SONOCHEMICAL SYNTHESIS AND CHARACTERIZATIONS OF NANOSIZED METAL COORDINATION POLYMERS DERIVED FROM 5-(3-PYRIDYL)-1,3,4-OXADIAZOLE-2-THIOLE AND 2-AMINOTHIAZOLE

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Nanosized coordination polymers of Co(II), Ni(II), Cu(II) and Cd(II) of mixed ligand derived from 5-(3-pyridyl)-1,3,4-oxadiazole-2-thiole (POZT) and 2-aminothiazole (AZ) were synthesized. The compounds were characterized by elemental analysis, IR and electronic spectral studies. Thermogravimetry (TG), derivative thermogravimetry (DTG) and differential thermal analysis (DTA) have been used to study the thermal decomposition steps of the compounds and to calculate the thermodynamic parameters of the nanosized 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 four compounds prepared under ultrasonic irradiation (average size 23-60 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.

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Introduction

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.[1-3] Nanometer-sized particles of metal coordination polymers are of interest to explore, since their unique properties are controlled by the large number of surface molecules, leading to an entirely different environment than those in a bulk crystal.[4] Therefore, they are of potential use as materials for nanotechnological applications. The variety of pyridyl connectors have been extensively applied in this respect.[5] The important role played by organosulfur compounds, in chemical or biological processes are well documented.[6] The pyridyl-oxadiazoles are suitable bridging ligands for the synthesis of coordination polymers and several papers have been published on using cyclized pyridyl 1,3,4-oxadiazoles for the preparation of metal complexes.[7-9] Azoles represent a very interesting class of compounds because of their pharmaceutical, analytical and industrial applications.[10] We now report the preparation and characterization of nanosized Co(II), Ni(II), Cu(II) and Cd(II), 5-(3-pyridyl)-1,3,4-oxadiazole-2-thiole and 2-aminothiazole complexes.

Experimental

High purity 5-(3-pyridyl)-1,3,4-oxadiazole-2-thiole (POZT) and 2-aminothiazole (AZ) were supplied from Sigma Aldrich and Merck. All other chemicals were of AR grade.

Preparation of the coordination polymers

Preparation of the mixed ligand complexes of POZT and AZ with Co(II), Ni(II), Cu(II) and Cd(II) followed essentially the same procedure. The preparation of $[Co(POZT)(AZ)Cl(H_2O)_2]_n$ is given below as a typical example.

To an ethanolic solution (15 mL) of $CoCl_2.6H_2O$ (0.5 mmol), a hot solution (15 mL) of POZT (0.5 mmol) was added dropwise with stirring, and then a solution of AZ (10 mL ethanol, 0.5 mmol) was added to the mixture. The mixture was refluxed and then cooled to room temperature. Subsequently, the solution mixture was stirred for 40 min under ultrasonic irradiation and then the blue precipitate was separated, washed with distilled water and EtOH and dried over $CaCl_2$ in a desiccator.

Physical Measurements

Stoichiometric analyses (C, H, N, S) were performed using Analyischer Funktionstest Vario El Fab-Nr.11982027 elemental analyzer. IR 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 MSB-Auto. The conductance was measured using a conductivity Meter model 4310 JENWAY. Thermal studies were carried out in dynamic air on a Shimadzu DTG 60-H thermal analyzer at a heating rate 10 °C min^{-1}. XRD-diffraction patterns were recorded on a diffractometer Model PW 1710 control unit Philips, anode material Cu 40 K,V 30 M, aoptics: automatic divergence slit. Scanning electron microscope was of the type 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 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 conicals 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 dimethylsulphoxide (DMSO) at 2%w/v (= 20 mg/mL) were pipetted in the cavities (20 ul /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.[11]

Result and discussion

The compounds were prepared by the reaction of 5-(3-pyridyl)-1,3,4-oxadiazole-2-thiole, metalchlorides and 2-aminothiazole (dissolved in EtOH). The prepared complexes were found to react in a molar ratio of 1:1:1 of metal, POZT and AZ.The complexes are air-stable, they are insoluble in common organic solvents but partially soluble in DMF and DMSO. The conductivity values, measured in DMSO at room temperature, lie within the range for nonelectrolytes. The compositions of the complexes are supported by the elemental analysis provided in table 1.

