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Synthesis, characterization, and thermal analysis of ternary complexes of nitrilotriacetic acid and alanine or phenylalanine with some transition metals

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Abstract Ternary complexes of Co(II), Ni(II), Cu(II), and Zn(II) with nitrilotriacetic acid as a primary ligand and alanine or phenylalanine as secondary ligand were prepared in slightly acidic medium. The structures of the complexes were elucidated using elemental, IR, molar conductance, magnetic moment, UV–Vis spectrophotometry, and thermal analyses. The ternary complexes were isolated in 1:1:1 (M:HNTA:alaH) ratios, and the molecular structures were found to be $[M(HNTA)(alaH)(H_2O)_2]$. Thermogravimetric analysis confirmed this structure and that the water present is coordinated to the central metal atom. UV–Vis spectra showed that the complexes have octahedral symmetry.

Keywords Alanine · Mixed-ligand complexes · Nitrilotriacetic acid · Phenylalanine ternary complexes · Thermal analyses

Introduction

Ternary complexes of metal (II) containing nitrogen and oxygen-donor ligands have received much attention recently as they can display exceptionally high stability [1–4]. Ternary complexes have been employed as probes for biological redox centers [5], and study of the structure of model ternary complexes provides information about how biological systems achieve their specificity and stability [6, 7]. Nitrilotriacetic acid (H_3NTA) is saturated aliphatic multicarboxic ligand, and its flexibility is due to the rotation of the single-bonded carbon chains with high specificity for various polyvalent metal ions. The uses of transition metal complexes of iminodiacetic acid and nitrilotriacetic acid (H_3NTA) [8, 9] have been widely adopted in biology, and are gaining increasing use in biotechnology, particularly in the protein purification technique known as Immobilised Metal-ion Affinity Chromatography (IMAC) [10]. Because of the great biological applications, much of the studies on the coordination of (H_3NTA) with transition metal to form binary or ternary complexes have been done in neutral or slightly basic media, where such ligands are the deprotonated acids (NTA^{3-}) [11–14]. Also, because of the flexibility of the NTA^{3-}, it exhibits interesting conformation and coordination versatility to form polymeric structure. It has been noted that the structural characterized divalent d-block metal NTA^{3-} complexes are mainly the mixed ligand [15, 16] except for $\{[CoNa(NTA)(H_2O)_3]\cdot 2H_2O\}_n$ [17], while some trivalent lanthanide [18] and monovalent transition metal [19] complexes are the non-mixed ligand coordination polymers. Recently, an unusual self-complementary self-assembly process, containing Cu(II) and Na(I) ions and NTA^{3-} ligand generated coordination polymer [20]. On the other hand, synthesis of different types of complexes using various amino acids is becoming increasingly important primarily because of the various applications of such complexes in biological fields [21–24]. Study of the thermal decomposition process of various aminoacid complexes is helpful to the understanding of the coordination structure of the complexes [25].

In the previous study, ternary complex of ternary complexes of Co(II), Ni(II), Cu(II), and Zn(II) with nitrilotriacetic acid as a primary ligand and glycine as secondary ligand were prepared and their molecular structures were found to be $[M(HNTA)(glyH)(H_2O)_2]$ [26]. In this study,

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preparation and characterization of ternary complexes of the same metals with nitrilotriacetic acid as a primary ligand and alanine or phenylalanine as secondary ligand in slightly acidic medium will be discussed.

Experimental

Chemicals

All chemicals used in this study are reagent grade. H_3NTA, alanine, and phenylalanine Merk products were used without further purification. $CuCO_3 \cdot Cu(OH)_2 \cdot H_2O$, $NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$, $CoCO_3 \cdot 3Co(OH)_2$, $ZnCO_3 \cdot 2Zn(OH)_2 \cdot H_2O$ B.D.H. products were used.

General procedure for preparation of the (1:1:1) metal nitrilotriacetate alanine and metal nitrilotriacetate phenylalanine ternary complexes

The calculated amounts of metal carbonate, H_3NTA, and alanine or phenylalanine to give the 1:1:1 complex were mixed together in 100 mL of distilled water, and the mixture was heated nearly to boiling. After complete reaction 96% ethanol was added until dense precipitate was obtained. Then after filtration of the precipitate it was washed with alcohol and dried in an oven at 100 °C then placed in the desiccator over night. This procedure was followed for the preparation of all the 1:1:1 complexes.

Potentiometric and conductometric measurements

Determination of the acidity of the prepared complexes was carried out by a potentiometric titration of a given mass of the acid against standard potassium hydroxide solution at 25 ± 0.2 °C using a Fisher pH meter. Conductivity measurements of 10^{-3} M solutions in bidistilled water thermostated at 25 °C were carried out using WTW D-812 Weilheium conductivity meter, model LBR, fitted with a cell model LTA 100.

