

Synthesis, characterization and thermogravimetric study of Cu(II) adducts with 3- and 4-amino-1,2,4-triazole, 2-mercaptothiazoline and 2-mercaptopyridine

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Abstract: The adducts $\text{CuCl}_2 \cdot (3\text{amt})$, $\text{CuCl}_2 \cdot 2(3\text{amt}) \cdot 2\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 3(3\text{amt})$, $\text{CuCl}_2 \cdot (4\text{amt})$, $\text{CuCl}_2 \cdot 2(4\text{amt})$, $\text{CuCl}_2 \cdot 3(4\text{amt}) \cdot 2\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot (2\text{mct}) \cdot \text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2(2\text{mct}) \cdot 2.5\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 3(2\text{mct}) \cdot 2\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot (2\text{mcp})$ and $\text{CuCl}_2 \cdot 2(2\text{mcp}) \cdot \text{H}_2\text{O}$, where 3-amino-1,2,4-triazole = 3amt, 4-amino-1,2,4-triazole = 4amt, 2-mercaptothiazoline = 2mct and 2-mercaptopyridine = 2mcp, were synthesized by a solid state route and characterized by CHN elemental analysis and infrared spectroscopy. A thermogravimetric study was also performed. It was verified that 4amp is a molecule with a higher ability to act as a bridging ligand in comparison with 3amp. It was also found that, for all compounds, the mono adducts were the most thermally stable ones. Such a fact is in agreement with a higher ionic and covalent character of the metal–ligand bond in such compounds.

Keywords: Cu(II) chloride, IR spectra, adducts, thermogravimetry, triazoles, mercaptothiazoline, mercaptopyridine.

INTRODUCTION

Thermogravimetry has been successfully employed to evaluate, from an energetic point of view, the degree of interaction between metal cations and species of biological interest, such as amino acids¹ and caffeine,² as well as molecules the chemical composition and structure of which resemble those of compounds of biological interest, e.g., ethyleneurea, propyleneurea and ethylenethiourea.³ Furthermore, thermogravimetric data exhibit very close relationships with calorimetric⁴ and spectroscopic data.⁵

The present study is significant in the previously mentioned context. The aim of this publication is to report the synthesis, characterization and a thermogravimetric study of Cu(II) adducts with 3- and 4-amino-1,2,4-triazole, 2-mercaptothi-

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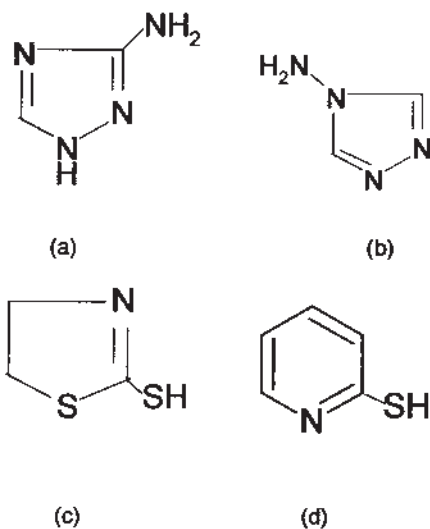


Fig. 1. Structural formulae for (a) 3-amino-1,2,4-triazole, (b) 4-amino-1,2,4-triazole, (c) 2-mercaptothiazoline and (d) 2-mercaptopyridine.

azoline and 2-mercaptopyridine. The structural formulae of these ligands are shown in Fig. 1. Hereafter, these ligands will be abbreviated as follows: 3-amino-1,2,4-triazole = 3amt, 4-amino-1,2,4-triazole = 4amt, 2-mercaptothiazoline = 2mct and 2-mercaptopyridine = 2mcp.

EXPERIMENTAL

All the used reagents were of analytical grade (Aldrich) and were employed without further purification.

All adducts were synthesized through a solid state route by grinding stoichiometric amounts of the metal halide and ligands in a mortar for 70 min, at room temperature (27 °C). Such a solid state route has been successfully employed to promote coordinative reactions⁶⁻⁹ as an alternative to the traditional synthesis in solution. Since the syntheses were performed at room temperature, the thermal stability of the ligands was not affected, and as no solvent was employed, any undesirable interaction of the metal cation was avoided.

Infrared spectra obtained for the free ligands and adducts confirm that there are no free ligand molecules after the grinding process. The synthesized adducts were dried under vacuum at room temperature for 24 h.

C, H and N elemental analyses were performed using a Perkin-Elmer 2400 analyzer. The infrared spectra (as KBr discs) were recorded in a Gengis II FTIR instrument in the 4000–400 cm⁻¹ range, with a resolution of 4 cm⁻¹. Thermogravimetric curves were obtained using a Shimadzu TG-50H apparatus under a N₂ atmosphere at a heating rate of 15 °C min⁻¹.

RESULTS AND DISCUSSION

The obtained CHN analysis results, which are in good agreement with the proposed formulae, are summarized in Table I. The obtained infrared spectra are shown in Figs. 2–5. The main IR bands are summarized in Tables II–V.