Fourier transform infrared spectroscopy (FT-IR)

The main FT-IR frequencies can be seen in table 2. The bands observed in the 1608-1620 cm^{-1} regions are assigned to the υ(C=N) stretching vibration of the 5-(3-pyridyl)-1,3,4-oxadiazole-2-thiole.[12] It is found that the CSC band of the 2-aminothiazole at ~740 cm^{-1} is almost unchanged in the respective complexes, indicating that the thiazole-S is not involved in the bonding.[13] The same is true for the υC=N stretching vibration of the azole for all complexes where no appreciable shift was noticed. However, the stretching vibration of the amino group in the free AZ observed at 3220 cm^{-1} is shifted to a lower wave number, appearing in the range 3150-3172 cm^{-1} in the complexes and suggesting coordination of the amino nitrogen to the metal(II) ions.[14] Furthermore, it is found that the bands at 3445 cm^{-1} in the spectra of compound (**2**) is assigned to υOH of water of crystallization[15] whereas the υOH stretching vibrations of the coordinated water molecules are located in the range 3197-3202 cm^{-1} for all compounds.[16] Metal-oxygen and metal-nitrogen bonding are manifested by the appearance of a band in the 513-543 cm^{-1} and 428-446 cm^{-1} regions, respectively.[17]

Electronic spectra

The UV-Vis spectra of the compounds were recorded in DMSO. The spectra displayed two absorption maxima located in the regions35,714-37,037 and 29,411-31,746 cm^{-1} which are attributed to $\pi\rightarrow\pi^*$ and n$\rightarrow\pi^*$ transitions within the POZT and AZ ligands [18,19]. The Co(II), Ni(II) and Cu(II) coordination polymers exhibit a band at 18,685, 19,801 and 17,518 cm^{-1} respectively corresponding to the d-d transitions. In the visible spectra, there were characteristic bands attributed to the d-d transitions in the complexes typical of octahedral structures. The structure of the coordination polymers can be postulated as follows (Figures 2 and 3).

Magnetic measurements

The magnetic moments of the compounds were measured and it has been found that the cobalt(II) compound (**1**) has a magnetic moment of 4.38 B.M typical for octahedral complexes,[20] whereas the magnetic moment values 2.13 and 1.88 B.M that were found for the Ni(II) and Cu(II) compounds respectively suggest their octahedral structures.[21,22]

Thermal analysis

The thermal decomposition of the compounds has been investigated in dynamic air from ambient temperature to 700 °C. The thermal decomposition data of the compounds are collected in table 3. As a representative example the thermal behaviour of the Co(II) complex (**1**) will be described. The thermogram of the complex shows three decomposition stages. The first stage corresponds to the release of the two water molecules (calc. 8.81 %, found 7.41 %). The DTG curve displays this step at 177 °C and an endothermic peak appears at 179 °C in the DTA trace. The second and third steps correspond to the decomposition products of the ligands. These two steps are manifested by two DTG peaks at 331 and 500 °C and are associated with two exothermic peaks at 333 and 503 °C in the DTA curve, respectively. The final product was identified on the basis of mass loss consideration as CoO (calc. 18.33 %, found 17.61 %) (Scheme 1).
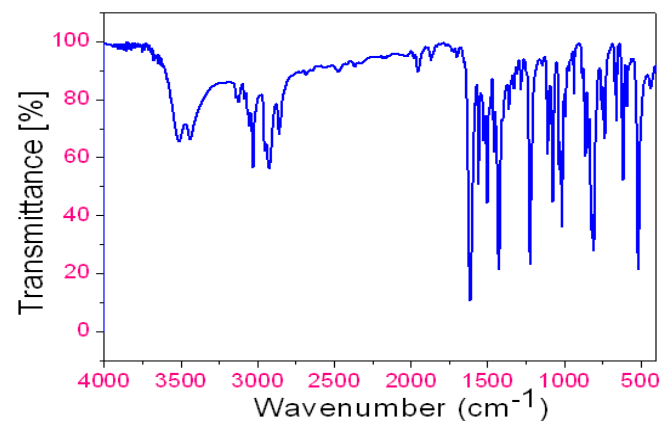

Figure 1. FT-IR spectrum of Ni(II) compound (**2**).

