10 mL) of POZT (0.1 g, 0.5 mmol) was slowly added into a hot methanolic solution (10 mL) of CoCl₂·6H₂O (0.132 g, 0.5 mmol) and to it a methanolic solution (10 mL) of benzimidazole (0.066 g, 0.5 mmol) was added drop wise. The resultant mixture was stirred for 1 h and filtered. The dark blue precipitate was separated, washed with distilled water and EtOH and then dried over CaCl₂ in a desicator. Anal. Calc. for Co₃H₅,N₃ClO₄·3H₂O: C, 33.42; H, 4.37; N, 14.01; S, 7.98. IR data: νOH 3495 (s), 3192 (m), νC=N 1612 (s), νC=N 1466 (s), 906 (s) νM-O 572 (m), νM-N 440 (s) cm⁻¹, m.p. 276°C.

[Co(POZT)(BIMZ)Cl(H₂O)]ₙ (4): The same synthetic procedure as that for 1 was adopted except that CoCl₂·6H₂O (0.132 g, 0.5 mmol) was replaced by CdCl₂·2H₂O (0.127 g, 0.5 mmol) (Figure 2). A white product was isolated. Anal. Calc. for Cd₃H₅,N₃ClO₄·3H₂O: C, 31.52; H, 3.59; N, 13.13; S, 6.01. Found: C, 33.96; H, 4.25; N, 11.72; S, 7.22. IR data: νOH 3500 (s), 3190 (m), 1483 (s), 928 (m), νM-O 550 (m), νM-N 430 (m) cm⁻¹, m.p. 298°C.

[NI(POZT)(BIMZ)Cl(H₂O)]ₙ (5): A mixture of equimolar quantity (0.5 mmol) of UO₂(ac)_2·2H₂O (0.236 g) and POZT (0.1 g) in a methanolic solution (15 mL) was mixed with a methanolic solution (10 mL) of BIMZ (0.066 g, 0.5 mmol) and heated for 2 h, then gradually cooled to room temperature (Figure 3). A yellow compound was isolated. Anal. Calc. for UO₂C₅H₅,N₃ClO₄·3H₂O: C, 49.21; H, 2.20; N, 10.90; S, 6.00. Found: C, 49.30; H, 2.37; N, 9.96; S, 6.78. IR data: νOH 3200 (m), νC=N 1618 (s), νC=N 1410 (m), 924 (m), νM-O 520 (m), νM-N 430 (m) cm⁻¹, m.p. 298°C.

Results

The coordination polymers were prepared by the reaction of 5-(3-pyridyl)-1,3,4-oxadiazole-2-thiol (neutralized with NaOH), metal chlorides or acetate, and benzimidazole (dissolved in EtOH or MtOH). The prepared compounds were found to react in the molar ratio 1:1:1 metal: POZT: BIMZ. The complexes are air stable, insoluble in chlorides or acetate, and benzimidazole (dissolved in EtOH or MtOH).
common organic solvents but partially soluble in DMSO. The electrical conductivity of the coordination polymers adequately supported their non-electrolytic nature.

**Fourier transform infrared spectroscopy (FT-IR)**

The main IR bands of each compound are cited in the experimental part. The bands observed in the 1606-1620 cm⁻¹ regions are assigned to the ν(C=N) stretching vibration of the POZT [17]. BIMZ exhibits two bands in the regions 906-964, 1414-1485 cm⁻¹ which can be assigned to ν(C-N) ring [12]. Furthermore, it is found that the bands at 3385-3500 cm⁻¹ in the spectra of compounds 2, 3 and 4 are assigned to νOH of water of crystallization [18] whereas the νOH stretching vibrations of the coordinated water molecules are located in the range 3150-3200 cm⁻¹ for all compounds [19]. Metal-oxygen and metal-nitrogen bonding are manifested by the appearance of a band in the 520-572 cm⁻¹ and 424-440 cm⁻¹ region, respectively [20].

