

Research Article

Preparation and Thermogravimetric and Antimicrobial Investigation of Cd (II) and Sn (II) Adducts of Mercaptopyridine, Amino Triazole Derivatives, and Mercaptothiazoline Organic Ligand Moieties

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The solid adducts of $\text{SnCl}_2 \cdot (3\text{amt}) \cdot \text{H}_2\text{O}$, $\text{SnCl}_2 \cdot 2(3\text{amt}) \cdot \text{H}_2\text{O}$, $\text{CdCl}_2 \cdot (3\text{amt})$, $\text{CdCl}_2 \cdot 2(3\text{amt})$, $\text{SnCl}_2 \cdot (2\text{mct}) \cdot 0.5\text{H}_2\text{O}$, $\text{SnCl}_2 \cdot 2(2\text{mct})$, $\text{CdCl}_2 \cdot (2\text{mct})$, $\text{CdCl}_2 \cdot 2(2\text{mct}) \cdot \text{H}_2\text{O}$, $\text{SnCl}_2 \cdot (2\text{mcp}) \cdot 1.5\text{H}_2\text{O}$, $>_2 \cdot 2(2\text{mcp}) \cdot 4\text{H}_2\text{O}$, $\text{CdCl}_2 \cdot (2\text{mcp})$, $\text{CdCl}_2 \cdot 2(2\text{mcp})$, $\text{SnCl}_2 \cdot (4\text{amt}) \cdot 4\text{H}_2\text{O}$, $\text{SnCl}_2 \cdot 2(4\text{amt}) \cdot 1.5\text{H}_2\text{O}$, $\text{CdCl}_2 \cdot (4\text{amt}) \cdot \text{H}_2\text{O}$, and $\text{CdCl}_2 \cdot 2(4\text{amt})$ (where the 3amt, 4amt, 2mct, and 2mcp represent 3-amino-1,2,4-triazole, 4-amino-1,2,4-triazole, 2-mercaptothiazoline, and 2-mercaptopyridine simple organic chelates, respectively) were prepared using a solid-state route and investigated by CHN elemental analysis and infrared spectroscopy. Additionally, we investigated the thermogravimetric characterization and antimicrobial proprieties. It is verified that for 3amt and 4amt adducts, the coordination occurs through nitrogen atom. For 2mct compounds, the coordination occurs through nitrogen (Sn) or sulfur (Cd). For 2mcp adducts, both coordination sites nitrogen and sulfur are involved. By examination of TG curves, it is confirmed that for each hydrated compounds, the first mass loss step is linked with the release of water molecules followed by the release of ligand molecules and sublimation of the metal chloride. Furthermore, it is verified that, considering only the release of ligand molecules (3amp, 4amp, 2mct, or 2mcp), the cadmium adducts are always more stable than the correspondent tin adducts probably due to the formation of cross-linking bonds in these compounds. Finally, of these 16 adducts, 14 showed antimicrobial activities against different bacterial and fungal strains.

1. Introduction

In the past decades, the problem of multidrug-resistant microorganisms has reached an alarming level worldwide, and the synthesis of new antimicrobial compounds has become an urgent need to treat microbial infections. Organic compounds that include heterocyclic ring systems continue to attract significant interest due to their wide range of biological elements [1]. The nucleus 1,2,4-triazole is incorporated into a variety of important therapeutic agents, which mainly exhibit antimicrobial activities [1, 2]. Among the various five-membered heterocyclic systems, 1,2,4-triazoles and 1,3,4-

thiadiazoles and their derivatives gain importance because they constitute the structural features of many bioactive compounds [2]. Triazole and thiadiazole rings are known to be included in the structure of various drugs [3, 4]. From these classes of heterocyclic compounds, the synthesis of novel derivatives of 1,2,4-triazole-3-thionate and 2-amino-1,3,4-thiazole has attracted great interest due to various biological properties such as antibacterial [5, 6], antifungal [7], anti-tuberculosis [8, 9], interferon [10], antioxidant [11], antitumor [12], anti-inflammatory [13, 14], and anticonvulsant [15].

The thermogravimetry analysis technique is employed to identify the acceptability level regarding the coordination

nature in between the central metal ions and different kinds of interesting biomolecule chelates, such as amino acids [16], caffeine molecule [17], or chemical materials that have a biological behavior as ethylene- and propylene-urea as well as ethylene-thiourea [18]. Moreover, the thermogravimetric information shows very close relationships with the calorimetric data [19] and the spectral data [20].