Table 1. Colors, elemental analysis and melting points of the compounds.

Compound	Mol. Wt	Color	Found (Calcd. %)				m.p.°C
			C	H	N	S	(decom.)
{[Co(POZT)(AZ)Cl(H₂O)₂]}ₙ (**1**)	$C_{10}H_{12}CoN_5O_3S_2Cl$, 408.72	Blue	29.10	2.86	17.04	15.49	274
			29.38	2.95	17.13	15.68	
{[Ni(POZT)(AZ)Cl(H₂O)₂].H₂O}ₙ(**2**)	$C_{10}H_{14}NiN_5O_4S_2Cl$, 426.48	Light green	28.02	3.12	16.33	14.95	281
			28.16	3.30	16.42	15.03	
{[Cu(POZT)(AZ)Cl(H₂O)₂]}ₙ (**3**)	$C_{10}H_{12}CuN_5O_3S_2Cl$, 413.34	Brown	28.97	2.86	16.90	15.48	269
			29.05	2.90	16.94	15.51	
{[Cd(POZT)(AZ)Cl(H₂O)₂]}ₙ (**4**)	$C_{10}H_{12}CdN_5O_3S_2Cl$, 462.20	White	25.66	2.50	15.09	13.79	290
			25.98	2.59	15.15	13.87	

Table 2. Infrared spectral data of the coordination polymers.

No.	ν(OH)	ν(NH₂)	ν(C=N)	ν(C-N)	ν(C-S)	ν(M-O)	ν(M-N)
(**1**)	3198	3164	1616	1487	736	543	428
(**2**)	3445, 3200	3150	1620	1456	733	538	437
(**3**)	3197	3158	1608	1470	728	513	446
(**4**)	3202	3172	1615	1483	724	530	431

Table 3. Thermal decomposition data of the compounds.

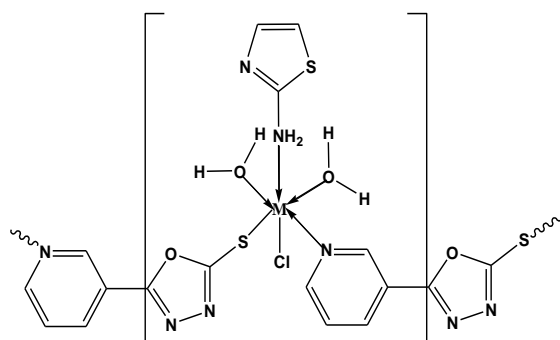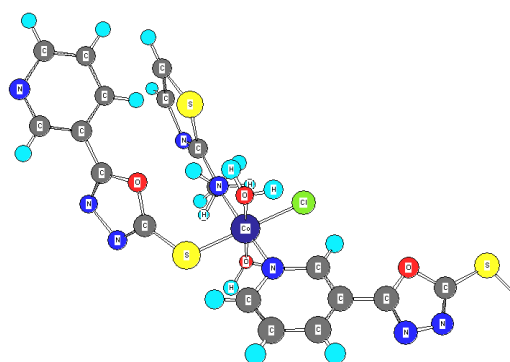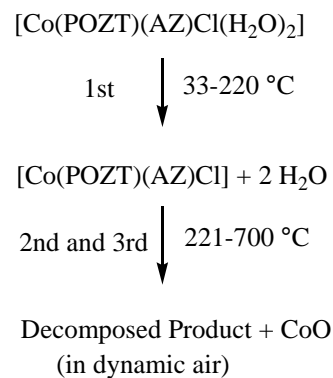|	Step	TG/DTG			Mass loss (%)
		T_i	T_m	T_f	
(**1**)	1st	33	177	220	7.41
	2nd	221	331	386	23.88
	3rd	387	500	700	51.10
(**2**)	1st	29	60	130	11.77
	2nd	131	213	285	22.15
	3rd	286	394	436	8.08
	4th	437	502	700	41.94
(**4**)	1st	35	109	250	6.98
	2nd	251	321	435	28.75
	3rd	436	583	700	38.13

Figure 2. Proposed structure of the metal complex.

