

SYNTHESIS, CHARACTERIZATION, THERMAL STUDY, AND EVALUATION OF MIXED LIGAND COMPLEXES OF (MALONIC ACID, NICOTINIC ACID, AND 2-AMINOPYRIDINE) WITH SOME TRANSITION METAL IONS

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ABSTRACT. Six mixed ligand complexes were prepared from malonic acid (MA), nicotinic acid (NA), and 2-aminopyridine (AP) in a (1:1:1:1) molar ratio (M: MA: NA: AP.), using aqueous ethanol as a reaction medium. The prepared compounds were analyzed by flame atomic absorption, (C.H.N.) analysis, and FTIR, UV-Vis, and mass spectroscopy, as well as conductivity measurement and magnetic susceptibility studies. Based on the combined analytical data, the prepared complexes were proposed to adopt an octahedral geometry. A urinary tract infection (UTI) is a bacterial infection that affects any part of the urinary tract. The emergence of antibiotic-resistant bacteria and fungi has led to poor patient outcomes and limited treatment options, prompting interest in mixed ligand-metal complexes as potential antimicrobial agents. Accordingly, this study evaluated the inhibitory activity and effectiveness of the free ligands, metal complexes, and DMSO (as a control) at a concentration of 10⁻³ mg/mL against clinically isolated UTI (*S. aureus*, *S. epidermidis*, *E. coli*, *K. pneumoniae*, and *C. albicans*). The results demonstrated that both the ligands and complexes exhibited varying degrees of activity against the tested.

KEY WORDS: Malonic acid (MA), Nicotinic acid (NA), 2-Aminopyridine (AP), Metal complexes, Spectral analysis, Biological activity

INTRODUCTION

Transition metal ions have played a major role in human biological processes. Coordination compounds have the characteristics of metals and have a wide range of coordination numbers, variable oxidation states, geometric shapes, and the ability to bind different organic ligands or mix ligands to achieve optimal stability and biological activity. On this basis, many drugs are made based on coordination with metal ions or inhibition when forming the metal enzyme [1-3]. Malonic acid (MA) is a dicarboxylic acid with the structure CH₂(COOH)₂. The ionized form of malonic acid, as well as its esters and salts, is known as a malonate. For example, diethyl malonate is the diethyl ester of malonic acid, an organic compound containing two carboxylic acid functional groups. Malonic acid is called propanedioic acid by IUPAC nomenclature. Malonic acid is an extremely hydrophobic, practically insoluble in water, and relatively neutral molecule found in all living organisms, from bacteria to humans. It participates in a number of enzymatic reactions, e.g., malonic acid, acetic acid, and acetoacetic acid, which mediate the synthesis of fatty acids. In humans, malonic acid has been associated with a number of diseases, including eosinophilic esophagitis, malonic aciduria, combined methylmalonic acid, and preeclampsia. Malonic acid has also been studied for its activity against bacteria and fungi [5-9]. Nicotinic acid, also known as vitamin B₃ or niacin (3-pyridine carboxylic acid), is a white, transparent crystalline solid with a carboxyl side chain at position 3 [10]. Pyridine carboxylic acids are known to be of great importance for their biological and metabolic activities, including skin health, blood circulation, cellular respiration, and the metabolism of fats, proteins, and carbohydrates [11]. It is found in a wide range of natural products, including vitamins, fluorides, and coenzymes [12]. Nicotinic acid contains two oxygen donor atoms and thus can form many mineral compounds

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[13]. Pyridine-carboxylate metal complexes are interesting as model systems with diverse pharmacological properties [14,15]. Aminopyridine is known to be an organic compound containing an amino and pyridine group in an aromatic heterocyclic form and has three isomers: 2-aminopyridine, 3-aminopyridine, and 4-aminopyridine [16]. In aminopyridine, the coordination of pyridine is through the nitrogen atom to form additional hydrogen bonds through the amino nitrogen atom in pyridine [17]. In addition, it has the ability to form chelates with a bidentate coordination mode through the nitrogen atoms of pyridine and the external cyclic amino [18]. Metal complexes containing N-, O-, or S-donor atoms have been developed as potential drugs [19]. The high pharmacological activity of heterogeneous aromatic amines has stimulated numerous research efforts to synthesize compounds of this structural type [20, 21]. Six mixed-ligand complexes (malonic acid, nicotinic acid, aminopyridine, and orthoaminopyridine) were synthesized with six metal salt ions (chromium, manganese, iron, cobalt, nickel, and lanthanum). Their various chemical and physical properties, such as flame atomic absorption spectra (IR, UV, mass spectrometry, and thermal analysis), and magnetic properties were studied. The biological activity of the six coordination complexes prepared from three different ligands was also investigated, including the antibacterial and antifungal activity of the six coordination complexes prepared from three different ligands.