For 3amt and 4amt, only nitrogen atoms are available as possible coordination sites. On the other hand, for 2mct and 2mcp, as well as nitrogen there are also sulfur atoms as possible electron donor species. Furthermore, for the four ligands, there

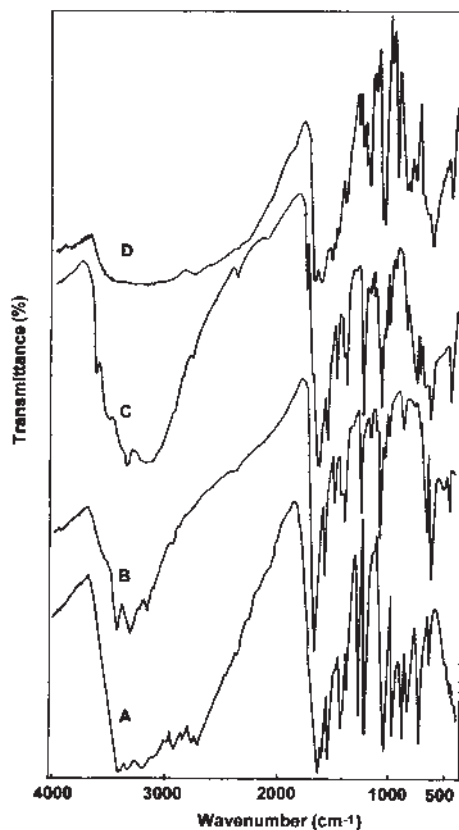


Fig. 2. Infrared spectra for: (a) 3-amino-1,2,4-triazole, (b) $\text{CuCl}_2 \cdot (3\text{amt})$, (c) $\text{CuCl}_2 \cdot 2(3\text{amt}) \cdot 2\text{H}_2\text{O}$ and (d) $\text{CuCl}_2 \cdot 3(3\text{amt})$.

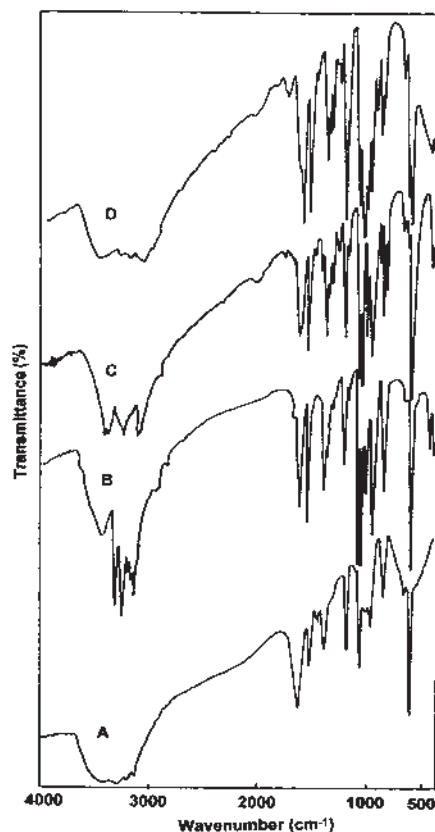


Fig. 3. Infrared spectra for: (a) 4-amino-1,2,4-triazole, (b) $\text{CuCl}_2 \cdot (4\text{amt})$, (c) $\text{CuCl}_2 \cdot 2(4\text{amt})$ and (d) $\text{CuCl}_2 \cdot 3(4\text{amt}) \cdot 2\text{H}_2\text{O}$.

are several possible coordination sites, enabling them in the first moment to act as cross-linking ligands.

TABLE I. Carbon, hydrogen and nitrogen elemental analysis results for the studied compounds

Adducts	FW	% C		% H		% N	
		Calcd.	Found	Calcd.	Found.	Calcd.	Found
$\text{CuCl}_2 \cdot (3\text{amt})$	218.53	10.98	10.76	1.83	1.85	25.63	25.55
$\text{CuCl}_2 \cdot 2(3\text{amt}) \cdot 2\text{H}_2\text{O}$	338.61	14.17	14.12	3.54	3.66	33.08	32.98
$\text{CuCl}_2 \cdot 3(3\text{amt})$	386.69	18.62	18.58	3.10	3.08	43.45	43.38
$\text{CuCl}_2 \cdot (4\text{amt})$	218.53	10.98	11.07	1.83	1.85	25.63	25.60
$\text{CuCl}_2 \cdot 2(4\text{amt})$	302.61	15.86	15.79	2.64	2.62	37.01	36.95
$\text{CuCl}_2 \cdot 3(4\text{amt}) \cdot 2\text{H}_2\text{O}$	422.69	17.03	17.18	3.78	3.86	39.74	39.71
$\text{CuCl}_2 \cdot (2\text{mct}) \cdot \text{H}_2\text{O}$	271.66	13.25	13.44	2.58	2.55	5.15	5.19
$\text{CuCl}_2 \cdot 2(2\text{mct}) \cdot 2.5\text{H}_2\text{O}$	417.87	17.23	17.30	2.85	2.88	6.70	6.64

TABLE I. Continued

Adducts	FW	% C		% H		% N	
		Calcd.	Found	Calcd.	Found.	Calcd.	Found
CuCl ₂ ·3(2mct)·2H ₂ O	528.08	20.45	20.30	3.60	3.70	7.95	7.92
CuCl ₂ ·(2mcp)	245.62	24.43	24.42	2.04	2.03	5.70	5.66
CuCl ₂ ·2(2mcp)·H ₂ O	374.79	32.02	32.00	3.20	3.26	7.47	7.45

