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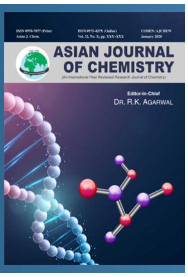

Synthesis and Properties of Two Fe(III) Coordination Polymers Based on 2-Amino-4-methylthiazole, 2-Mercaptobenzothiazole and Aromatic Polycarboxylate

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Two of coordination polymers of the general formula $[Fe(BDC)(AMTZ)Cl]\cdot 2H_2O$ and $[Fe(BDC)(MBT)Cl]\cdot H_2O$, BDC = 1,4-benzenedicarboxylic acid, AMTZ = 2-amino-4-methyl-thiazole and MBT = 2-mercaptobenzothiazole, have been synthesized and characterized. Structure of both coordination polymers has been evaluated on the basis of elemental analysis, thermal, FT-IR, UV-vis spectra and the charges been carried by the atoms, caused a dipole moment of 2.4346 debye and total energy -382×10^3 Kcal mol^{-1}. Biological activity of the two synthesized complexes was tested against some fungal and bacterial strains.

Keywords: Coordination polymers, Properties, Iron(III) organic frameworks and biological activity.

INTRODUCTION

Coordination polymers have many fields like inorganic and organic chemistry, material science, electrochemistry, pharmacology and biochemistry with many potential applications has led to extensive study of these coordination polymers [1-5]. Supramolecular coordination polymer is a coordination compound or an inorganic or organometallic polymer structure having metal cation centers connected by organic ligands with repeating coordination entities extending in one, two or three dimensions [6]. Metal organic frameworks (MOFS), according to O'Keeffe [7] used to be interchangeably used as coordination polymers, but it specifically apply to materials with frameworks built by linking polyatomic clusters formed holistically by strong covalent bonds unlike coordination polymers which have some interplay of weaker bonds and lower stability. The atom or ion and particularly filled *d*-orbitals can hybridize differently. This depends on the environment of the transition metals, like iron, copper and gold ions that have fully filled *d*-orbitals in their outer shell as neutral atoms exhibit multiple coordination geometries because of their electronic structure [8].

The coordination polymer is formed by a ligand when it has the capability to form redoubled coordination bonds and acts as a bridge between redoubled metal ion centers. 1,4-Benzenedicarboxylic acid is a commodity chemical, used principally as a precursor to the polyester PET, used to make plastic bottles and clothing. Metal organic frameworks based on aromatic polycarboxylic acid ligands, such as 1,4-benzenedicarboxylic acid has been widely studied because of the diversity of coordination modes and the pH-sensitivity of the carboxylate groups [9]. 1,4-Benzenedicarboxylic acid can be partially or fully deprotonated to adopt different coordination modes in their reactions with metal ions [10]. Thiazoles for example 2-amino-4-methylthiazole (AMTZ) and 2-mercaptobenzothiazole (MBT) illustrate a very interesting category of complexes because of their analytical, pharmaceutical and industrial applications, also AMTZ and MBT ligands had been extensively used as medicine due to their antibacterial and anti-inflammatory properties [11-16]. A number of iron(III) complexes consist of both aromatic carboxylates and *N*-heterocyclic ligands have been reported [17-19]. In present study, a flexible *N*-heterocyclic ligands *viz*. 2-amino-4-methylthiazole and 2-mercaptobenzothiazole were chosen as the bridging ligands and 1,4-benzenedicarboxylic acid as auxiliary ligands in order to construct d^{10} transition metal complexes and to explore mixed-ligand Fe(III) compounds. Herein, the synthesis and characterization of two new coordination polymers *viz.* [Fe(BDC)(AMTZ)Cl]·2H_2O and [Fe(BDC)(MBT)Cl]·H_2O are discussed.

EXPERIMENTAL

High purity iron(III) chloride, 1,4-benzenedicarboxylic acid (BDC), 2-amino-4-methylthiazole (AMTZ) and 2-mercaptobenzothiazole (MBT) were supplied from Sigma-Aldrich and used without purification.