EXPERIMENTAL

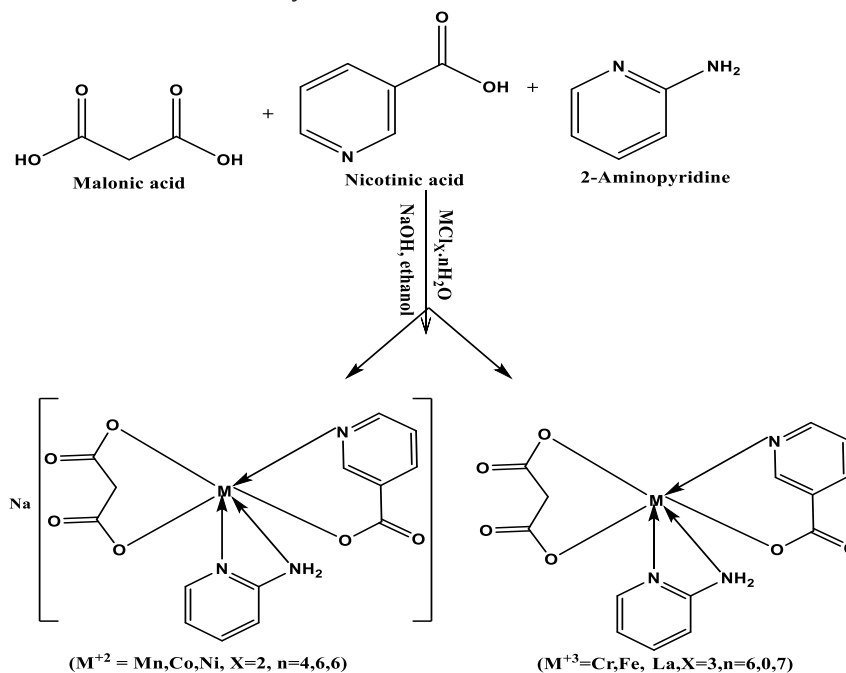
Materials and methods

All reagents and solvents used in this research were from commercial sources, without any further purification, and included: malonic acid, nicotinic acid, ortho-aminopyridine, ethyl alcohol, sodium hydroxide, and dimethylglyoxime (from Merck and Aldrich Chemicals). As for the metal salts such as $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, FeCl_3 , $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, and $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ (from Merck, BDH, and Riedel), unpurified. The molar conductance for ligands and mixed ligand metal complexes has been measured employing a CON 510 Conductivity at dry DMSO (10^{-3} M) solution at room temperature. While metal complexes were determined during Atomic Absorption (A.A) Technique / Flame Emission Spectrophotometer utilizing AA – 680. Elemental (C, H, N.) micro-analysis, to search using the EA 3000 single V.3 model vector device. Infrared (FT.IR) spectra have been registered on a 4000-400 cm^{-1} range for three ligands as well as metal complexes on a Shimadzu IR-470 Spectrophotometer employing KBr. UV-Vis spectrum has been registered on a Shimadzu UV-160. Ultraviolet spectrometer employing DMSO solution 10^{-3} on a range (200-1000) nm for ligands as well as mixed ligand complexes. The mass spectra for all complexes were registered on an Agilent 6211 mass spectrometer. Sherwood's application of the Auto Magnetic Susceptibility at 25 °C allowed scientists to refine the magnetic characteristics of the prepared coordination complexes. Melting points have been obtained at the Stuart Melting Point Apparatus for the ligands as well as mixed ligand complexes. The thermal analysis was conducted at the College of Education/University of Basra, using a Bruker 400 MHz UltraShield spectrometer.