The main goal of this article is to investigate the synthesis, thermal analyses, and antimicrobial data of the sixteen solid adducts for the Cd (II) and Sn (II) metal ions coordinated with the 3amt, 4amt, 2mct, or 2mcp organic molecules. The molecular structural formulas of 3amt, 4amt, 2mct, and 2mcp are displayed in Figure 1. The sixteen solid adducts are $\text{SnCl}_2 \cdot (3\text{amt}) \cdot \text{H}_2\text{O}$, $\text{SnCl}_2 \cdot 2(3\text{amt}) \cdot \text{H}_2\text{O}$, $\text{CdCl}_2 \cdot (3\text{amt})$, $\text{CdCl}_2 \cdot 2(3\text{amt})$, $\text{SnCl}_2 \cdot (2\text{mct}) \cdot 0.5\text{H}_2\text{O}$, $\text{SnCl}_2 \cdot 2(2\text{mct})$, $\text{CdCl}_2 \cdot (2\text{mct})$, $\text{CdCl}_2 \cdot 2(2\text{mct}) \cdot \text{H}_2\text{O}$, $\text{SnCl}_2 \cdot (2\text{mcp}) \cdot 1.5\text{H}_2\text{O}$, $\text{SnCl}_2 \cdot 2(2\text{mcp}) \cdot 4\text{H}_2\text{O}$, $\text{CdCl}_2 \cdot (2\text{mcp})$, $\text{CdCl}_2 \cdot 2(2\text{mcp})$, $\text{SnCl}_2 \cdot (4\text{amt}) \cdot 4\text{H}_2\text{O}$, $\text{SnCl}_2 \cdot 2(4\text{amt}) \cdot 1.5\text{H}_2\text{O}$, $\text{CdCl}_2 \cdot (4\text{amt}) \cdot \text{H}_2\text{O}$, and $\text{CdCl}_2 \cdot 2(4\text{amt})$.

2. Materials and Methods

All used reagents were purchased from Sigma-Aldrich and were utilized with no additional purification.

All solid Cd(II) and Sn(II) adducts were prepared by the solid-state pathway by grinding stoichiometric amounts of metal halides and organic moieties (3amt, 4amt, 2mct, and 2mcp) in a mortar for 70 minutes at room temperature (27°C). The prepared solid adducts were dried under vacuum at room temperature for 24 h. This solid-state pathway was successfully used to enhance coordination reactions [21–24] as an alternative to conventional synthesis in solution. The synthesis is performed at room temperature, and where no solvent is used, any unwanted reaction to the metal cation is avoided. The infrared spectra result considering both free organic ligands and sixteen solid adducts proved that there are no free ligand particles after the grinding process.

C, H, and N elemental analysis were performed using a Perkin-Elmer 2400 analyzer. Infrared spectra of the solid adducts as a powder in *situ* KBr discs were scanned using a Gengis II FTIR apparatus within the 4000–400 cm^{-1} range, with a resolution of 4 cm^{-1} . Thermogravimetric diagrams under N_2 atmosphere were analyzed on the Shimadzu TG-50H apparatus with a heating rate of 15°C min^{-1} .

Tin(II) and cadmium(II) contents were determined by gravimetry by the direct ignition of the adducts at 600°C for 3 h till constant weight. The residue was then weighted in the forms of SnO and CdO, respectively. The Mohr method uses chromate ions as an indicator in the titration of chloride ions with a silver nitrate standard solution. After all the chloride precipitated as white silver chloride, the first excess of titrant results in the formation of a silver chromate precipitate, which signals the end point.

Preparation of standard AgNO_3 solution: 9.0 g of AgNO_3 was weighed out, transferred to a 500 mL volumetric flask, and made up to volume with distilled water. The resulting solution was approximately 0.1 M. This solution was standardized against NaCl. Reagent-grade NaCl was dried overnight and cooled to room temperature. 0.25 g portions

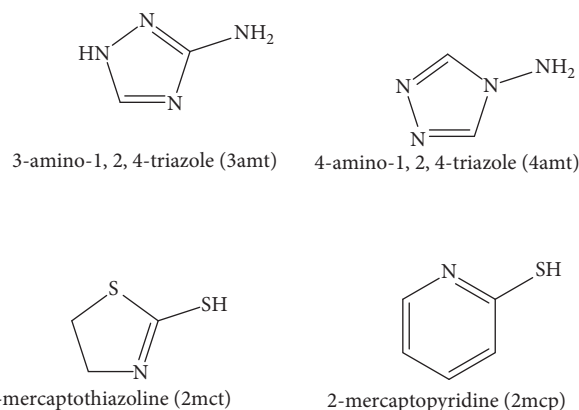


FIGURE 1: The structural forms of 3amt, 4amt, 2mct, and 2mcp.

of NaCl were weighed into Erlenmeyer flasks and dissolved in about 100 mL of distilled water. In order to adjust the pH of the solutions, small quantities of NaHCO_3 were added until effervescence ceased. About 2 mL of K_2CrO_4 was added, and the solution was titrated to the first permanent appearance of red Ag_2CrO_4 .

The antimicrobial activity of all adducts were performed as previously explained in detail by Gaber et al. [21]. *Escherichia coli* and *Pseudomonas aeruginosa* were used as Gram-negative bacteria, whereas *Bacillus subtilis* and *Staphylococcus aureus* were used as Gram-positive bacteria. In addition, *Aspergillus flavus* and *Candida albicans* were used as fungal strains. Diameters of the inhibition zones around the hole were calculated [21].

3. Results and Discussion

Table 1 shows the data of the elemental analysis. These results are like the proposed formulas. Additionally, the main infrared bands are displayed in Tables 2–5. Before a discussion on the infrared data, it is important to note that considering (3amt and 4amt) and (2mct and 2mcp), organic molecules have a rich electron donor sites through the lone pair of electrons presented on the nitrogen and sulfur atoms, respectively. Moreover, for the four chelates, there is more than one potential coordination site, which makes them able, at the very first moment, to act as cross-links.