Synthesis of coordination polymers

Synthesis of [Fe(BDC)(AMTZ)Cl]·2H_2O complex (1): Synthesis of Fe(III) mixed ligand coordination polymer of 1,4-benzenedicarboxylate and 2-amino-4-methyl-thiazole follows essentially to an EtOH solution (20 mL) of iron(III) chloride (0.78 g, 4.8 mmol) a solution of 1,4-benzenedicarboxylate (0.8 g H_2BDC in 25 mL 0.1 M NaOH, 4.8 mmol) was added dropwise addition and with stirring, then AMTZ solution (0.55 g in 20 mL ethanol, 4.8 mmol) was added to the mixture. The mixture was refluxed and then cooled. Dark brown precipitate separated, which was filtered, washed with distilled water, ethanol and dried.

Synthesis of [Fe(BDC)(MBT)Cl]·H_2O complex (2): A mixture of equimolar quantity, an ethanolic solution (20 mL) (4.8 mmol) of $FeCl_3$ (0.7 g) and a solution 20 mL of BDC (0.8 g, 0.1 M sodium hydroxide, 4.8 mmol) was added with stirring and then a solution of MBT (20 mL distilled water, 0.8 g, 4.8 mmol) was added to the mixture and heated for 2 h, then progressively cooled. A light brown complex was isolated.

Physical measurements and biological activity: The stoichiometric analyses C, H, N, S, were performed using Analyischer Funktions test Vario El Fab-Nr. 11982027 elemental analyzer; The physical measurements and biological activity were measured as reported earlier [20].

RESULTS AND DISCUSSION

The complexes were prepared by the reaction of BDC, iron(III) chloride and azole derivatives (AMTZ and MBT) dissolved in ethanol. The synthesized two complexes were found to react in the molar ratio 1:1:1 Fe(III):BDC:AMTZ or MBT. [Fe(BDC)(AMTZ)Cl]·2H_2O and [Fe(BDC)(MBT)Cl]·H_2O are insoluble in common organic solvents but partially soluble in DMSO and air stable. The results are listed in Table-1 together with the colour and melting points of the compounds.

FT-IR: The important FT-IR spectral bands of the mixed coordination polymers **1** and **2** are given in Table-2 and illustrated in Fig. 1. Coordination of 1,4-benzenedicarboxylate (BDC) is manifested by the appearance of a sharp band with a shoulder in the region 1384-1352 and 1568-1534 cm^{-1}, which indicates symmetric and asymmetric stretching vibration of the carboxylic groups of the BDC coordinated to the iron(III) center. The bands in the region of 1715-1680 cm^{-1} typical of protonated carboxylate groups of BDC were not observed [21] and a complete deprotonation of the BDC molecule occurs upon coordination. Furthermore, in the IR spectra of the complexes, the separation value of $\Delta\nu \leq 184$ was found indicating bidentate nature of coordination for the carboxylate group [22]. It is found that the C=S=C band of azoles showing at ~740 cm^{-1} is nearly unchanged in the respective complex **1**, indicating that thiazol-S is not involved in the bonding. The stretching vibration of ν(C=N) of the thiazole ligand for the complex **1** undergoes no