Preparation of the mixed ligand complexes

Six mixed ligand complexes were prepared, each involving malonic acid (MA, 0.104 g, 1 mmol), nicotinic acid (NA, 0.123 g, 1mmol), and 2-aminopyridine (AP, 0.094 g, 1mmol). Each ligand was dissolved separately in hot water (20 mL). For MA and NA, sodium hydroxide was used with each of six metal salts individually. The metal salts used were $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (0.197 g, 1 mmol), $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ (0.267 g, 1 mmol), FeCl_3 (0.162 g, 1 mmol), $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.237 g, 1 mmol), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.237 g, 1 mmol), and $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ (0.371 g, 1mmol). Each salt was dissolved in water (20 mL) and added to the ligand mixture, then refluxed for three hours in a (1:1:1:1) molar ratio

of M:(MA):(NA):(AP) (Scheme 1), affording six mixed-coordination complexes. After refluxing, the solutions were left at room temperature to complete precipitation. Each resulting complex was filtered, washed with ether and dry.



Scheme 1. Preparation of the six complexes by mixing different ligands.

Antimicrobial susceptibility testing

Bacterial and fungal suspensions were prepared by transferring 1-2 colonies of clinically isolated strains *E. coli*, *K. pneumoniae*, *S. epidermidis*, *S. aureus*, and *C. albicans* from patients with urinary tract infection into 3 mL normal saline. The turbidity of each suspension was adjusted to a 0.5 McFarland standard containing 1.5×10^8 cells/mL. The inoculated plates were left at room temperature for 15 minutes to allow culture absorption. Wells were then created in the agar using a cork borer, and 10^{-3} M concentration of the following test compounds were added the control (DMSO), the free ligands malonic acid (MA), nicotinic acid (NA), 2-aminopyridine (AP), and the six mixed ligand complexes $[Cr(MA)(NA)(AP)]$, $Na[Mn(MA)(NA)(AP)]$, $[Fe(MA)(NA)(AP)]$, $Na[Co(MA)(NA)(AP)]$, $Na[Ni(MA)(NA)(AP)]$ and $[La(MA)(NA)(AP)]$. The plates were incubated at 37 °C for 18 - 24 hours, and the complex was tested in duplicate. After 24 hours, the diameters of the inhibition zones were measured using a ruler [22, 23].

RESULTS AND DISCUSSION

The six coordination complexes prepared from the reaction of the three ligands with the metal salts in a (1:1:1:1) molar ratio (M: MA:NA:AP) were characterized. The results showed good agreement with the calculated values (Table 1), which summarizes selected physical properties. The molar conductivity of each complex was measured in DMSO at a concentration of (10^{-3} M) to the values indicated a 1:1 electrolytic ratio [24], and the data are presented in Table 2.

Table 1. Elemental analysis and some physical features of various ligands, as well as prepared complexes.

Compounds	Empirical formula	M.wt (g/mol)	Color (Yield %)	m.p (°C)	Analysis calc (Found)			
					M%	C%	H%	N%
Malonic acid (MA)	C ₃ H ₄ O ₄	104.06	White	(135-136)	-	-	-	-
Nicotinic acid (NA)	C ₆ H ₅ NO ₂	123.11	White-off-white	(236-239)	-	-	-	-
2-Aminopyridine (AP)	C ₅ H ₆ N ₂	94.12	white	58	-	-	-	-
[Cr(MA)(NA)(AP)]	C ₁₄ H ₁₂ CrN ₃ O ₆	370.26	Purple (85)	225 Dec.	14.04 (12.60)	45.41 (44.25)	3.27 (2.14)	11.35 (10.05)
Na[Mn(MA)(NA)(AP)]	C ₁₄ H ₁₂ MnN ₃ NaO ₆	396.19	White (87)	(253-255)	13.87 (11.90)	42.44 (41.19)	3.06 (2.32)	10.61 (9.34)
[Fe(MA)(NA)(AP)]	C ₁₄ H ₁₂ FeN ₃ O ₆	374.11	Yellow-green (79)	145	14.93 (13.85)	44.94 (43.72)	3.24 (2.09)	11.23 (10.21)
Na[Co(MA)(NA)(AP)]	C ₁₄ H ₁₂ CoN ₃ NaO ₆	400.19	Dark green (81)	120	14.73 (12.91)	42.01 (41.22)	3.03 (2.41)	10.50 (9.38)
Na[Ni(MA)(NA)(AP)]	C ₁₄ H ₁₂ NiN ₃ NaO ₆	399.95	Light green (78)	230	14.68 (13.50)	42.04 (41.15)	3.03 (2.42)	10.51 (9.32)
[La(MA)(NA)(AP)]	C ₁₄ H ₁₂ LaN ₃ O ₆	457.17	White (90)	210	30.38 (28.92)	36.78 (35.59)	2.65 (1.43)	9.19 (8.28)