In case of 3amt adducts, the overall decrease observed for the symmetrical and asymmetrical N-H bands suggests that the NH_2 group is engaged with the coordination. Furthermore, positive shifts observed for the δ_b bands reinforce this statement. It is worth noting that the observed shifts are more intense to Sn(II) adducts than to Cd(II), which is probably due to the higher acidity of Sn(II) (larger nuclear effective charge: 5.65 for Sn and 4.35 for Cd). It is verified that the symmetrical N-H bands are more sensitive to this acidity difference since a positive shift is observed for Cd(II) adducts, whereas a negative shift of this band is verified to Sn(II) adducts.

In case of 4amp approximation, the same general orientation is observed for asymmetric and symmetric N-H bands. This fact indicates that in this case, NH_2 is involved to a slight degree in the metallic coordination. This hypothesis is reinforced by the fact that for 4amp, the ringed breathing

TABLE 1: Mass weight and carbon, hydrogen, and nitrogen elemental analysis data for the examined compounds.

Adducts	M.wt	% C		% H		% N	
		Calc.	Found	Calc.	Found	Calc.	Found
SnCl ₂ ·(3amt)·H ₂ O	291.68	8.22	8.11	2.05	2.02	19.19	18.94
SnCl ₂ ·2(3amt)·H ₂ O	375.76	12.77	12.25	2.66	2.61	29.81	29.44
CdCl ₂ ·(3amt)	267.37	8.97	8.89	1.49	1.45	20.94	20.73
CdCl ₂ ·2(3amt)	351.47	13.65	13.62	2.27	2.20	31.87	31.48
SnCl ₂ ·(2mct)·0.5H ₂ O	317.81	11.33	10.99	1.89	1.84	4.40	4.35
SnCl ₂ ·2(2mct)	428.02	16.82	16.32	2.33	2.28	6.54	6.43
CdCl ₂ ·(2mct)	302.52	11.90	11.74	1.65	1.59	4.62	4.55
CdCl ₂ ·2(2mct)·H ₂ O	439.73	16.37	16.22	2.73	2.68	6.37	6.18
SnCl ₂ ·(2mcp)·1.5H ₂ O	327.77	18.31	18.19	2.44	2.41	4.27	4.15
SnCl ₂ ·2(2mcp)·4H ₂ O	483.94	24.80	24.57	3.72	3.68	5.78	5.74
CdCl ₂ ·(2mcp)	294.48	20.37	20.22	1.69	1.68	4.75	4.72
CdCl ₂ ·2(2mcp)	405.65	29.58	29.29	2.46	2.45	6.90	6.84
SnCl ₂ ·(4amt)·4H ₂ O	345.68	6.94	6.91	3.47	3.41	16.19	15.98
SnCl ₂ ·2(4amt)·1.5H ₂ O	384.76	12.48	12.34	2.86	2.79	29.11	28.96
CdCl ₂ ·(4amt)·H ₂ O	285.37	8.40	8.34	2.10	2.07	19.62	19.48
CdCl ₂ ·2(4amt)	351.47	13.65	13.51	2.27	2.26	31.87	31.83

TABLE 2: Major infrared bands (cm⁻¹) for 3amt and its Cd(II) and Sn(II) adducts.

3amt	CdCl ₂ ·(3amt)	CdCl ₂ ·2(3amt)	SnCl ₂ ·(3amt)	SnCl ₂ ·2(3amt)	Assignments
3398 s	3419 ms	3340 ms	3312 w	3349 vw	ν_{as} (N-H); NH ₂
3326 mw	3356 w 3316 mw			3310 vw 3258 vw	
3182 mw	3213 w 3131 w	3212 ms 3153 vw	3155 mw	3155 ms	ν_s (N-H); NH ₂
1647 vs	1652 vs	1645 w, sh	1688 vs	1677 vs	δ_b (NH ₂)
1590 s	1573 w	1594 vs	1569 ms	1566 ms	$\nu_{(C=N)}$
1533 s	1537 s 1480 w	1560 vs 1479 vs			$\nu_{(N=N)}$
1418 s	1429 ms	1374 vs	1405 mw	1415 w	Ring breathing bands
1389 ms	1373 w 1332 ms		1339 ms	1326 s	
1275 vs	1283 s	1248 vs	1257 ms	1263 w	ρ_r (NH ₂)
1217 vs	1250 vw 1219 vs 1144 w	1213 ms 1144 vs	1125 vw	1125 ms	$\nu_{(C-N)}$
1045 vs	1088 w	1083 vs	1048 s	1066 s	ρ_w (NH ₂)
945 vs	1057 s 991 s	1011 vs	951 vs	950 vs	
873 vs	901 s	884 s	860 ms	867 s	ρ_t (NH ₂)
830 s	740 ms	747 sh	748 w, sh	773 ms	
729 vs	693 vw 644 vs	726 ms 694 vs 642 ms			

s = strong; w = weak; m = medium; sh = shoulder; v = very; br = broad; ν = stretching; δ = bending.