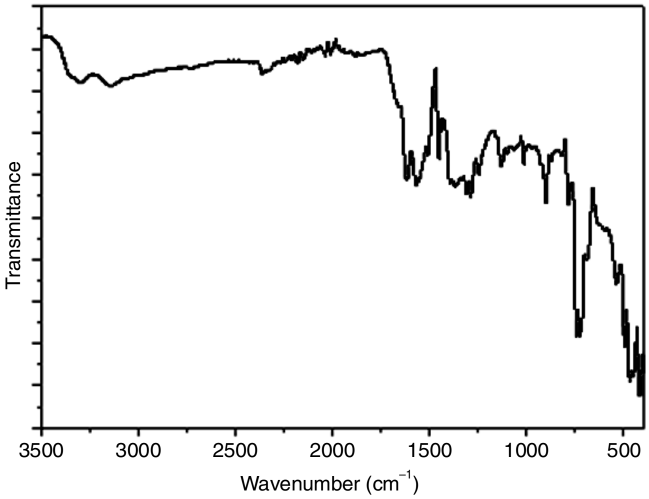

Fig. 1. FT-IR of Fe(III) coordination polymer **1**

TABLE-1
COLOURS, C.H.N.S AND MELTING POINTS OF Fe(II) COORDINATION POLYMERS

Compound	m.f. (m.w)	Colour	Elemental analysis (%): Found (calcd.)				m.p. (°C) (Decom.)	Λ_m (Scm^2 mol^{-1})
			C	H	N	S		
[Fe(BDC)(AMTZ)Cl]·2H_2O (**1**)	$C_{12}H_{14}N_2SFeClO_6$ (404.58)	Brown	36.05 (35.59)	3.60 (3.48)	6.98 (6.92)	7.04 (7.92)	206	43
[Fe(BDC)(MBT)Cl]·H_2O (**2**)	$C_{15}H_{10}NS_2FeClO_5$ (439.48)	Dark brown	40.01 (40.95)	2.13 (2.29)	3.35 (3.19)	14.87 (14.58)	198	50

TABLE-2
FT-IR SPECTRAL DATA (cm^{-1}) OF Fe(III) COORDINATION POLYMERS

Complex	ν(OH)	ν(NH_2)	ν(COO) asym.	ν(COO) sym.	Δν	ν(C=N)	ν(C-N)	ν(C-S)	ν(M-N)	ν(M-O)
1	3346	3105	1534	1352	182	1621	812	742	420	516
2	3388	3132	1568	1384	184	1602	816	690	426	522

shift comparing to assigned to ν(C=N) of 2-amino-4-methylthiazole (AMTZ) (1621 cm^{-1}). Furthermore, the ν_{as}(N-H_2) and ν_s(N-H_2) bands of the amino group in free AMTZ, detected at 3218 cm^{-1} [22] is shifted to a lower wave number and displays bands at 3132-3105 cm^{-1} in the complexes suggesting coordination of the amino nitrogen to iron(III) ions. The ν(C-S) mode of vibration in 2-mercaptobenzothiazole (MBT) is observed at 599 cm^{-1}, which residue very strong in Fe(III) complex. A 690 cm^{-1} stretching vibration for Fe(III) complex **2** is due to C-S stretching of heterocyclic ring system [23]. The bands at 3388-3346 cm^{-1} in the spectrum of the complexes **1** and **2** is assigned to ν(OH) of the coordinated water molecules [24]. Iron(III)-oxygen and iron(III)-nitrogen bondings are manifested by the appearance of a bands in the 522-516 and 426-420 cm^{-1} regions, respectively (Table-2).

Electronic spectra and magnetic moments: The band observed in the electronic spectra in DMSO of the Fe(III) ternary coordination polymers of BDC, AMTZ and MBT which located in the region 35,428-38,846 cm^{-1} assigned to a $\pi\rightarrow\pi^*$ transition due to molecular orbital energy levels originating in the BDC moiety. On the other hand in the region 23,848-28,654 cm^{-1} attributed to $n\rightarrow\pi^*$ transitions within the azole moieties (AMTZ and MBT), respectively. In the visible spectra, there were typical bands attributed to the *d-d* transitions in the Fe(III) compounds characteristic of octahedral structure (Fig. 2). The *d-d* bands at 19,186-19,268 cm^{-1} were observed for Fe(III) complex **1** and **2**, respectively. The magnetic moment value for the Fe(III) coordination polymers were 2.84-2.96 B.M typical for octahedral compounds **1** and **2** [25-27]. The structures for BDC mixed ligand compounds are shown in Figs. 2-5.

In Fig. 6, showed that, the charges been carried by the atoms, cause dipole moment 2.4346 debye and total energy -382 × 10^3 k Cal mol^{-1}.