Mass spectra

Mass spectral from the prepared compounds were exposed, the peaks were concentrated at m/z = 370.26, 396.19, 374.11, 400.19, 399.95 as well 457.17 belong into formulas [C₁₄H₁₂N₃O₆Cr], Na[C₁₄H₁₂N₃O₆Mn], [C₁₄H₁₂N₃O₆Fe], Na[C₁₄H₁₂N₃O₆Co], Na[C₁₄H₁₂N₃O₆Ni], as well as [C₁₄H₁₂N₃O₆La]. The general pattern from segmentation is according on Figures 1 to 4.

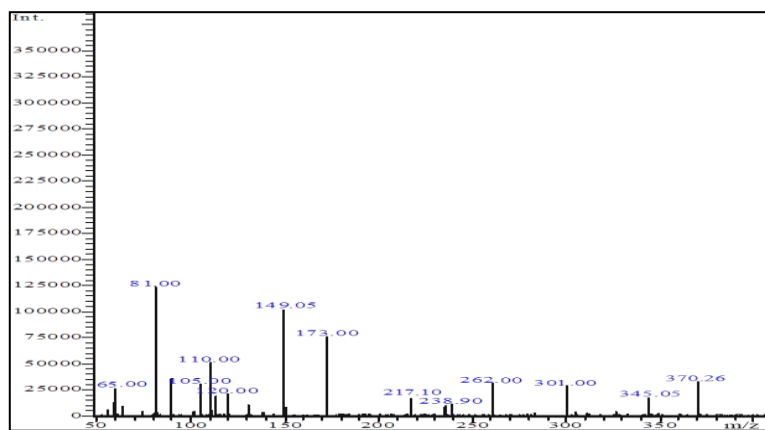


Figure 1. Mass spectrum for [Cr(MA)(NA)(AP)] complex.

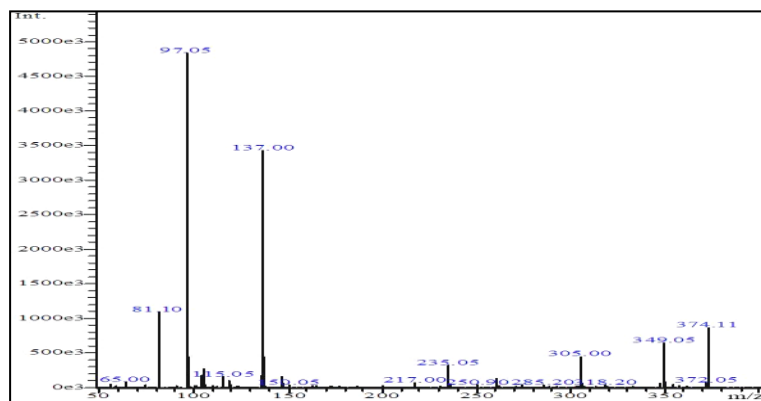


Figure 2. Mass spectrum for Na[Mn(MA)(NA)(AP)]complex.

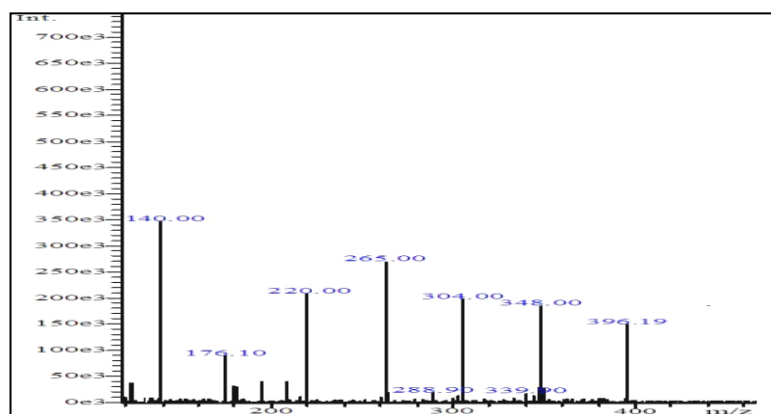


Figure 3. Mass spectrum [Fe(MA)(NA)(AP)]complex.