TABLE II. Main infrared bands (cm⁻¹) for 3amt and its Cu(II) adducts

3amt	CuCl ₂ ·(3amt)	CuCl ₂ ·2(3amt)·2H ₂ O	CuCl ₂ ·3(3amt)	Assignments ^{a,b}
3398 <i>s</i>	3412 <i>ms</i> 3312 <i>ms</i>	3484 <i>w</i>	3455 <i>vw</i>	$\nu_{\text{as(N-H)}}$; NH ₂
3326 <i>mw</i>		3340 <i>ms</i>	3326 <i>vw</i>	
3182 <i>mw</i>	3197 <i>w</i> 3154 <i>ms</i>	3226 <i>w</i>	3211 <i>vw</i>	$\nu_{\text{s(N-H)}}$; NH ₂
		3139 <i>w</i>	3139 <i>vw</i>	
1647 <i>vs</i>	1676 <i>vs</i> 1561 <i>s</i>	1705 <i>ms</i>	1690 <i>ms</i>	$\delta_{\text{b}}(\text{NH}_2)$
1590 <i>s</i>		1619 <i>vs</i>	1619 <i>s</i>	$\nu_{\text{(C=N)}}$
1533 <i>s</i>		1547 <i>s</i>	1533 <i>mw</i>	$\nu_{\text{(N=N)}}$
1418 <i>s</i>	1475 <i>s</i>	1461 <i>s</i>	1504 <i>ms</i>	Ring breathing bands
1389 <i>ms</i>	1389 <i>vs</i>	1389 <i>sh</i>	1475 <i>w</i>	
		1361 <i>vs</i>	1418 <i>ms</i>	
1275 <i>vs</i>	1217 <i>s</i> 1145 <i>ms</i>	1289 <i>w</i>	1289 <i>ms</i>	$\rho_{\text{r}}(\text{NH}_2)$
1217 <i>vs</i>		1231 <i>vs</i>	1260 <i>ms</i>	$\nu_{\text{(C-N)}}$
		1174 <i>w</i>	1217 <i>w</i>	
		1131 <i>w</i>	1188 <i>s</i>	
			1131 <i>ms</i>	
1045 <i>vs</i>	1074 <i>vs</i> 1016 <i>mw</i> 988 <i>mw</i>	1074 <i>vs</i>	1059 <i>vs</i>	$\rho_{\text{w}}(\text{NH}_2)$
945 <i>vs</i>		1031 <i>ms</i>	959 <i>s</i>	
		988 <i>s</i>	930 <i>vs</i>	
		930 <i>w</i>		
873 <i>vs</i>	873 <i>ms</i> 772 <i>w</i>	830 <i>s</i>	859 <i>w</i>	$\rho_{\text{t}}(\text{NH}_2)$
830 <i>s</i>	729 <i>w</i>	758 <i>s</i>	815 <i>w</i>	
729 <i>vs</i>		715 <i>ms</i>	772 <i>s</i>	

(a) *s* = strong, *w* = weak, *m* = medium, *sh* = shoulder, *v* = very; (b) ν = stretching; δ = bending; ρ = rocking.

TABLE III. Main infrared bands (cm⁻¹) for 4amt and its Cu(II) adducts.

4amt	CuCl ₂ ·(4amt)	CuCl ₂ ·2(4amt)	CuCl ₂ ·3(4amt)·2H ₂ O	Assignments ^{a,b}
3312 <i>w</i>	3312 <i>s</i> 3254 <i>s</i>	3398 <i>w</i>	3283 <i>w</i>	$\nu_{\text{as(N-H)}}$; NH ₂
	3211 <i>w</i>	3297 <i>sh</i>		
		3240 <i>ms</i>		

TABLE III. Continued

4amt	CuCl ₂ ·(4amt)	CuCl ₂ ·2(4amt)	CuCl ₂ ·3(4amt)·2H ₂ O	Assignments ^{a,b}
3197 <i>w</i>	3182 <i>w</i> 3139 <i>ms</i>	3139 <i>ms</i>	3197 <i>w</i>	$\nu_{s(N-H)}$; NH ₂
3139 <i>w</i>				
1647 <i>vs</i>	1619 <i>vs</i> 1547 <i>vs</i>	1633 <i>vs</i>	1762 <i>ms</i>	$\delta_b(NH_2)$
1533 <i>s</i>		1547 <i>s</i>	1619 <i>vs</i>	
			1561 <i>vs</i>	
1475 <i>ms</i>	1404 <i>s</i>	1432 <i>s</i>	1418 <i>s</i>	Ring breathing bands
1404 <i>s</i>	1375 <i>sh</i>	1389 <i>mw</i>	1389 <i>w</i>	
		1347 <i>mw</i>	1361 <i>ms</i>	
1188 <i>s</i>	1231 <i>s</i>	1303 <i>ms</i>	1289 <i>ms</i>	$\rho_r(NH_2)$
1074 <i>s</i>	1188 <i>mw</i>	1217 <i>vs</i>	1246 <i>vs</i>	$\nu_{(C-N)}$
	1088 <i>vs</i>	1102 <i>vs</i>	1203 <i>ms</i>	
	1059 <i>vs</i>	1074 <i>vs</i>	1102 <i>vs</i>	
			1074 <i>vs</i>	
1016 <i>vw</i>	1016 <i>s</i>	1031 <i>s</i>	1045 <i>ms</i>	$\rho_w(NH_2)$
959 <i>ms</i>	959 <i>vs</i>	988 <i>vs</i>	1002 <i>s</i>	
		930 <i>ms</i>	959 <i>ms</i>	
873 <i>s</i>	844 <i>s</i>	887 <i>vs</i>	902 <i>ms</i>	$\rho_r(NH_2)$
672 <i>w</i>	700 <i>s</i>	844 <i>s</i>	873 <i>ms</i>	

(a): *s* = strong, *w* = weak, *m* = medium, *sh* = shoulder, *v* = very; (b): ν = stretching; δ = bending; ρ = rocking.