TABLE 3: Major infrared bands (cm⁻¹) for 4amt and its Cd(II) and Sn(II) adducts.

4amt	CdCl ₂ ·(4amt)	CdCl ₂ ·2(4amt)	SnCl ₂ ·(4amt)	SnCl ₂ ·2(4amt)	Assignments
3312 w	3467 ms 3368 ms 3307 ms	3303 s 3258 vw	3417 w 3317 ms	3418 w, br 3277 w, br	ν_{as} (N-H); NH ₂
3197 w	3199 s	3198 s	3127 ms	3129 w, br	ν_s (N-H); NH ₂
3139 w	3136 s	3105 s			
1647 vs	1618 vs	1618 vs	1623 vs	1685 w	δ_b (NH ₂)

TABLE 3: Continued.

4amt	CdCl ₂ -(4amt)	CdCl ₂ -2(4amt)	SnCl ₂ -(4amt)	SnCl ₂ -2(4amt)	Assignments
1533 s	1543 s	1537 s	1539 ms	1631 vs 1529 s	
1475 ms 1404 s	1474 mw 1398 s 1341 s	1470 w 1394 w 1346 w	1465 vw 1402 vw 1366 vw 1318 vw	1465 vw 1412 vw 1363 vw 1323 vw	Ring breathing bands
1188 s 1074 s	1209 s 1145 vw 1082 vs	1209 ms 1078 s	1207 ms 1164 vw 1135 vw 1075 s	1205 s 1075s	ρ_r (NH ₂) $\nu_{(C-N)}$
1016 vw 959 ms	1025 s 980 vs	1015 s 984 ms	1034 s 934 ms	1033 s 935 ms	ρ_w (NH ₂)
873 s 672 w	908 w 874 s 689 ms	894 ms 845 vw 686 ms	871 ms 690 w, sh	875 ms 661 ms	ρ_t (NH ₂)

s = strong; w = weak; m = medium; sh = shoulder; v = very; br = broad; ν = stretching; δ = bending.

TABLE 4: Major infrared bands (cm⁻¹) for 2mct and its Cd(II) and Sn(II) adducts.

2mct	CdCl ₂ -(2mct)	CdCl ₂ -2(2mct)	SnCl ₂ -(2mct)	SnCl ₂ -2(2mct)	Assignments
2852 w	3258 s 2948 vw	3258 s 3136 ms 2998 w 2947 w 2844 w	3443 s, br 3206 ms 3144 vw 2997 w 2929 w 2845 w	3447 ms, br 3207 w 3136 w 2997 w 2848 vw	ν_s (C-H); -CH ₂ ν (O-H); H ₂ O
2709 mw 2565 mw	—	—	—	—	$\nu_{(SH)}$
1518 vs	1515 vs	1515 vs	1539 vs	1539 w, sh 1514 s	$\nu_{(C=N)}$ Ring breathing bands
1260 w 1217 w 1160 w 1102 s	1308 s 1250 vw 1192 ms 1142 w 1045 vs	1305 s 1249 w 1193 s 1045 vs	1307 s 1253 w 1208 w 1167 w 1038 s	1294 s 1250 vw 1205 vw 1041 s	ν_{as} (C-N) ν_s (C-N) + ν (C-C) $\nu_{(C-S)}$; C-SH

s = strong; w = weak; m = medium; sh = shoulder; v = very; br = broad; ν = stretching; δ = bending.

TABLE 5: Major infrared bands (cm⁻¹) for 2mcp and its Cd(II) and Sn(II) adducts.

2mcp	CdCl ₂ -(2mcp)	CdCl ₂ -2(2mcp)	SnCl ₂ -(2mcp)	SnCl ₂ -2(2mcp)	Assignments
—	3458 ms, br 3196 ms 3126 ms 3087 s	3448 ms, br 3172 ms	3421 ms, br 3216 ms 3135 w	3423 ms, br 3073 vw	$\nu_{(OH)}$; H ₂ O
2709 mw 2537 mw	—	—	—	—	$\nu_{(SH)}$
1576 vs 1504 s 1446 ms 1418 s	1602 vs 1517 s 1443 s 1378 s	1585 vs 1513 s 1443 s 1370 s	1582 vs 1550 sh 1517 s 1438 vs 1360 s	1578 vs 1551 sh 1438 vs 1366 w	Ring breathing bands
1275 ms 1246 ms 1188 vs	1262 s 1160 ms	1252 s 1163 s	1259 vs 1155 w, sh	1262 s 1179 vw	$\nu_{(C=N)}$; aromatic δ (C-H); in-plane bend
1145 vs 1102 vw	1134 vs 1111 vw	1132 vs 1109 vw	1131 s 1080 ms	1136 s 1081 ms	$\nu_{(C-S)}$; C-SH

s = strong; w = weak; m = medium; sh = shoulder; v = very; br = broad; ν = stretching; δ = bending.

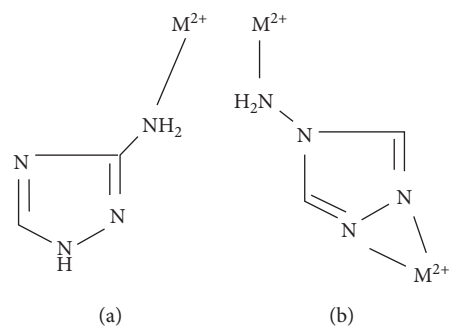


FIGURE 2: Schematic representation of the suggested coordinative characteristics for (a) 3amt and (b) 4amt adducts.