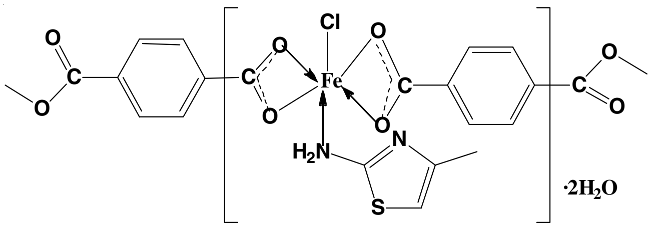

Fig. 2. Structure of [Fe(BDC)(AMTZ)Cl]·$2H_2O$

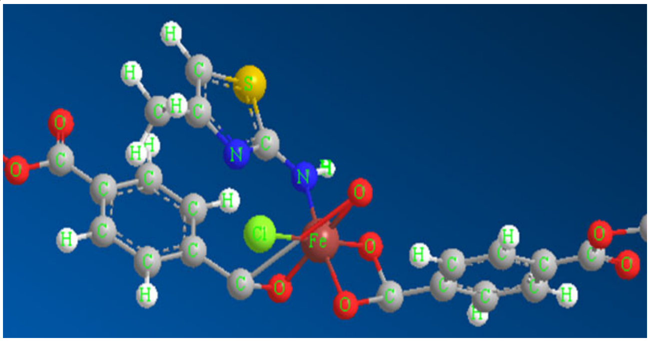

Fig. 3. A perspective view of the complete coordination around Fe(III) complex **1**

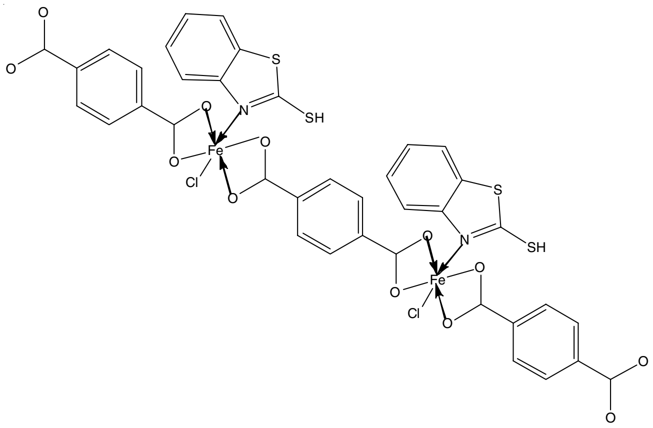

Fig. 4. Structure of [Fe(BDC)(MBT)Cl]·H_2O

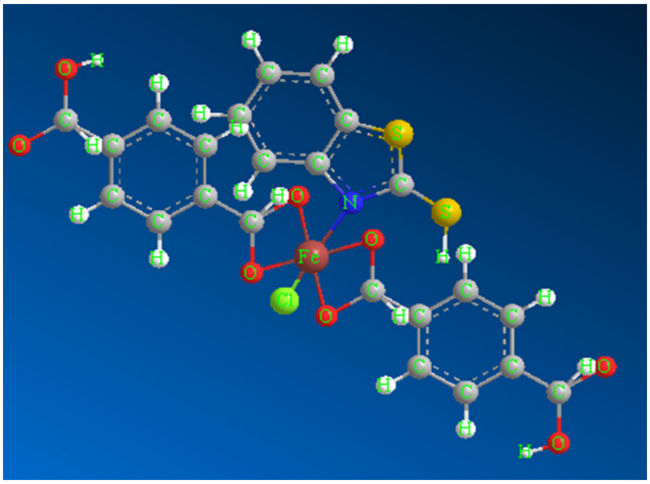

Fig. 5. A perspective view of the complete coordination around Fe(III) complex **2**

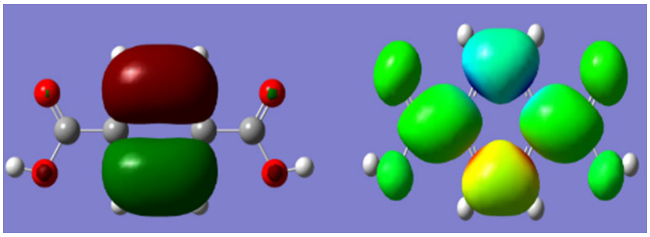

Fig. 6. Charges been carried by the atoms BDC ligand, cause dipole moment in debye and total energy in (k Cal mol^{-1})

Thermal studies: Both Fe(III) coordination polymers **1** and **2** have been explained from ambient temperature to 750 °C in dynamic. As a representative, thermogram of Fe(III) coordination polymer **1** is depicted in Fig. 7. Thermolysis of [Fe(BDC)-(AMTZ)Cl]·$2H_2O$ consists of four decomposition steps, namely at 56-186, 187-298, 299-445 and 447-750 ºC. The first mass loss correlates well with the release of two water molecules (calcd. 8.89%, found 8.58%) (DTG peak at 124 °C) with an endothermic peak in the DTA trace at 126 °C. The second, third and fourth steps indicate decomposition of the product with a corresponding three DTG peaks at 248, 402 and 548 °C, respectively and three exothermic peaks at 250, 404 and 550 °C, respectively in the DTA trace. The remaining residue may beiron(III) oxide (calc. 17.75%, found 16.96%).