Instrumentation

All measurements were carried out at the microanalytical laboratories of Cairo University, Ain Shams University and the National Research Center, Cairo. C, H, and N were determined by Vario El Elementar. Co, Ni, Cu, and Zn percentages were determined by atomic absorption spectrometry (AAS), using a Perkin-Elmer AAS 3100. IR spectra of the solid complexes were recorded on a Jasco FTIR-300 E Fourier Transform Infrared Spectrometer, using KBr disks in the range 400–4,000 cm^{-1} and CsI technique in the range 200–630 cm^{-1}. Thermogravimetric analysis was carried out using a Perkin-Elmer 7 series thermal analyzer. The measurements were carried out under nitrogen atmosphere at a heating rate 10 °C min^{-1}. Magnetic susceptibilities of the paramagnetic metal complexes were measured by using a magnetic susceptibility balance Johnson Mtthy, Alfa products; model No MKI at room temperature. The electronic UV–Vis spectra were measured at room temperature on a Jasco model V-550 UV/Vis spectrophotometer. Mass spectra were recorded at 350 °C and 70 eV on a GL/MS finnigan mat SSQ 7000 apparatus.

Results and discussion

Elemental analysis and physical properties

Elemental analyses and physical and chemical properties of the eight complexes are given in Table 1. All the prepared complexes have some common features such as thermal decomposition before melting, effervescence and evolution

Table 1 Elemental analysis, mass spectrometry data, and physical properties of the complexes

Complexes	Color	Molecular mass	*m*/*e*	Magnetic moment	Conductivity/ microS	Elemental analysis found/calc.			
						C/%	H/%	N/%	Metal/%
$[Co(HNTA)(ala)(H_2O)_2]$	Pink	373.18	333	4.08	821	28.22/28.97	5.13/4.86	7.17/7.51	15.68/15.79
$[Ni(HNTA)(ala)(H_2O)_2]$	Green	372.94	373	2.97	717	27.22/28.98	5.10/4.86	6.82/7.57	15.71/15.74
$[Cu(HNTA)(ala)(H_2O)_2]$	Blue	377.79	372	1.85	623	28.00/28.44	5.00/5.26	7.12/7.37	16.48/16.82
$[Zn(HNTA)(ala)(H_2O)_2]$	White	379.66	375	Diam.	594	28.10/28.47	5.04/4.78	7.00/7.38	16.97/17.23
$[Co(HNTA)(pheH)(H_2O)_2]$	Pink	449.27	450	5.0	874	40.10/38.55	4.94/5.18	6.24/5.99	12.93/13.12
$[Ni(HNTA)(pheH)(H_2O)_2]$	Green	449.03	450	3.33	961	39.88/40.12	5.12/4.94	6.19/6.24	12.88/13.07
$[Cu(HNTA)(pheH)(H_2O)_2]$	Blue	453	454	1.7	850	39.15/39.69	4.08/4.89	6.00/6.17	13.91/14.00
$[Zn(HNTA)(pheH)(H_2O)_2]$	White	455.75	453	Diam.	684	39.11/39.53	4.16/4.78	6.00/6.15	14.01/14.35

of carbon dioxide on reaction with sodium bicarbonate. The molecular masses of the eight complexes suggest the presence of two water molecules, Table 1. Comparing the 10 Dq values of the complexes of this study with the literature values of Co, Ni, and Cu octahedral complexes, respectively, it was concluded that the octahedral structure is recommended for the ternary complexes of this study and the two water molecules are coordinated to the metal. The pH values of the solution at which all the complexes under study were crystallized ranged from 2.8 to 4.0. In this pH range $HNTA^{2-}$ and alaH or pheH in their zwitter form predominate. At this pH, $HNTA^{2-}$ has three coordination sites (N and two COO^{-}) while alaH or phenylalanine coordinate in slightly acid medium via its carboxylic oxygen after being converted into the zwitter ion form (H_3N^{+} CH_2COO^{-}). This means that under the reaction condition used in this study, the amino acids coordinated as monodentate ligand. Accordingly, the metal coordinates to four sites and to form an octahedral structure, two water molecules could be coordinated to the metal. The proposed structure of the 1:1:1 complex is thus as shown in Fig. 1. From the proposed structure, there are two ionisable protons, one due uncoordinated COOH group and the other