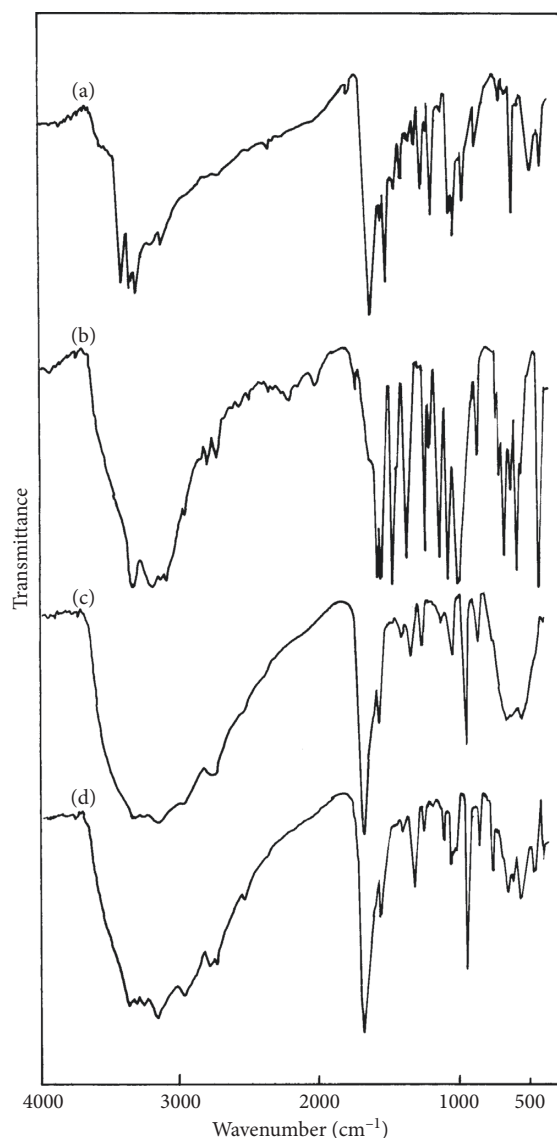


FIGURE 3: Infrared spectra for (a) $CdCl_2 \cdot (3amt)$, (b) $CdCl_2 \cdot 2(3amt)$, (c) $SnCl_2 \cdot (3amt) \cdot H_2O$, and (d) $SnCl_2 \cdot 2(3amt) \cdot H_2O$.

bands exhibit a negative shift (compared to free chelates and synthesized solid adducts), whereas positive shifts are observed in 3amp. Therefore, for 4amp adducts, the two “isolated” nitrogen atoms are the main coordination sites.

Suggested coordination modes for 3amp and 4amp molecules are shown schematically in Figure 2.

As explicatory examples, the infrared spectra of 3amt solid adducts are shown in Figure 3.