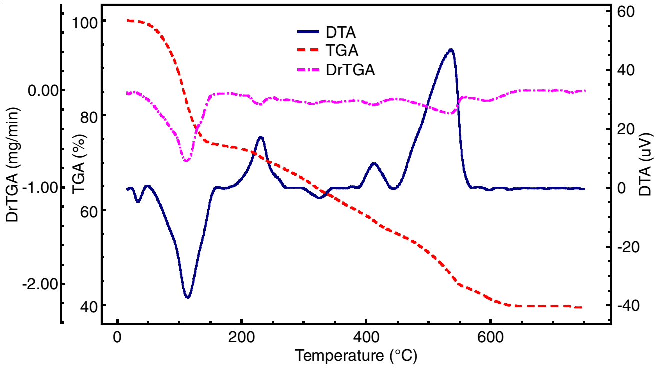

Fig. 7. TG, DTG and DTA thermograms of Fe(III) complex **1**

$$\begin{tikzcd}\lbrack \mathrm{Fe(BDC)(AMTZ)Cl}\rbrack\cdot 2H_2O \arrow[r, "56\text{-}186\ ^{\circ}C"] & \lbrack \mathrm{Fe(BDC)(AMTZ)}\rbrack + 2H_2O \arrow[d, "187\text{-}750\ ^{\circ}C"'] \\ & \text{Decomposition products} + \mathrm{FeO}\end{tikzcd}$$

Scheme-I

XRD studies: The XRD patterns were recorded for both coordination polymers **1** and **2**. The crystal lattice variables of coordination polymers were computed with the computer program TREOR. The diffraction patterns indicate that the two compounds are crystalline, also the crystal data for the iron(III) complexes belong to the crystal system triclinic (XRD of Fe(III) coordination polymer **1** is depicted in Fig. 8). The crystal data together with particle size of two complexes are recorded in Table-3.

TABLE-3
XRD POWDER DIFFRACTION CRYSTAL DATA OF THE IRON(III) COORDINATION POLYMERS

Parameters	Complex **1**	Complex **2**
Empirical formula	$C_{12}H_{14}N_2O_6SFeCl$	$C_{15}H_{10}NO_5S_2FeCl$
Formula weight	404.58	439.48
Crystal system	Triclinic	Triclinic
a (Å)	7.895	6.936
b (Å)	12.315	13.393
c (Å)	13.802	13.172
α (°)	58.165	90.339
β (°)	95.396	94.385
γ (°)	63.248	52.123
Volume of unit cell (Å^3)	915.83	961.87

Scanning electron micrographs (SEM): SEM analysis of iron complexes revealed the poly aggregated granules of the particles, also the arboreal gatherings shape of the majority of the particles. The scanning electron micrographs of iron(III) complexes as representatives are shown in Figs. 9 and 10. The figures show the different morphologies of the two coordination polymers.