**Electronic Spectra**

The UV-Vis spectra of the coordination polymers in dimethylsulphoxide (DMSO) display two absorption maxima located in the regions 34,482-39,682 and 21,186-27,777 cm⁻¹ which are attributed to π→π* and n→π* transitions within the POZT and BIMZ ligands [12,16]. The Co(II), Ni(II) and Cu(II) coordination polymers exhibit a band at 16,129, 17,543 and 15,337 cm⁻¹ respectively corresponding to the d-d transitions. Additionally, the magnetic moments of the compounds were measured and it has been found that the cobalt(II) compound 1 has a magnetic moment of 4.43 B.M typical for the octahedral complexes [21] whereas the magnetic moment values 1.90, 2.10 B.M were found for the Ni(II) 3 and Cu(II) 4 compounds respectively suggesting their octahedral structures [22,23]. However, the low value of magnetic moment for the Ni(II) complex may be attributed to the presence of a mixture of square planar and octahedral geometries [24]. The electronic spectral data are shown in (Table 1). From the above data the structure of the coordination polymers can be postulated as follows:

**Thermal Studies**

The thermal decomposition of the coordination polymers has been investigated in dynamic air from ambient temperature to 750°C (Table 2). As a following example the thermogram of the cadmium(II) compound 4 shows four stages in the temperature ranges 53-92, 93-176, 177-235 and 236-750°C (Figure 4). The first and second stages correspond to the release of the two coordinated and the three crystalline water molecules (calc.16.89 %, found 15.32 %). The DTG curve shows these two steps at 63 and 131°C and two endothermic peaks at 66 and 133°C are recorded in the DTA trace. The third and forth steps represent decomposition of the organic ligands. These two steps are manifested by two DTG peaks at 200 and 525°C and are associated with two exothermic peaks at 201 and 527°C in the DTA curve. The final product was identified on the basis of mass loss considerations to be CdO (calc.24.07 %, found 25.76 %). (Scheme 1).

**Kinetic analysis:** Non-isothermal kinetic analysis of the complexes was carried out applying two different procedures: the Coats-Redfern [24] and the Horowitz-Metzger [25] methods.

(i) **The Coats-Redfern equation**

\[
\ln\left[\frac{1-(1-\alpha)^n}{1-(1-\alpha)^T}\right] = M / T + B \quad \text{for} \quad n \neq 1 \quad (1)
\]

\[
\ln\left[-\ln(1-\alpha)/T\right] = M / T + B \quad \text{for} \quad n = 1 \quad (2)
\]

where \(\alpha\) is the fraction of material decomposed, \(n\) is the order of the decomposition reaction and \(M = -E/R\) and \(B = ZR/\Phi E\); \(E, R, Z\) and \(\Phi\) are the activation energy, gas constant, pre-exponential factor and heating rate, respectively.

(ii) **The Horowitz-Metzger equation**

\[
\ln\left[\frac{1-(1-\alpha)^1}{1-n/1-n}\right] = \ln Z R T s^2 / \Phi E - E / RT s + E/RT s 2 \quad \text{for} \quad n \neq 1 \quad (3)
\]

\[
\ln\left[-\ln(1-\alpha)\right] = E/RT s 2 \quad \text{for} \quad n = 1 \quad (4)
\]
where $\theta = T - T_s$, $T_s$ is the temperature at the DTG peak. The correlation coefficient $r$ is computed using the least squares method for equations (1), (2), (3) and (4). Linear curves were drawn for different values of $n$ ranging from 0 to 2. The value of $n$, which gave the best fit, was chosen as the order parameter for the decomposition stage of interest. The kinetic parameters were calculated from the plots of the left hand side of equations (1), (2), against $1/T$ and against $\theta$ for equations (3) and (4) (Figure 5, 6). The kinetic parameters for compounds 1, 4 and 5 were calculated for the first step according to the above two methods and are cited in Table 3, 4. The thermodynamic parameters $\Delta S^*$, $\Delta H^*$ and $\Delta G^*$ for the three complexes 1, 4 and 5 were computed using the following equations:

\[
\Delta S^* = R \left[ \ln \frac{Z_n h}{kT_s} \right] \tag{5}
\]

\[
\Delta H^* = \Delta E^* - RT_s \tag{6}
\]

\[
\Delta G^* = \Delta H^* - T_s \Delta S^* \tag{7}
\]
where $h$, Planck’s constant, $k$, Boltzmann constant, $R$, gas constant and $T_s$, temperature at the DTG peak. Negative $\Delta S^*$ value for the different stages of decomposition of the complexes suggest that the activated complex is more ordered than the reactants and that the reactions are slower than normal [26-28]. The more ordered nature may be due to the polarization of bonds in the activated state, which might happen through charge transfer electronic transition [29]. The different values of $\Delta H^*$ and $\Delta G^*$ of the complexes refer to the effect of the structure of the metal ions on the thermal stability of the complexes [30]. The positive values of $\Delta G^*$ indicate that the decomposition reaction is not spontaneous.

![Figure 11: Microbiological screening of compound 4 against Candida albicans.](image1)

![Figure 12: Microbiological screening of compound 5 against Serratia marcescens(-ve).](image2)

**X-ray powder diffraction of the complexes**

The X-ray powder diffraction patterns were recorded for the coordination polymers 3 and 4. The diffraction patterns indicate that the compounds are crystalline. The crystal lattice parameters were computed with the aid of the computer program TREOR. The crystal data for 3 and 4 metal mixed-ligand compounds belong to the crystal system triclinic (Table 5). The significant broadening of the diffraction patterns suggests that the particles are of nanometer dimensions. XRD of compound 3 is depicted in Figure 7. Scherrer’s equation (8) was applied to estimate the particle size of the coordination polymers:

$$D = \frac{K\lambda}{\beta \cos \theta}$$

(8)

where $K$ is the shape factor, $\lambda$ is the X-ray wavelength typically 1.54 Å, $\beta$ is the line broadening at half the maximum intensity in radians and $\theta$ is Bragg angle, $D$ is the mean size of the ordered (crystalline) domains, which may be smaller or equal to the grain size. The crystal data together with the particle size are recorded in

![Figure 13: Comparison of coordination polymers of antibacterial activity.](image3)

**Table 2: Thermal decomposition data of the compounds in dynamic air.**

| Compound | Step | TG/DTG | Mass Loss(%) |
|----------|------|--------|-------------|
|          | Ti   | Tm     | Tf          |
| 1        | 1st  | 50     | 68          | 156       | 5.37 |
|          | 2nd  | 157    | 217         | 244       | 2.93 |
|          | 3rd  | 245    | 325         | 371       | 19.69 |
|          | 4th  | 372    | 475         | 750       | 44.07 |
| 4        | 1st  | 53     | 64          | 92        | 11.01 |
|          | 2nd  | 93     | 131         | 176       | 4.31 |
|          | 3rd  | 177    | 201         | 236       | 26.30 |
|          | 4th  | 236    | 525         | 750       | 32.62 |
| 5        | 1st  | 150    | 210         | 230       | 1.42 |
|          | 2nd  | 231    | 312         | 463       | 33.97 |
|          | 3rd  | 464    | 560         | 750       | 18.38 |

$T_i$=Initial temperature, $T_m$=Maximum temperature, $T_f$=Final temperature.

**Biological activity**

In testing the antibacterial and antifungal activity of these compounds we used more than one test organism to increase the chance of detecting antibiotic principles in tested materials. The data showed that in some cases the ligand has a higher or similar antimicrobial and antifungal activity than the selected standards (chloramphenicol and clotrimazole). Also, the complexes of certain metal ions enhanced the
antimicrobial activity and in some case a higher or similar activity than the selected standards were shown Table 6. Figure 10-13 show the antimicrobial effect for these compounds.

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