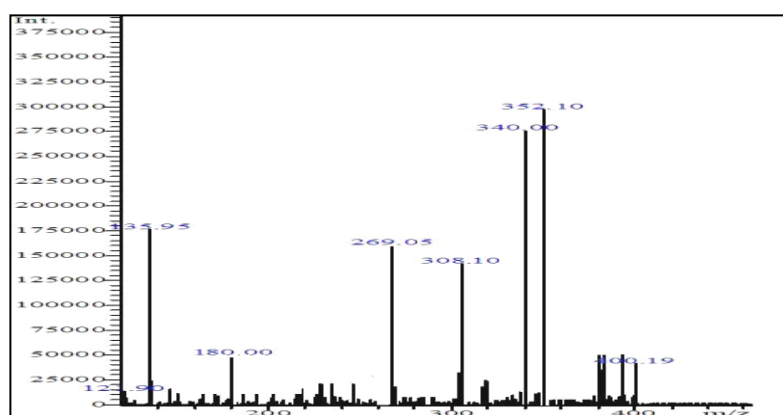


Figure 4. Mass spectrum for Na[Co(MA)(NA)(AP)] complex.

Electronic spectra measurements

After measuring the UV spectra of the produced compounds that were dissolved in DMSO (10-3 M/L), the results obtained were listed in Table 2. Appearance of peaks in the UV spectrum of malonic acid was at 264 nm and 306 nm, which appropriated it to light energy ($\pi-\pi^*$) and transition ($n-\pi^*$) [25]. The spectrum of nicotinic acid has peaks at 268 and 346 due to ($\pi-\pi^*$) and ($n-\pi^*$) [26]. The spectrum of 2-aminopyridine shows peaks at 264 and 297 due to ($\pi-\pi^*$) and ($n-\pi^*$) [27]. Cr(III) spectrum shows peaks at 268 and 306 nm, indicating intra-ligand transitions; the peak at 769 nm corresponds to the electronic transition $4A_2g \rightarrow 4T_2g$. The obtained magnetic moment for the prepared complex was 3.72 B.M. It was found to be very close to an octahedral structure [28]. Mn(II) spectrum shows peaks at 266 and 301 nm, corresponding to intra-ligand transitions; another peak at 780 nm corresponds to the electronic transition ${}^6A_1g \rightarrow {}^4E_g(D)$. The obtained magnetic moment for the prepared complex was 5.88 B.M. It was found to be very close to an octahedral structure [29]. The iron(III) spectrum shows a peak at 295 nm due to intra-ligand transitions, and another peak at 792 nm due to electronic transitions ${}^6A_1g \rightarrow {}^4E_g(D)$. The obtained magnetic moment for the prepared complex was 5.65 B.M. It was found to be very close to an octahedral structure [30]. Co(II) spectrum appeared peaks on 266, 301, and 395 nm due to intra-ligand and charge transfer (C.T). Peaks on 703 and 819 nm are allocated to electronic transition type ${}^4T_{1g(F)} \rightarrow {}^4A_{2g(F)}$ and ${}^4T_{1g(F)} \rightarrow {}^4T_{2g(F)}$, respectively [31]. The obtained magnetic moment for the prepared complex was 4.73 B.M. It was found to be very close to an octahedral structure [32]. Ni(II) complex width peaks on 294 and 395, which were considered by their qualification in internal ligand and charge transfer. Else peaks at 829 and 9860 nm, which were referred to as electronic transition type $3A_2g(F) \rightarrow 3T_{1g(F)}$ and $3A_2g(F) \rightarrow 3T_{2g(F)}$, respectively. The obtained magnetic moment for the prepared complex was 2.81 B.M. It was found to be very close unto octahedral structure [33]. La(III) spectrum appearance peak on 295 nm lead onto intra ligand, and diamagnetic moment [34].

Table 2. UV Spectra data, molar conductivity as well as magnetic moment for ligands also mixed ligand complexes.