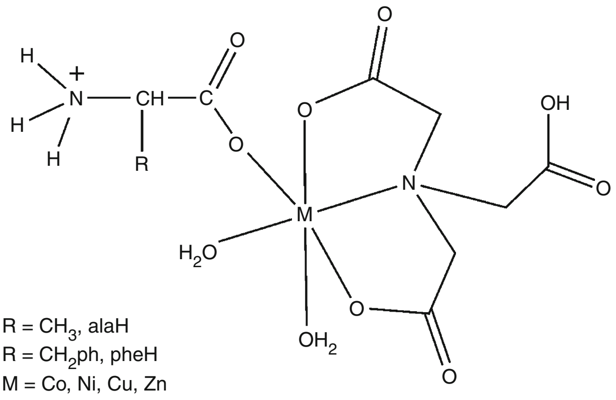

Fig. 1 The proposed structure of the ternary complexes

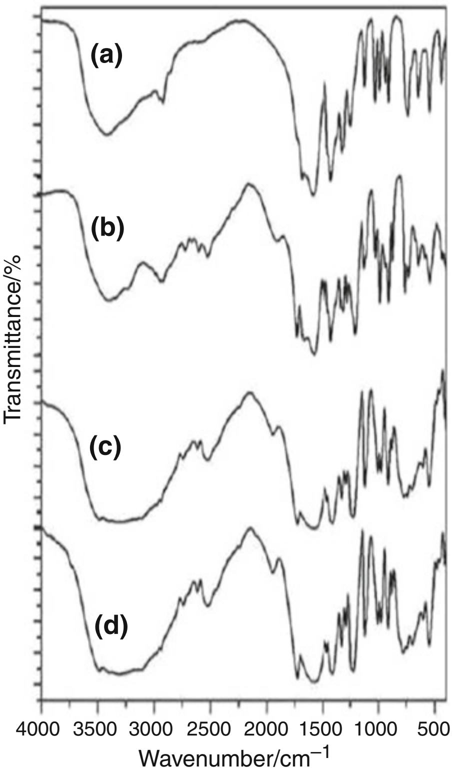

Fig. 2 IR spectra of (*a*) $[Co(HNTA)(ala)(H_2O)_2]$, (*b*) $[Co(HNTA)(pheH)(H_2O)_2]$, (*c*) $[Ni(HNTA)(ala)(H_2O)_2]$, (*d*) $[Ni(HNTA)(pheH)(H_2O)_2]$

Table 2 Infrared data of the ternary complexes

Complex	νOH	νCO	νCOO	νM–O	νM–N
$[Co(HNTA)(alaH)(H_2O)_2]$	3396(m,br)	1734 (s)	1668 (s), 1581 (vs) 1468 (m), 1451 (s) 1425 (s)	298	541
$[Ni(HNTA)(alaH)(H_2O)_2]$	3489 (m)	1729 (s)	1583 (vs), 1463 (m) 1408 (s)	354	547
$[Cu(HNTA)(alaH)(H_2O)_2]$	3588 (m) 3429 (m)	1729 (s)	1653 (s), 1600 (vs) 1409 (s)	350	457
$[Zn(HNTA)(alaH)(H_2O)_2]$	3464 (m)	1731 (m)	1639 1584	304	563
$[Co(HNTA)(pheH)(H_2O)_2]$	3412 (m)	1730 (w, sh)	1685 (s) 1588 (vs) 1424 (s)	285	541
$[Ni(HNTA)(pheH)(H_2O)_2]$	3484 (s, br)	1730 (s)	1587 (vs) 1462 (vs) 1410 (s)	368	548
$[Cu(HNTA)(pheH)(H_2O)_2]$	3589 (s)	1730 (s)	1642 (sh) 1601 (vs) 1407 (s)	357	635
$[Zn(HNTA)(pheH)(H_2O)_2]$	3464 (m)	1728 (m)	1641 (s) 1581 (vs)	468, 359	522

one from the protonated uncoordinated NH_2 group of amino acids used. Potentiometric titrations of the eight acid complexes were carried out for the determination of their acidities. Metal complexes solution was prepared by dissolving the complex in about 20 mL bidistilled water then the volume was then made up to 50 mL by distilled water to give 5×10^{-3} M solutions and titrated potentiometrically against potassium hydroxide solution. As expected the eight prepared complexes showed that they have two ionized protons. The obtained results confirm our structure proposed. In the following sections IR spectra, thermal analysis, mass spectra, and conductivity measurements will be discussed to support the above conclusion about octahedral structure of the complexes.