Figure 3. A perspective view of coordination round Co(II).

$[Co(POZT)(AZ)Cl(H_2O)_2]$

1st ↓ 33-220 °C

$[Co(POZT)(AZ)Cl] + 2 H_2O$

2nd and 3rd ↓ 221-700 °C

Decomposed Product + CoO
(in dynamic air)

Scheme 1. Thermal decomposition of Co-compound

Table 4. Kinetic and thermodynamic parameters for the thermal decomposition of the compounds

Compound	Step	Coats-Redfern equation				ΔS^*	ΔH^*	ΔG^*
		r	n	E	$Zx10^2$	J mol^{-1} K^{-1}	kJ mol^{-1}	kJ mol^{-1}
(**1**)	1st	1.0000	0.50	55.6	6.52	-192.5	50.53	167.78
(**2**)	1st	0.9997	2.00	126.2	2.54	-186.4	120. 7	244.61
(**4**)	1st	1.0000	0.66	44.6	8.95	-194.1	39.65	155.18

Kinetic analysis

Non-isothermal kinetic analysis of the complexes was carried out applying two different procedures: the Coats-Redfern[23] and the Horowitz-Metzger[24] methods.

Coats-Redfern equation

$$\ln[1-(1-\alpha)^{1-n}/ (1-n)T^2] = M/T + B \quad (\text{for } n \neq 1) \qquad (1)$$

$$\ln[-\ln(1-\alpha)/ T^2] = M/T + B \qquad (\text{for } n = 1) \qquad (2)$$

where

α 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 Φ are the activation energy, gas constant, pre-exponential factor and heating rate, respectively.

Horowitz-Metzger equation for $n \neq 1$

$$\ln[1-(1-\alpha)^{1-n}/1-n]= \ln ZRT_s^2/\Phi E - E/RT_s+ E\theta/RT_s^2 \quad (3)$$

for $n = 1$

$$\ln[-\ln(1-\alpha)] = E\theta/RT_s^2 \qquad (4)$$

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 θ for equations (3) and (4). The kinetic parameters were calculated according to the above two methods and are cited in Table 4.

The negative ΔS^* values 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.[25-27] The more ordered nature may be due to the polarization of bonds in the activated state, which might happen through charge transfer electronic transition.[28] The different values of ΔH^* and ΔG^*

of the compounds refer to the effect of the structure of the metal ions on the thermal stability of the complexes.[29] The positive values of ΔG^* indicate that the decomposition reaction is not spontaneous.

X-ray powder diffraction of the compounds

The X-ray powder diffraction patterns were recorded for four of the coordination polymers. 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 Co(II), Ni(II), Cu(II) and Cd(II) metal mixed-ligand compounds belong to the crystal system triclinic. The significant broadening of the diffraction patterns suggests that the particles are of nanometer dimensions. Scherrer's equation (eqn. 5) was applied to estimate the particle size of the coordination polymers.

$$D = \frac{K\lambda}{\beta \cos\theta} \qquad (5)$$

Table 5. X-ray diffraction crystal data of the compounds

Parameters	(1)	(2)	(3)	(4)
Mol. Wt.	408.72	645.67	413.34	462.20
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
a (Å)	7.34	8.53	9.02	3.47
b (Å)	10.05	9.00	8.53	6.37
c (Å)	11.96	10.98	13.75	7.51
α (°)	103.81	86.19	90.00	65.80
β(°)	117.00	65.09	52.67	110.31
γ(°)	82.44	59.21	120.74	62.92
Volume of unit cell (Å^3)	763.97	645.67	646.18	102.09
Particle size (nm)	35	60	23	56

Scanning electron microscopy

The scanning electron micrographs of the Co(II), Ni(II), Cu(II) and Cd(II) ternary coordination polymer prepared bysonication is illustrated in Figures 4-6. The micrograph shows the morphology of this nanostructured compounds. The nano crystals aggregate to a great extent in the form of cornel reefs for cadmium compound.