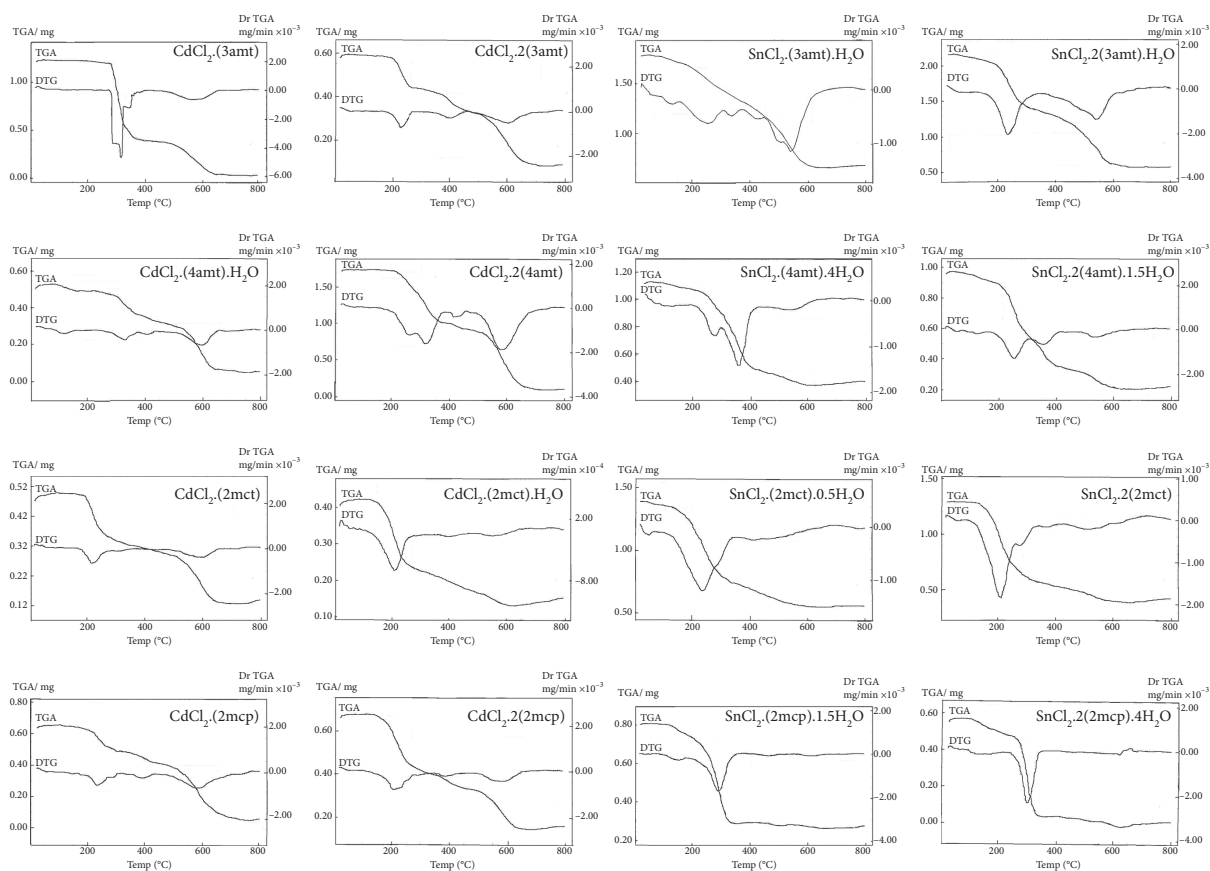


FIGURE 4: Thermogravimetric curves for the 16 solid adducts.

TABLE 6: TG data summary for Sn(II) and Cd(II) adducts with 3amt, 4amt, 2mcp, and 2mcp.

Adduct	Step	t_i (°C)	Degradation t_f (°C)	Process onset (°C)	Mass loss (%)
SnCl ₂ .(3amt).H ₂ O	1	55	382	238	26.7
	2	385	560	473	35.5
SnCl ₂ ,2(3amt).H ₂ O	1	45	102	76	5.1
	2	160	445	320	40.0
CdCl ₂ (3amt)	3	447	606	517	27.2
	1	280	331	307	53.7
CdCl ₂ ,2(3amt)	2	332	406	348	12.8
	3	478	660	569	29.3
CdCl ₂ ,2(3amt)	1	188	271	234	24.1
	2	348	448	401	16.8
CdCl ₂ ,2(3amt)	3	449	681	587	43.0
	1	31.4	83	50	3.3
SnCl ₂ .(2mct).0.5H ₂ O	2	127	344	237	43.2
	3	346	461	404	7.5
SnCl ₂ .(2mct).0.5H ₂ O	4	462	615	513	6.2
	1	120	260	204	44.0
SnCl ₂ ,2(2mct)	2	261	341	288	10.2
	3	342	430	378	4.7
SnCl ₂ ,2(2mct)	4	431	595	513	8.9
	5	596	656	607	1.1
CdCl ₂ .(2mct)	1	181	276	223	30.2
	2	497	650	583	41.3
CdCl ₂ .(2mct)	1	136	276	207	43.2
	2	277	485	384	15.4
CdCl ₂ ,2(2mct).H ₂ O	3	486	628	551	9.3

TABLE 6: Continued.

Adduct	Step	t_i (°C)	Degradation t_f (°C)	Process onset (°C)	Mass loss (%)
SnCl ₂ .(2mcp).1.5H ₂ O	1	110	199	154	8.0
	2	200	355	285	55.4
	3	421	654	534	3.1
SnCl ₂ .2(2mcp).4H ₂ O	1	103	221	154	14.3
	2	222	349	302	82.1
	3	584	670	585	1.8
CdCl ₂ .(2mcp)	1	186	309	244	23.3
	2	310	459	391	12.6
	3	460	647	576	47.0
CdCl ₂ .2(2mcp)	4	648	751	675	8.6
	1	139	274	215	35.8
	2	276	349	301	5.2
SnCl ₂ .(4amt).4H ₂ O	3	351	482	399	10.1
	4	483	649	572	26.9
	1	46	145	110	2.8
SnCl ₂ .2(4amt).1.5H ₂ O	2	210	299	269	15.7
	3	300	425	355	37.0
	4	428	616	515	10.2
CdCl ₂ .(4amt).H ₂ O	1	63	191	133	6.8
	2	192	319	257	39.2
	3	320	407	358	18.2
CdCl ₂ .2(4amt)	4	497	619	545	14.2
	1	88	176	123	6.7
	2	274	381	328	21.1
CdCl ₂ .2(4amt)	3	382	459	407	7.9
	4	460	655	583	51.3
	1	195	289	256	17.9
CdCl ₂ .2(4amt)	2	290	390	324	23.7
	3	392	456	420	4.8
	4	457	679	583	47.5

t_i and t_f are the initial and final temperatures of the thermal degradation process, respectively.

TABLE 7: Antimicrobial activities (inhibition zone diameter, mm/ μ g sample) of papaverine and its metal complexes against Gram-positive bacteria, Gram-negative bacteria, and two types of fungi.