Compounds	λ (nm)	ABS	Wave number (cm ⁻¹)	$\epsilon_{\max}$ (L.mol ⁻¹ .cm ⁻¹)	Assignments	Molar conductivity Λ_m .cm ² .Mol ⁻¹ 10 ⁻³ M in DMSO	μ_{eff} (B.M)
Malonic acid (MA)	264	0.117	37878	117	$\pi-\pi^*$	10.18	-
	306	0.148	32679	148	$n-\pi^*$		
Nicotinic acid (NA)	268	1.868	37313	1868	$\pi-\pi^*$	10.63	-
	346	0.129	28901	129	$n-\pi^*$		
2-aminopyridine (AP)	264	0.301	37878	301	$\pi-\pi^*$	13.79	-
	297	0.116	33670	116	$n-\pi^*$		
[Cr(MA)(NA)(AP)]	268	1.408	37313	1408	intra ligand intra ligand ${}^4A_2g \rightarrow {}^4T_2g$	24.91	3.72
	302	1.925	33112	1925			
	769	0.013	13003	13			

Na[Mn(MA)(NA)(AP)]	266	1.081	37593	1081	intra ligand	48.6	5.88
	301	1.338	33222	1338	intra ligand		
	780	0.012	12820	12	${}^6A_{1g} \rightarrow {}^4E_g(D)$		
[Fe(MA)(NA)(AP)]	295	2.304	33898	2304	intra ligand	35.4	5.65
	815	0.014	12269	14	${}^6A_{1g} \rightarrow {}^4E_g(D)$		
Na[Co(MA)(NA)(AP)]	266	1.040	37593	104	intra ligand	35.06	4.73
	301	1.312	33222	1312	intra ligand		
	395	0.049	25316	49	C.T. ${}^4T_{1g(F)} \rightarrow {}^4A_{2g(F)}$		
	703	0.009	14224	9	${}^4T_{1g(F)} \rightarrow {}^4T_{2g(F)}$		
	819	0.009	12210	9			
Na[Ni(MA)(NA)(AP)]	294	2.406	34013	2406	intra ligand	40.34	2.81
	395	0.108	25316	108	C.T. ${}^3A_{2g} \rightarrow {}^3T_{1g(F)}$		
	829	0.032	12062	32	${}^3A_{2g} \rightarrow {}^3T_{2g(F)}$		
	986	0.045	10141	45			
[La(MA)(NA)(AP)]	295	2.288	33898	2288	intra ligand	22.06	Dia

Infrared spectra measurements

From FTIR spectra measurements to the mixed ligands and their metal chelates, by tabulating the data according to Table 3. The existing bands of the malonic acid (Figure 5S) and nicotinic acid (Figure 6S) spectra on 3409, 3384, and 3427 cm^{-1} are described in the extended vibration on $\nu(\text{OH})$ for carboxyl, also the disappearance at this range with all complexes indicates deprotonation of the carboxyl group in the coordination of the metal ion [35, 36]. Existing bands of the 2-aminopyridine spectrum (Figure 7S) on 3446 and 3240 cm^{-1} due to $\nu(\text{NH}_2)$, these bands reach the highest frequency in the spectra of all prepared complexes, which indicates coordination with the metal ion [37]. $\nu(\text{C}=\text{N})$ bands in spectra of nicotinic acid and 2-aminopyridine on 1641 and 1629 cm^{-1} , respectively, these bands reach the lowest frequency in the spectra for prepared complexes (Figure 8S to 13S), which indicates coordination with metal ion [38, 39]. The bands on 1635, 1596 cm^{-1} as well as 1514, 1492 cm^{-1} have been appropriated onto stretching vibration for $\nu(\text{COO}^-)$ asymmetric as well as symmetric malonic acid and nicotinic acid, respectively. These bands have been shifted to the lowest frequency, which is due to the coordination with the metal ion [40, 41]. As well as extending frequency bands belonging to metal-nitrogen at other than metal-oxygen, which are more [42, 43], and this ensures their presence at ranges at a rate of 435-518 cm^{-1} .

Table 3. Infrared spectral data for three ligands and their complexes (cm⁻¹).