IR spectra

The IR spectra of the H_3NTA, alanine, phenylalanine, and their metal complexes were carried out in the range of 4,000–400 cm^{-1} and the important bands were listed in Table 2. IR spectra of the cobalt and nickel complexes with H_3NTA and alanine or phenylalanine are shown in Fig. 2. The ir spectrum of nitrilotriacetic acid (H_3NTA) showed bands at 3,041 and 1,733 cm^{-1} which were attributed to υOH with intermolecular hydrogen bonding and undissociated carboxylic groups, respectively. The IR spectra of the ternary complexes with alanine or phenylalanine as secondary ligand exhibited bands 1,728–1,734 cm^{-1}, Table 2, suggesting the presence of non-coordinated free carboxylic group of H_3NTA ligand. On the other hand, the ternary complexes with alanine exhibited new strong absorption at 1668, 1583, 1653 and 1639 cm^{-1} for Co, Ni, Cu and Zn complexes, respectively. These new bands can be assigned to the stretching vibration υ(CO) of the coordinated carboxylate group, COOM [27]. Similar data for phenylalanine ternary complexes were observed with appropriate shift of COOM due to complex formation, Table 2. The IR spectra the free ligands show sharp bands at 1,594 and 1,409 cm^{-1} for alanine and at 1,561 and 1,407 cm^{-1} for phenylalanine assigned for asymmetric and

Table 3 Temperature values for the decomposition along with the species lost in each step

Complexes	Molecular mass	TG range/K	DTG/K	Found/calculated		Assignment
				Mass loss	Total mass loss	
[Co(HNTA)(alaH)(H_2O)$_2$]	373.18	303–503	453.8	18.83/18.3	79.27	$2H_2O + CH_3OH$
		503–873	704.2–833.8	60.47/60.83		Organic compounds
		873–1273	Above 873	20.37/20.12		CoO
[Ni(HNTA)(alaH)(H_2O)$_2$]	372.94	303–563	543.7	19.47/18.3	73.52	$2H_2O + CH_3OH$
		563–673	658.7	54.05/57.66		Organic compounds
		673–1273	Above 673	26.48/23.69		Mix., Ni and NiO
[Cu(HNTA)(alaH)(H_2O)$_2$]	377.79	303–373	357.8	5.2/4.8	77.1	$1H_2O$
		473–773	506–556.4	59.8/61.1		$1H_2O + CH_3OH$ + organic cpd
		773–1173	813–1163	12.1/11.7		CO_2
		1173–1273	Above 1173	22.9/22.6		Mix Cu and CuO
[Zn(HNTA)(alaH)(H_2O)$_2$]	379.66	303–573	168–527	17.4/17.9	76.96	$2H_2O + CH_3OH$
		573–1213	683–1186	59.56/59.8		Organic compounds
		1213–1273	Above 1223	24.04/21.4		Mix., Zn + ZnO
[Co(HNTA)(pheH)(H_2O)$_2$]	449.27	303–513	504.5	28.95/28.93	82.75	$2H_2O$ + phenol
		633–718	669.1–713.62	53.8/54.2		Organic compounds
		718–1273	Above 718	17.25/16.7		CoO
[Ni(HNTA)(pheH)(H_2O)$_2$]	449.03	303–573	562.6	29.21/28.95	82.16	$2H_2O$ + phenol
		673–773	688.19–746.2	52.95/54.1		Organic compounds
		773–1273	Above 773	17.68/16.64		Mix., Ni and NiO
[Cu(HNTA)(pheH)(H_2O)$_2$]	453	303–373	343.6	4.00/3.97	75.54	$1H_2O$
		473–673	503.3	61.3/64.8		$1H_2O$ + phenol + organic cpd
		673–873	796.2	10.24/9.7		CO_2
		873–1273	Above 873	24.46/24.8		Mix Cu and CuO
[Zn(HNTA)(pheH)(H_2O)$_2$]	455.75	303–513	436.3–509.2	27.8/28.5	76.4	$2H_2O$ + phenol
		573–873	614.7–670.8	48.6/48.5		Organic compounds
		873–1273	Above 873	23.6/24.0		CO_2 + Zn

symmetric stretching vibrations of the carboxylate moiety, respectively. These two bands of the free ligands are either shifted to lower or higher frequencies, indicating that these ligands coordinated to the metal ions via deprotonated carboxylate group [28]. On the other hand, the IR spectrum of alanine and phenylalanine showed medium broad bands at 3,087 and 3,135 cm^{-1}, respectively, which attributed to NH_3^+ group of the amino acid. The IR spectra then suggest that in ternary complexes $HNTA^{2-}$ is a tridentate ligand (two $-COO^-$) and (one nitrogen), and that the secondary ligands are monodentate (one $-COO^-$). All the prepared complexes exhibited bands in the range of 3,558–3,412 cm^{-1} signifying that H_2O molecules exist in these complexes. The mass spectra of the complexes support the proposed complexes with the two water molecules coordinated to the central atom to form an octahedral structure.