TABLE IV. Main infrared bands (cm⁻¹) for 2mct and its Cu(II) adducts

2mct	CuCl ₂ ·(2mct)·H ₂ O	CuCl ₂ ·2(2mct)·2.5H ₂ O	CuCl ₂ ·3(2mct)·2H ₂ O	Assignments ^{a,b}
2852 <i>w</i>	2852 <i>vw</i>	2881 <i>w</i>	2881 <i>mw</i>	$\nu_{s(C-H)}$; -CH ₂
			2738 <i>w</i>	
2709 <i>mw</i>				$\nu(SH)$
2565 <i>mw</i>				
1518 <i>vs</i>	1647 <i>ms</i> 1590 <i>s</i> 1547 <i>s</i>	1734 <i>vw</i>	1734 <i>ms</i>	$\nu_{(C=N)}$
		1676 <i>ms</i> 1604 <i>vs</i>	1690 <i>w</i>	Ring breathing bands
1260 <i>w</i>	1275 <i>s</i>	1275 <i>s</i>	1231 <i>vs</i>	$\nu_{as(C-N)}$
1217 <i>w</i>	1217 <i>ms</i> 1102 <i>vs</i>	1217 <i>sh</i>	1117 <i>mw</i>	$\nu_{s(C-N)+\nu(C-C)}$
1160 <i>w</i>		1117 <i>vs</i>		$\nu(C-S)$; C-SH
1102 <i>s</i>				

(a): *s* = strong, *w* = weak, *m* = medium, *sh* = shoulder, *v* = very; (b): ν - stretching; δ = bending.

TABLE V. Main infrared bands (cm^{-1}) for 2mcp and its Cu(II) adducts

2mcp	$\text{CuCl}_2 \cdot (2\text{mcp})$	$\text{CuCl}_2 \cdot 2(2\text{mcp}) \cdot 2\text{H}_2\text{O}$	Assignments ^{a,b}
2709 <i>mw</i>			$\nu(\text{SH})$
2537 <i>mw</i>			
1576 <i>vs</i>	1576 <i>vs</i>	1533 <i>ms</i>	Ring breathing bands
1504 <i>s</i>	1518 <i>s</i>	1475 <i>s</i>	
1446 <i>ms</i>	1461 <i>s</i>	1404 <i>s</i>	
1418 <i>s</i>	1418 <i>ms</i>		
1275 <i>ms</i>	1232 <i>w</i>	1188 <i>ms</i>	$\nu(\text{C}=\text{N})$; aromatic
1246 <i>ms</i>	1159 <i>vw</i>	1160 <i>s</i>	$\delta(\text{C}-\text{H})$; in-plane bend
1188 <i>vs</i>			
1145 <i>vs</i> 1102 <i>vw</i>	1117 <i>vs</i>	1074 <i>mw</i>	$\nu(\text{C}-\text{S})$; C-SH
	1031 <i>m</i>	1016 <i>s</i>	

(a) *s* = strong, *w* = weak, *m* = medium, *sh* = shoulder, *v* = very; (b) ν = stretching; δ = bending.

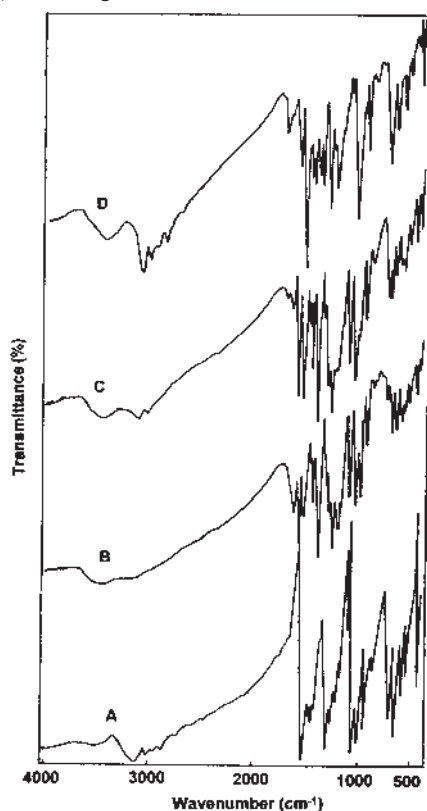


Fig. 4. Infrared spectra for: (a) 2-mercaptothiazoline, (b) $\text{CuCl}_2 \cdot (2\text{mct}) \cdot \text{H}_2\text{O}$, (c) $\text{CuCl}_2 \cdot 2(2\text{mct}) \cdot 2.5\text{H}_2\text{O}$ and (d) $\text{CuCl}_2 \cdot 3(2\text{mct}) \cdot 2\text{H}_2\text{O}$.

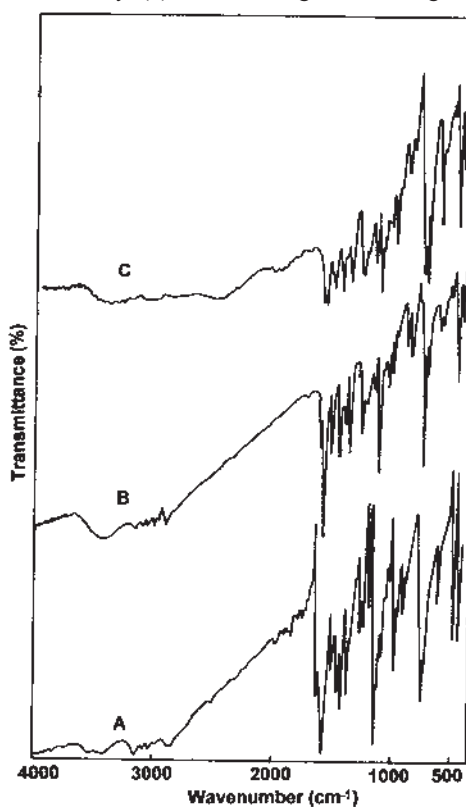


Fig. 5. Infrared spectra for: (a) 2-mercaptopyridine, (b) $\text{CuCl}_2 \cdot (2\text{mcp})$ and (c) $\text{CuCl}_2 \cdot 2(2\text{mcp}) \cdot \text{H}_2\text{O}$.