Compounds	ν (OH)	ν (NH ₂)	ν (C=N)	ν (COO ⁻) _{as,s}	ν (M-N) + ν (M-O)
Malonic acid (MA)	3409 br. 3384 br.	-	-	1635 sho. 1514 s.	-
Nicotinic acid (NA)	3427 br.	-	1641 s.	1596 sh. 1492 s.	-
2-Aminopyridine (AP)	-	3446 sh. 3305 sh.	1629 sh.		-
[Cr(MA)(NA)(AP)]	-	3417 s. 3375 s.	1623 sh.	1568 sho. 1481 s.	516 w. 462 w.
Na[Mn(MA)(NA)(AP)]	-	3373 s. 3348 s.	1611 sh.	1568 sh. 1487 sh.	518 w. 468 w.
[Fe(MA)(NA)(AP)]	-	3359 s. 3257 s.	1614 s.	1560 sh. 1487 sh.	514 w. 459 w.
Na[Co(MA)(NA)(AP)]	-	3394 s. 3367 s.	1612 sh.	1562 sh. 1488 sh.	516 w. 435 w.
Na[Ni(MA)(NA)(AP)]	-	3384 s. 3365 s.	1612 sh.	1544 sh. 1475 sh.	489 w. 443 w.
[La(MA)(NA)(AP)]	-	3386 s. 3365 s.	1602 sh.	1544 sh. 1475 sh.	468 w. 449 w.

Thermal measurements

Thermogravimetric analysis (TGA) was carried out for two of the prepared complexes. The thermal analysis of the (Fe and Mn, Figure 14S and 15S) complexes was performed under nitrogen (N₂) gas at temperatures ranging from 25 to 600 °C and a heating rate of 10 °C per minute. A brief overview of important aspects of this analysis is as follows:

The TGA curve and methodology: The TGA curve was recorded under nitrogen (N₂) gas at temperatures ranging from 25 to 600 °C and a heating rate of 10 °C per minute. The TGA oven combines humidity and thermal analysis, monitoring the sample temperature and weight over time until it stabilizes. TGA possesses high sensitivity to exothermic and endothermic processes, which play a key role in determining changes in physical and chemical properties related to temperature. Weight loss and decomposition stages: During the subsequent stages of decomposition, shown in Table 4, significant weight losses were observed, exceeding 80% of the total weight loss. The first stage of decomposition was the thermal evaporation of volatile compounds, which occurred after moisture evaporation. The second stage demonstrated the loss of molecules within the compounds. The decomposition of both (Mn and Fe) complexes occurred in three steps. The decomposition temperatures for both compounds ranged between 100 and 500 °C. The initial decomposition temperature was used to confirm the relative stability of the compound. Unlike manganese compounds, these compounds continued to decompose at temperatures exceeding 600 °C. Thermal decomposition statistics: The thermal decomposition data, relative stability, and decomposition patterns of manganese and iron compounds are shown in Table 4, in terms of molecular weight, decomposition processes, temperature ranges, proposed loss formulas, and predicted mass loss ratios.

Table 4. New various mixed-ligand complexes of thermal decomposition data.

Compound	Molecular M.Wt.	Step	Temp. range of the decomposition TG) °C	Suggested formula of loss	Mass loss %	
					Cal.	Found
Fe(MA)(NA)(AP)	C ₁₄ H ₁₂ FeN ₃ O ₆ 374.11	1	163 – 239	-2CO ₂ , -NO	31.54	26.58
		2	242 – 382	-CH ₃ OH	8.55	9.53
		3	382 – 571	-C ₃ H ₄ N	14.43	13.41
Na[Mn(MA)(NA)(AP)]	C ₁₄ H ₁₂ MnN ₃ NaO ₆ 396.19	1	69 - 228	-2CO ₂ , -Na	28.02	28.74
		2	236 - 348	-C ₃ H ₅ OH	14.63	14.06
		3	391 - 559	-C ₃ H ₄ N	13.62	13.8

The Effect of the three ligands and complexes of various ligands on the growth of clinically isolated bacteria and fungi