The adducts	Gram-negative bacteria		Gram-positive bacteria		Fungi	
	<i>E. coli</i>	<i>P. aeruginosa</i>	<i>B. subtilis</i>	<i>S. aureus</i>	<i>A. flavus</i>	<i>C. albicans</i>
Control: DMSO	0.0	0.0	0.0	0.0	0.0	0.0
Ampicillin (Antibacterial agent)	22	17	20	18	0.0	0.0
Amphotericin B (Antifungal agent)	0.0	0.0	0.0	0.0	17	19
SnCl ₂ .(3amt).H ₂ O	10	10	12	11	0.0	23
SnCl ₂ .2(3amt).H ₂ O	15	13	13	15	0.0	14
CdCl ₂ .(3amt)	0.0	0.0	0.0	0.0	0.0	0.0
CdCl ₂ .2(3amt)	12	12	12	15	0.0	11
SnCl ₂ .(2mct).0.5H ₂ O	9	0.0	10	10	0.0	0.0
SnCl ₂ .2(2mct)	9	9	9	21	0.0	0.0
CdCl ₂ .(2mct)	16	15	14	20	14	17
CdCl ₂ .2(2mct).H ₂ O	26	28	26	32	31	35
SnCl ₂ .(2mcp).1.5H ₂ O	16	15	16	21	0.0	9
SnCl ₂ .2(2mcp).4H ₂ O	13	14	14	14	0.0	0.0
CdCl ₂ .(2mcp)	11	10	11	10	0.0	16
CdCl ₂ .2(2mcp)	14	13	12	16	0.0	13
SnCl ₂ .(4amt).4H ₂ O	9	0.0	0.0	0.0	0.0	0.0
SnCl ₂ .2(4amt).1.5H ₂ O	10	9	12	13	0.0	9
CdCl ₂ .(4amt).H ₂ O	0.0	0.0	0.0	0.0	0.0	0.0
CdCl ₂ .2(4amt)	9	0.0	0.0	9	0.0	0.0

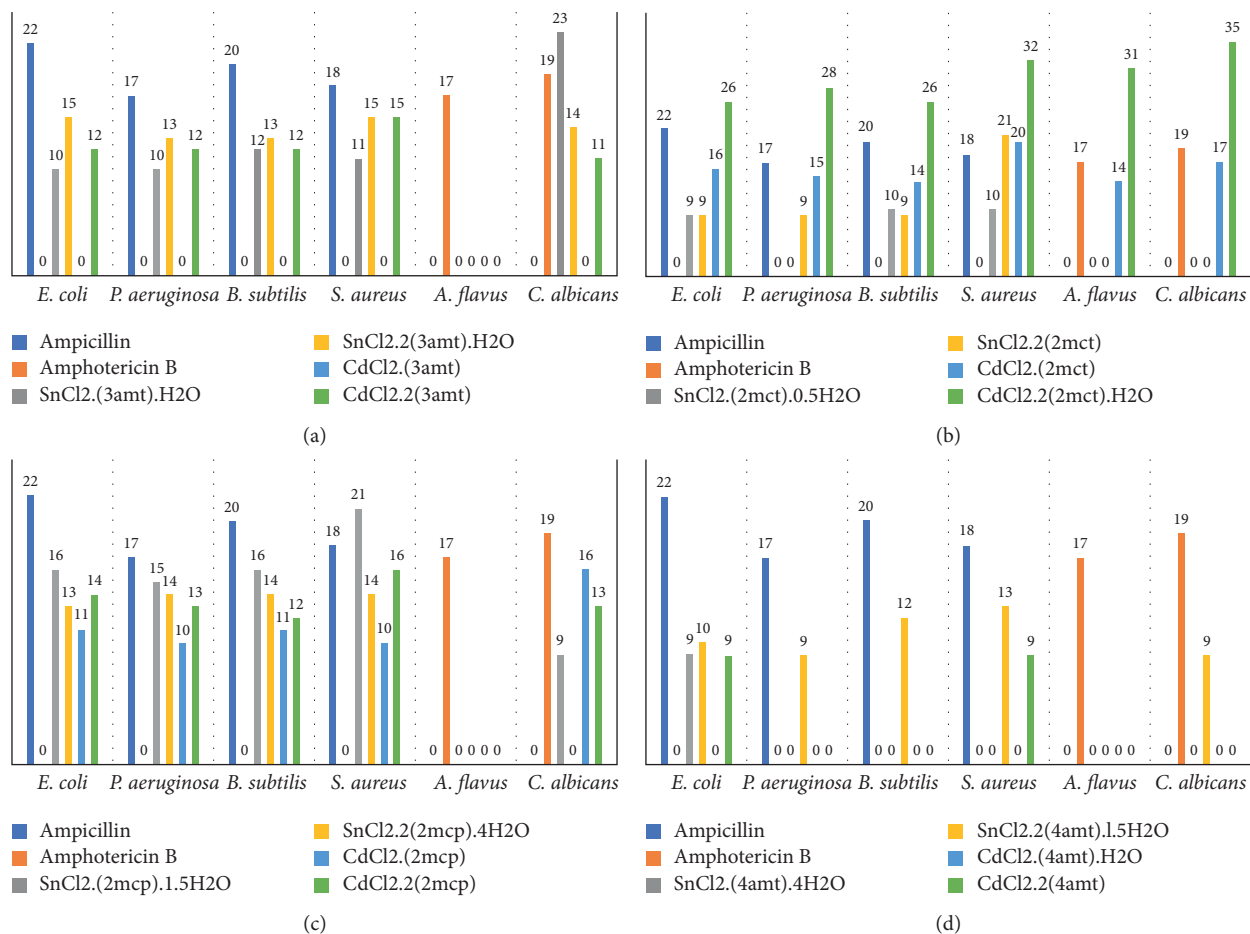


FIGURE 5: The antimicrobial effects of the 16 solid adducts. The number above the column indicates the inhibition zone diameter.