For the 3amt adducts, the general increase observed for the symmetrical and asymmetrical N–H bands indicates that the NH_2 group is involved in the coordination. In addition, the positive shifts observed for the δ_b bands (by comparison of the spectra of the free ligand and adducts) reinforces this statement. For the 4amt adducts, the same general trend for the asymmetric and symmetric N–H bands was observed, but to a minor extent. This suggests that in this case the NH_2 is involved to a minor extent in the metal coordination. Such a hypothesis is reinforced by the fact that the ring breathing bands for 4amt exhibit negative shifts (comparing the free ligand and the adducts) whereas positive shifts were observed for the 3amt adducts. Hence, for the 4amt adducts, the two "isolated" nitrogen atoms are the main coordination sites. The proposed coordination features for the 3amt and 4amt adducts are schematically shown in Fig. 6.

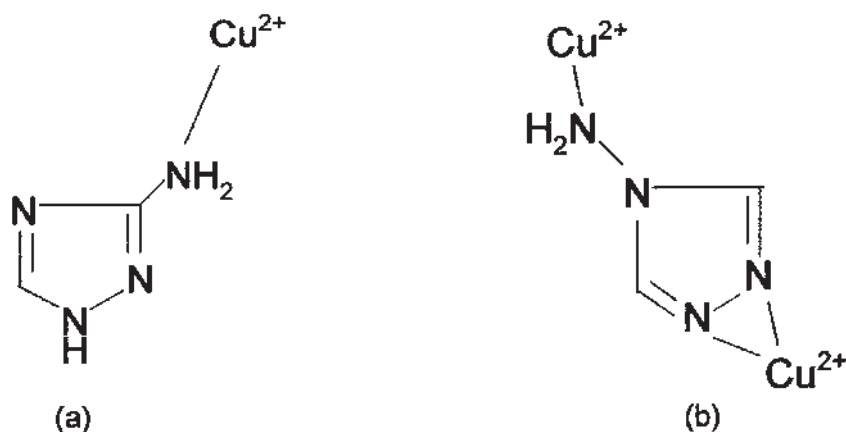


Fig. 6. Schematic representation of the proposed coordinative features for: (a) 3amt and (b) 4amt adducts.

For the 2mct adducts, the positive shifts observed for the $\nu(\text{C}=\text{N})$ band are consistent with a coordination involving the nitrogen atom. This is also consistent with the fact that Cu^{2+} is a borderline Pearson's acid and that sulfur is a softer base than nitrogen, making it less suitable for coordination with Cu^{2+} , as was previously verified for a copper-ethylenethiourea (etu) compound, for which solution and solid state calorimetric data have been obtained.¹⁰ Resonance phenomena similar to those proposed for etu can be suggested being responsible for both, the coordination through the nitrogen and the positive shifts observed for the $\nu(\text{C}=\text{N})$ band.¹⁰ Similar arguments can be used to propose a coordination through the nitrogen for the 2mcp adducts. In this case, however, a negative shift of the $\nu(\text{C}=\text{N})$ bands was observed, showing the effect of the aromatic electronic ring on the coordination features of such a molecule. The proposition of coordination through the nitrogen is also reinforced by the fact that negative shifts of the $\nu(\text{C}-\text{S}; \text{C}-\text{SH})$ bands were observed.