The result (Table 5, Figure 16S and 17S) shows that the ligand and complexes at a concentration of 10⁻³ M show high inhibitory activity against bacteria isolated from the urine of patients with urinary tract infection: Gram (+ve) *S. aureus*, *S. epidermidis* and gram (-ve) *K. pneumonia*, *E. coli*, and fungi *C. albicans*. The DMSO control and [Fe(MA)(NA)(AP)] didn't give any inhibitory activity, while there was clear effectiveness of malonic acid, which is better than that of other ligands (nicotinic acid and 2-aminopyridine), especially in inhibiting *K. pneumoniae* and *C. albicans*. The complex Na[Co(MA)(NA)(AP)] had the best inhibitory activity on pathogenic bacteria isolated from urine, especially *E. Coli* and *C. albicans*, with inhibitory diameters of 25 and 22 mm, respectively. But the free 2-aminopyridine (AP) was more effective against *S. epidermidis*; its inhibitory diameter was 18 mm. Na[Mn(MA)(NA)(AP)] and Na[Ni(MA)(NA)(AP)] gave an inhibitory effect of 19 and 16 mm, respectively, on the growth of *E. coli*. This effectiveness may result from the interaction of complexes with the cellular biology of bacteria and fungi through its effect on QS quorum sensing, inhibiting cell division, and the process of biofilm formation. It affects the bacterial membrane by dispersing the potassium ion (K⁺), which leads to damage to the membrane and the collapse of the cell permeability barrier. Thus, the cell membrane works to produce clumps and spontaneous assembly, and then cell death. Also, Metals have an impact on microbial populations through influencing growth, shape, and biochemical activities, which ultimately leads to a decrease in living mass [44, 45]. Heavy metals could break down the cell membrane, change enzymes specific to a specific biological species, disrupt cellular functions, and destroy DNA synthesis. Toxicity can also occur because of changes in the structure of nucleic acids and proteins, and interference with oxidative phosphorylation and osmotic balance. Heavy metal toxicity occurs through the displacement of essential metals from their original binding site or through interaction with surrounding molecules [46]. Metal toxicity occurs because of the formation of bonds that stabilize the active site and base of the enzyme, such as the sulfhydryl group. Metals have a broad effect on fungi by reducing populations, weakening diversification, and changing the fungi's external appearance and physiological activity by affecting growth rate, reproductive processes, and enzyme production. Its effect is not limited to fungal organisms, but also to the reproductive and vegetative structures of the same fungi [47, 48].

Table 5. Biological efficacy of three ligand and metal complexes against bacteria as well as fungi.

Compounds	<i>Staphylococcus aureus</i> (G+ve)	<i>Staphylococcus epidermidis</i> (G+ve)	<i>Escherichia coli</i> (G-ve)	<i>Klebsiella pneumoniae</i> (G-ve)	<i>Candida albicans</i> (Fungi)
Control (DMSO)	-	-	-	-	-
Malonic acid (MA)	10	15	15	20	17
Nicotinic acid (NA)	10	12	13	9	13
o-Aminopyridine (AP)	-	18	-	-	10
[Cr(MA)(NA)(AP)]	8	8	9	8	11
Na[Mn(MA)(NA)(AP)]	10	10	19	-	10
[Fe(MA)(NA)(AP)]	-	-	-	-	-
Na[Co(MA)(NA)(AP)]	17	15	25	17	22
Na[Ni(MA)(NA)(AP)]	10	12	16	9	11
La(MA)(NA)(AP)	-	8	-	10	-

CONCLUSION

In this research study, malonic acid, nicotinic acid, and 2-aminopyridine, organocarboxylates, were coordinated with chromium, manganese, iron, cobalt, nickel, and lanolin ions. These complexes were characterized using multiple analytical techniques; including Fourier transform infrared spectroscopy, UV-visible spectroscopy, mass spectrometry, elemental analysis, thermogravimetric analysis (TGA), and magnetic susceptibility. The spectroscopic and magnetic data showed that the prepared complexes adopt an octahedral conformation, confirming coordination through donor oxygen and nitrogen atoms. Thermogravimetric studies demonstrated the thermal stability of both the (Mn and Fe) complexes. In addition, antimicrobial screening against urinary tract infection-causing pathogens showed that most of the complexes possessed promising biological activity, with the cobalt and malonic acid complex exhibiting the most significant inhibitory effects. The results indicate that mixed metal complexes, particularly those containing biologically active ligands, could be potential candidates for antimicrobial therapy. This work provides a basis for further biochemical and pharmacological evaluation of these metal complexes.

Data availability

All the supporting information will be made available upon request.

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