In case of 2mct adducts, positive shifts of the $\nu\text{C}=\text{N}$ band are observed for Sn(II) adducts, whereas negative shifts are verified to Cd(II) adducts. Such fact suggests a coordination through nitrogen to Sn(II) and a coordination through sulfur to Cd(II) in agreement with the fact that the nitrogen atom is a hard base and that Sn(II) is a harder acid than Cd(II).

For 2mcp adducts, the negative shifts observed for the $\nu(\text{C}-\text{S})$; $\text{C}-\text{SH}$ and $\nu(\text{C}=\text{N})$ aromatic bands suggest that, in this case, both coordination sites N and S are involved in the coordination process for both cations considered.

The data of thermogravimetric curves for the 16 solid adducts are demonstrated in Figure 4. The main TG data are elucidated in Table 6.

For each TG curve, the experimental mass losses ($\pm 5\%$) are similar to the proposed formulas. It is possible to verify that for all hydrated compounds, the first mass loss step is associated with the release of water molecules followed by the release of ligand molecules and sublimation of the metal chloride. Furthermore, it is verified that, considering only the release of ligand molecules

(3amp, 4amp, 2mct, or 2mcp), the cadmium adducts are always more stable than the correspondent tin adducts. Since the infrared data suggest that the metal-to-ligand interaction is higher for tin adducts, this last result is an expected one, unless we take into account that the cadmium adducts generally polymerize [22–27] and so there is, probably for these compounds, the formation of cross-linking bonds, leading to more stable compounds, from a thermal point of view.

The antimicrobial effect of the adducts was measured against a variety of microorganisms including bacteria and fungus (Table 7 and Figure 5). The no-growth zones around the hole indicated the inhibiting activity of the adducts on the microbe. These were calculated and compared with the ampicillin as an antibacterial agent or amphotericin B as an antifungal agent. The adduct CdCl₂.(2mct).H₂O and CdCl₂.(2mct) showed the highest antimicrobial activities followed by SnCl₂.(2mcp).1.5H₂O among all other adducts. On other hand, the CdCl₂.(3amt) and CdCl₂.(4amt).H₂O have no effect on any bacteria or fungal strains (Table 7). The antimicrobial activities of these adducts might be caused by a

direct interaction of Cd (II) or Sn (II) ions with proteins, enzymes, nucleic acids, and membranes of microbe cells.

4. Conclusion

The adducts $\text{SnCl}_2 \cdot (3\text{amt}) \cdot \text{H}_2\text{O}$, $\text{SnCl}_2 \cdot 2(3\text{amt}) \cdot \text{H}_2\text{O}$, $\text{CdCl}_2 \cdot (3\text{amt})$, $\text{CdCl}_2 \cdot 2(3\text{amt})$, $\text{SnCl}_2 \cdot (2\text{mct}) \cdot 0.5\text{H}_2\text{O}$, $\text{SnCl}_2 \cdot 2(2\text{mct})$, $\text{CdCl}_2 \cdot (2\text{mct})$, $\text{CdCl}_2 \cdot 2(2\text{mct}) \cdot \text{H}_2\text{O}$, $\text{SnCl}_2 \cdot (2\text{mcp}) \cdot 1.5\text{H}_2\text{O}$, $\text{SnCl}_2 \cdot 2(2\text{mcp}) \cdot 4\text{H}_2\text{O}$, $\text{CdCl}_2 \cdot (2\text{mcp})$, $\text{CdCl}_2 \cdot 2(2\text{mcp})$, $\text{SnCl}_2 \cdot (4\text{amt}) \cdot 4\text{H}_2\text{O}$, $\text{SnCl}_2 \cdot 2(4\text{amt}) \cdot 1.5\text{H}_2\text{O}$, $\text{CdCl}_2 \cdot (4\text{amt}) \cdot \text{H}_2\text{O}$, and $\text{CdCl}_2 \cdot 2(4\text{amt})$ —where 3amt = 3-amino-1,2,4-triazole; 4amt = 4-amino-1,2,4-triazole; 2mct = 2-mercaptotriazole; and 2mcp = 2-mercaptopyridine—were synthesized by a solid-state route and characterized by CHN elemental analysis and infrared spectroscopy. A thermogravimetric study was also performed. It is verified that, for all compounds, the monoadducts are the most stable ones. Such fact agrees with a higher ionic and covalent character of the metal-ligand bond for such compounds. From the result, it can be concluded that 14 of the 16 compounds have a good biological activity against these microorganisms.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare no conflicts of interest.

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