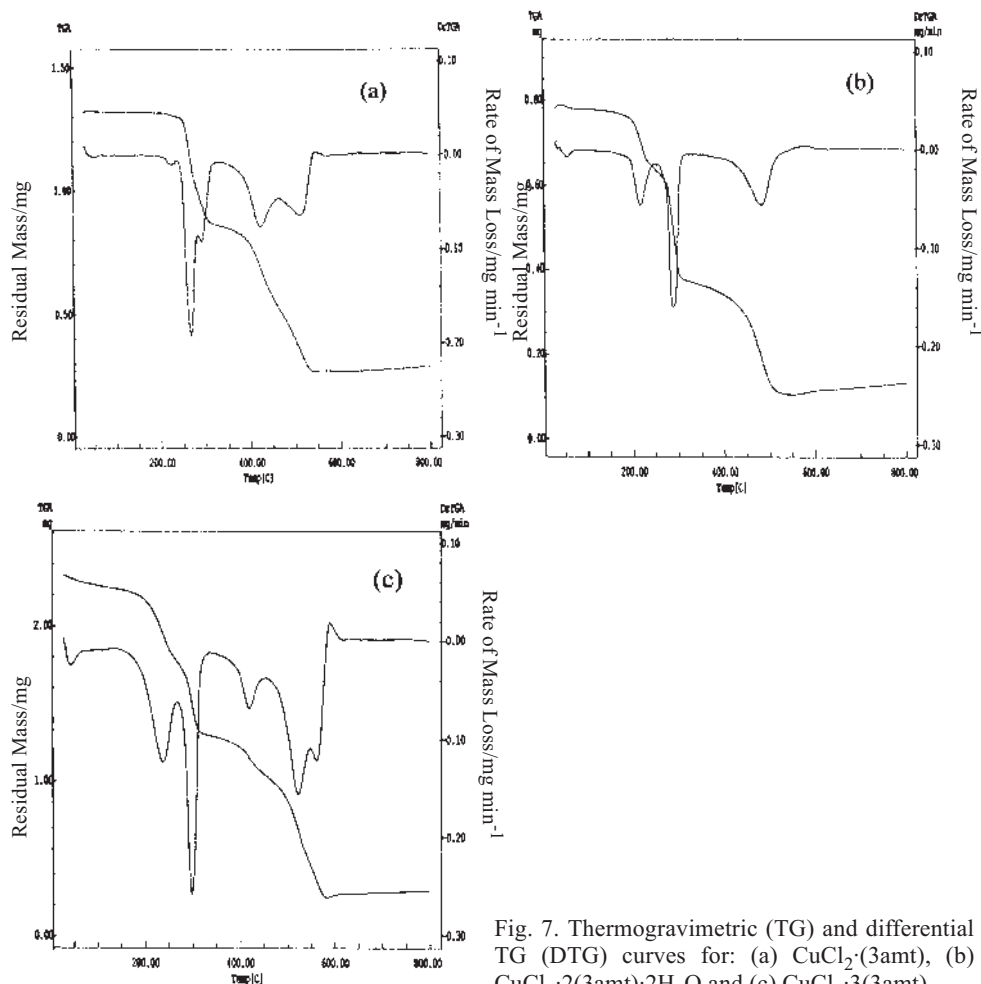


Fig. 7. Thermogravimetric (TG) and differential TG (DTG) curves for: (a) $\text{CuCl}_2 \cdot (3\text{amt})$, (b) $\text{CuCl}_2 \cdot 2(3\text{amt}) \cdot 2\text{H}_2\text{O}$ and (c) $\text{CuCl}_2 \cdot 3(3\text{amt})$.

Metal-triazole and related compounds have been investigated mainly taking into account the possible biological effects/applications of such compounds, that is as antifungal agents and anticancer drugs.^{11–14} Comparing the coordination features proposed in those studies (based on both spectroscopic and crystallographic data) with the present results, it is possible to state that there is, in a broad sense, good agreement between all the data sets. Special attention was devoted to the compound $\text{CuCl}_2 \cdot 2\text{L}^1$, where L^1 is 4-amino-3-aminomethyl-5-methyl-1,2,4-triazole, for which an ORTEP diagram has been presented.¹² For this compound, it was verified that the two Cl^- ions are in an axial position with relation to Cu^{2+} , whereas both ligand molecules are in the equatorial plane, each one bonded to the metal cation by two nitrogen atoms. Such a coordination feature resembles those proposed for the 4amt adducts and shown in Fig. 6(b).