The particle size of the compounds are in the range 23-60 nm. These results are in a good agreement with the size determined from XRD analysis by the Scherrer's equation (Table 5).
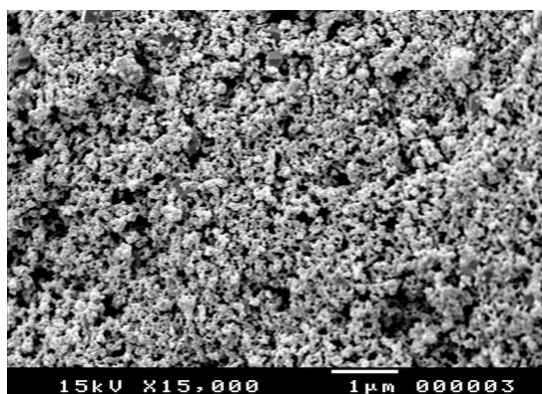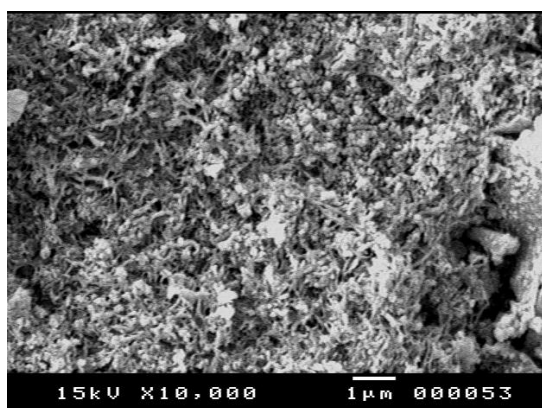
Figure 4. SEM picture of Cu(II) compound.

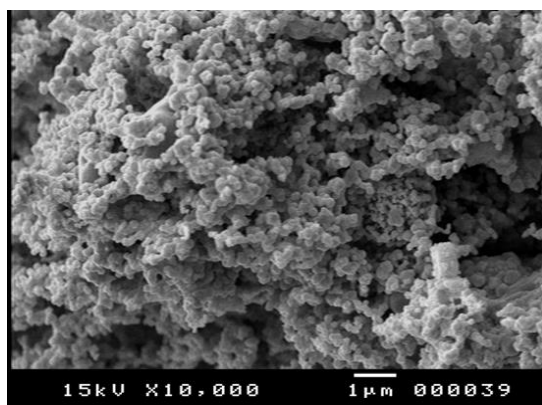**Figure 5.** SEM picture of Ni(II) compound.

Figure 6. SEM picture of Co(II) compound.

Biological Activity

For testing the antibacterial and antifungal activity of these compounds we used more than one test organism to increase the chance of detecting the antibiotic property of the 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 possessed enhanced antimicrobial activity and in some cases activity similar to the selected standards (Table 6).

Table 6. Microbiological screening of the compounds.

Microbes	Compound			
	(1)	**(2)**	**(3)**	**(4)**
*B. cereu*s (G+ve)	10	16	12	18
S. aureus (G+ve)	10	12	10	14
S. marcescens (G-ve)	10	11	8	16
E. coli (G-ve)	10	12	11	18
P. aeruginosa (G-ve)	10	12	10	14
T. rubrum	8	8	10	12
A. flavus	0	0	0	10
C. albicans	8	0	0	12
F. oxysporm	0	8	0	10
G. candidum	10	0	11	18
S. brevicaulis	0	8	8	12

The toxic action of the prepared coordination polymers against the growth of bacteria and fungi studied may be due to thiols, which are the vital constituents in the living cells, having a reduction potential for disulfide form at or below -200 mV, may be oxidized by the metals complexes. The complexes may cause disturbance in the respiration process due to the presence of (C=S) group in the azole complexes.[30-32]

Conclusion

The results presented in this work showed that synthesis of nanosized metal (II) coordination polymers derived from 5-(3-pyridyl)-1,3,4-oxadiazole-2-thiole and 2-aminothiazole can be achieved via the sonochemical method. Some of the complexes show a remarkable biological activity against bacteria and fungi indicating that they can be as potential antibacterial or antifungal drugs.

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