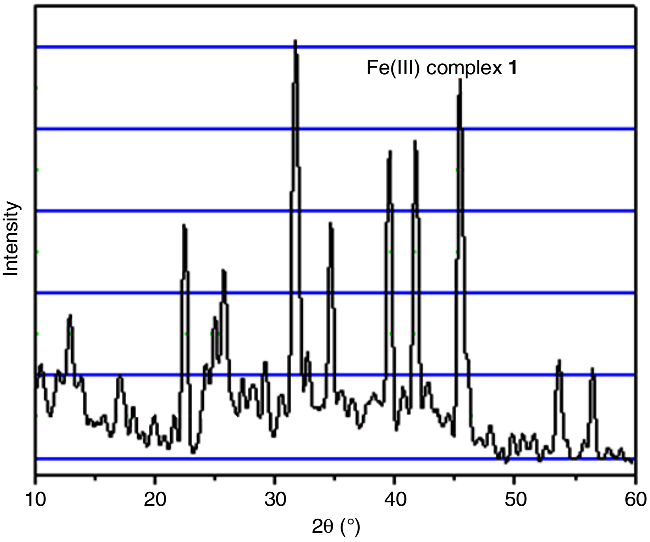

Fig. 8. X-ray of [Fe(BDC)(AMTZ)Cl]·2H$_2$O

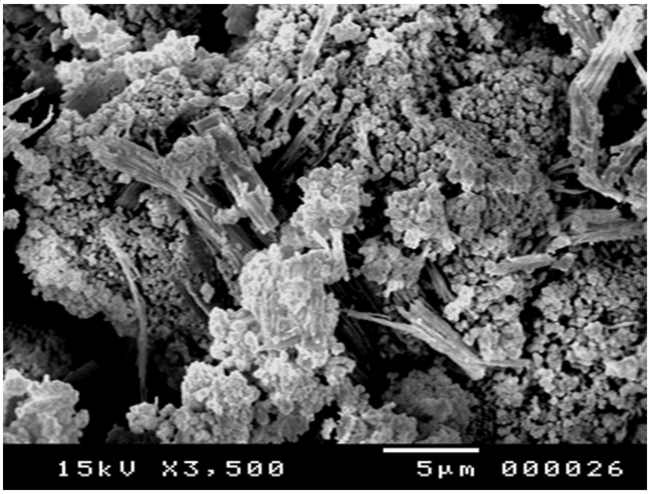

Fig. 9. SEM image of [Fe(BDC)(AMTZ)Cl]·2H$_2$O

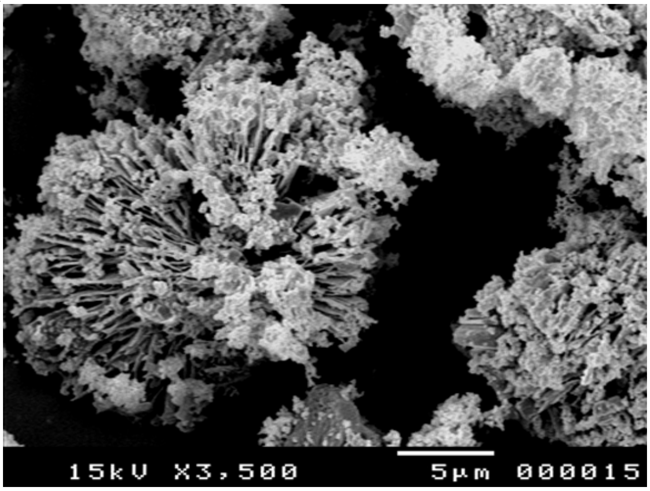

Fig. 10. SEM image of [Fe(BDC)(MBT)Cl]·H$_2$O

Antimicrobial activity: The synthesized iron(III) coordination polymers were tested against the bacterial and fungal strains. The examination of antibacterial screening appeared that the tested two Fe(III) coordination polymers showed mild to good bacterial inhibition for Gram-positive and Gram-negative bacteria. On other hand the concerning the antifungal activity, these compounds were effective against *Aspergillus flavus* and *Geotrichum candidum* (a yeast like human pathogen fungus) with the inhibitory activity exerted by compound **2**. It is assumed that the complexes interact mainly with bacteria and fungi through the 2-amino-4-methylthiazole and 2-mercaptobenzothiazole, moiety which possesses high antibacterial and fungal effect.

Conclusion

The solvothermal reactions of 1,4-benzenedicarboxylate and 2-amino-4-methylthiazole or 2-mercaptobenzothiazole with iron(III) chloride gave two new coordination polymers and the structure and properties of the obtained these compounds are octahedral geometry. The coupling length in Fe(III) coordination polymers may lead to higher conductivity, so this study may be advantageous for several applications. The antimicrobial activities of both Fe(III) coordination polymers have been evaluated against 5 bacterial and 6 fungal strains.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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