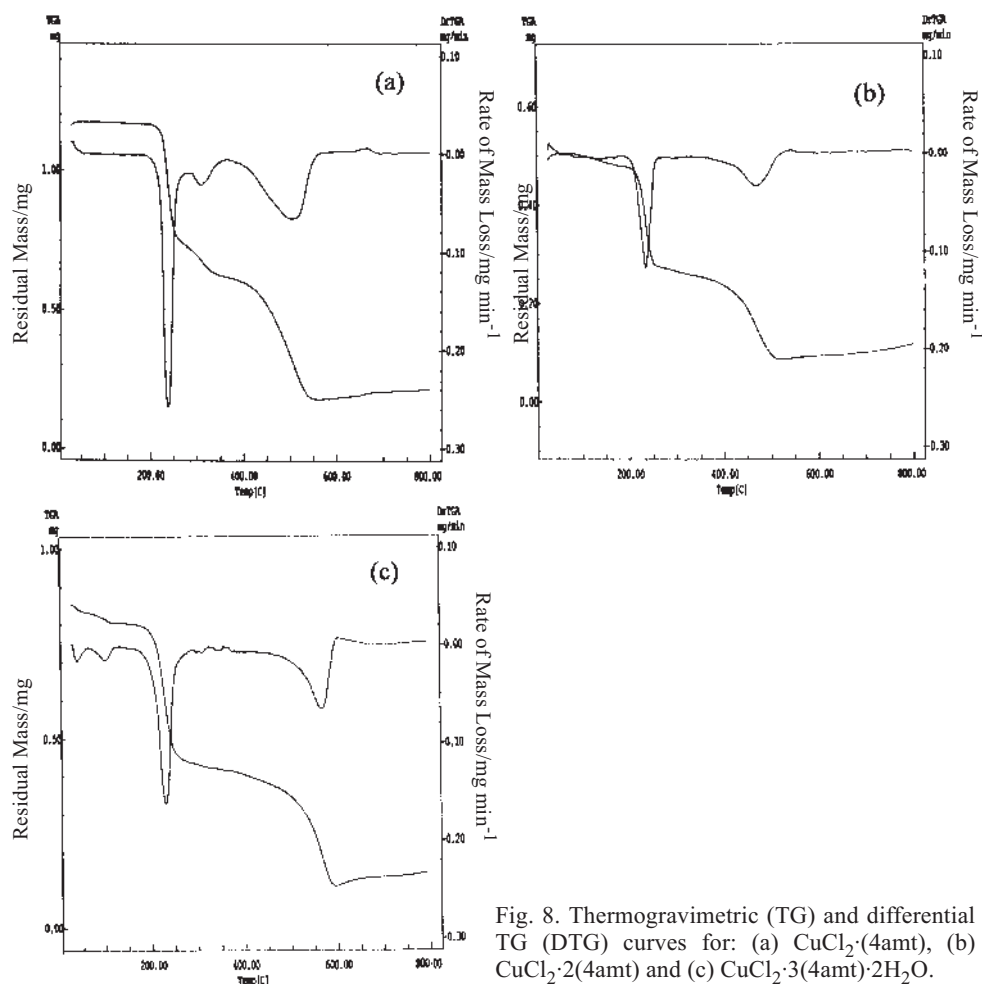


Fig. 8. Thermogravimetric (TG) and differential TG (DTG) curves for: (a) $\text{CuCl}_2 \cdot (4\text{amt})$, (b) $\text{CuCl}_2 \cdot 2(4\text{amt})$ and (c) $\text{CuCl}_2 \cdot 3(4\text{amt}) \cdot 2\text{H}_2\text{O}$.

The results obtained in the present work for 2mct and 2mcp adducts differ from those previously presented for sulfur containing triazole derivatives,¹¹ for which the participation of sulfur as a coordination site was shown.

The obtained thermogravimetric curves are shown in Figs. 7–10. As a general statement, the overall mass loss for all compounds is in good agreement ($\pm 5\%$) with the proposed formulae. For the hydrated compounds, the first mass loss step is associated with the release of water molecules, despite the fact that, for the mct and mcp adducts, such mass losses are superimposed with the release of ligand molecules. After the release of the hydration molecules, the release of ligands occurred.

For the 3amt adducts, the thermal stability decreased from the mono to the tris-adduct, with the release of the ligand molecules occurring at 223, 190 and 182 °C, respectively. On the other hand, for the 4amt compounds, the bis and tris adducts exhibit the same temperature for the release of the ligand molecules around

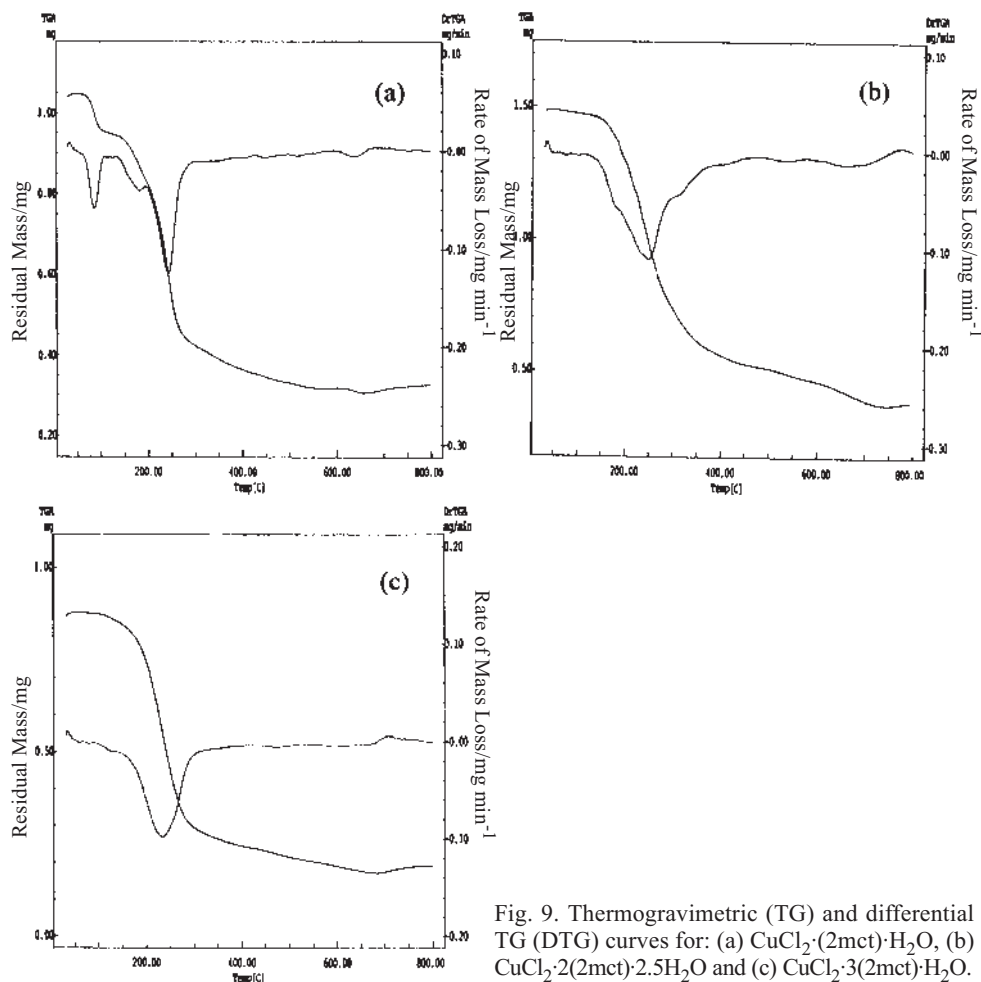


Fig. 9. Thermogravimetric (TG) and differential TG (DTG) curves for: (a) $\text{CuCl}_2 \cdot (2\text{mct}) \cdot \text{H}_2\text{O}$, (b) $\text{CuCl}_2 \cdot 2(2\text{mct}) \cdot 2.5\text{H}_2\text{O}$ and (c) $\text{CuCl}_2 \cdot 3(2\text{mct}) \cdot \text{H}_2\text{O}$.

180 °C, whereas the mono adduct is the most stable: 197 °C.

Taking into account that the 3amt mono adduct is thermally more stable than the 4amt mono adduct, and also the proposed coordination features (schematically illustrated in Fig. 6), it is supposed that the copper–nitrogen bond lengths are larger in the 4amt adduct than in the 3amt adduct.

For the 2mct adducts, it is worth noting that the temperature of the release of water molecules (all are hydrated) are higher the greater the number of water molecules. Hence, the adducts with 1, 2 and 2.5 water molecules start the release of water molecules at 62, 128 and 133 °C, respectively. Thus, two hypotheses can be proposed: a larger number of water molecules favours a structure in which they are closer to the metal cation and then strongly bonded to it and/or hydrogen bonds are formed between the water molecules and the ligand molecules in such a manner that a larger number of water molecules signifies a greater number of hydrogen

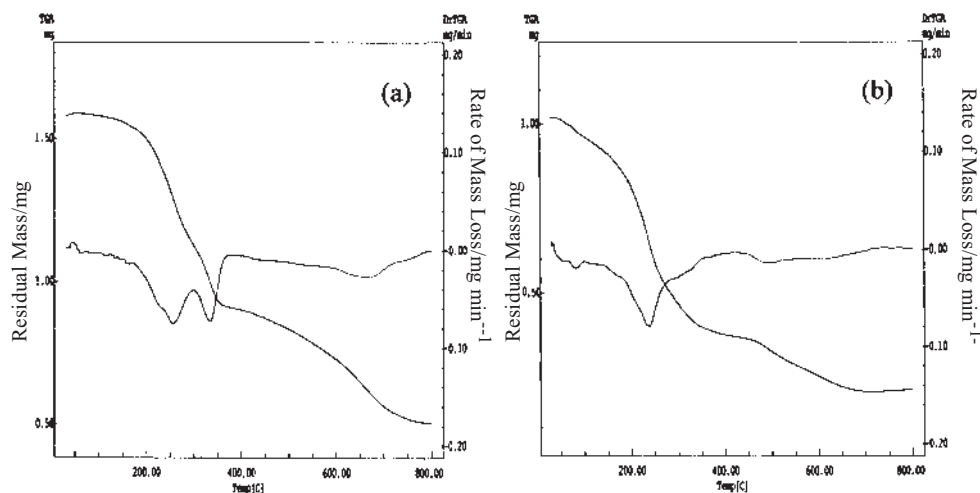


Fig. 10. Thermogravimetric (TG) and differential TG (DTG) curves for: (a) $\text{CuCl}_2 \cdot 2(2\text{mcp})$ and (b) $\text{CuCl}_2 \cdot 2(2\text{mcp}) \cdot \text{H}_2\text{O}$.

bonds and hence a stronger bond strength and thermal stability of the water molecules.

For the 2mcp compounds, it was also verified that the mono adduct is thermally more stable than the bis adducts. The temperature for the commencement of the release of ligand molecules were 173 and 156 °C, respectively.

CONCLUSIONS

(a) In comparison with 3amp, 4amp has a higher capability to act as a bridging ligand.

(b) For all compounds the mono adducts are thermally the most stable. This is in agreement with the hypothesis that both the ionic and covalent character of the metal–ligand bond are higher in these compounds, since only one ligand interacts with the metal cation (Lewis acid), provoking both the most intense positive–negative charge interactions and the most effective overlap of the metal–ligand frontier orbitals.

(c) For the hydrated 2mct adducts, the temperature of release of water molecules is higher the greater the amount of water. Hence, two hypotheses can be proposed: a larger number of water molecules favours a structure in which they are closer to the metal cation and strongly bonded to it and/or hydrogen bonds are formed between the water molecules and the ligands.

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ИЗВОД

СИНТЕЗА, КАРАКТЕРИЗАЦИЈА И ТЕРМОГРАВИМЕТРИЈСКО
ПРОУЧАВАЊЕ Cu(II) АДУКАТА СА 3- И 4-АМИНО-1,2,4-ТРИАЗОЛОМ,
2-МЕРКАПТОТИАЗОЛИНОМ И 2-МЕРКАПТОПИРИДИНОМ

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Адукти CuCl₂·(3amt), CuCl₂·2(3amt)·2H₂O, CuCl₂·3(3amt), CuCl₂·(4amt), CuCl₂·2(4amt), CuCl₂·3(4amt)·2H₂O, CuCl₂·(2mct)·H₂O, CuCl₂·2(2mct)·2,5H₂O, CuCl₂·3(2mct)·2H₂O, CuCl₂·(2mcp) и CuCl₂·2(2mcp)·H₂O, где је 3-амино-1,2,4-триазол = 3amt, 4-амино-1,2,4-триазол = 4amt, 2-меркаптотиазолин = 2mct и 2-меркаптопиридин = 2mcp су синтетисани поступком у чврстом стању и окарактерисани C, H, N елементалном анализом и инфрацрвеном спектроскопијом. Такође је изведено термогравиметријско проучавање. Потврђено је да 4амр молекула има израженију тежњу да буде мостовни лиганд него 3амр. Сем тога нађено је да су моно адукти за сва једињења најстабилнији са термичке тачке гледишта. Ова чињеница је сагласна са већим јонским и ковалентним карактером метал-лиганд везе за таква једињења.

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