Further elucidation of the participation of nitrogen and carboxylic groups in $HNTA^{2-}$ and the used amino acids was confirmed by recording the IR spectra of the complexes in the range 200–630 cm^{-1}. The υ(MO) frequencies of NTA^{3-} as ligand are at 343, 347, 380, and 355 cm^{-1} for Co, Ni, Cu and Zn complexes, respectively [29]. Thus one may assign the bands in the complexes in the range 285–468 cm^{-1} for the M–O vibrational frequencies, Table 2. The M–N band frequencies were found in the range 457–563 cm^{-1} for Co, Ni, Cu, and Zn complexes, respectively, Table 2.

Magnetic moments and electronic spectra

The UV–Visible spectra of the metal complexes were carried out in deionized H_2O (10^{-3} mol L^{-1}) solution. For ternary Co(II) complexes, the effective magnetic moment values are 4.08 B.M. and 5.10 B.M. for [Co(HNTA)(alaH)$(H_2O)_2$] and [Co(HNTA)(PheH)$(H_2O)_2$], respectively. These values are higher than spin only moment for three unpaired electrons 3.89 due to a considerable orbital contribution [30]. The UV–Vis spectra of the two complexes show one band at 19,685 cm^{-1} which are assigned to $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transition, assuming an octahedral geometry for Co(II) complex. For ternary Ni(II) complexes, the magnetic moments μ_{eff} of [Ni(alaH(HNTA)$(H_2O)_2$] and [Ni(HNTA)(PheH)$(H_2O)_2$] have values of 2.97 B.M. and 3.3 B.M., respectively, which suggest an octahedral geometry [30]. The electronic spectrum of Ni(II) complexes displays two bands in the range of 15,627 cm and 25,379 cm^{-1} assigned as $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$, respectively. The mixed-ligand complexes of Cu(II) with alaH and pheH showed magnetic moment values, μ_{eff}, in the range 1.77–1.85 B.M. These values correspond to one unpaired electron and thus offer evidence for mononuclear structures of the complexes. The UV–Vis spectrum of Cu(II) complexes consists of a broad band centered at 12,135 cm^{-1} that assigned as $^2E_g \rightarrow {}^2T_{2g}$

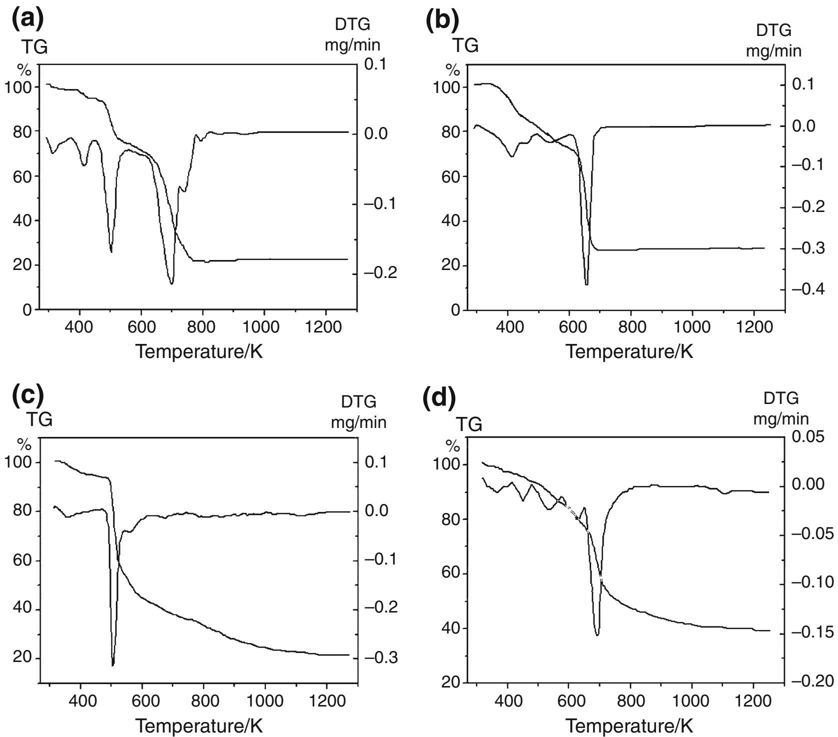

Fig. 3 TG and DTG of ternary complexes: **a** [Co(HNTA)(alaH)$(H_2O)_2$], **b** Ni(HNTA)(alaH)$(H_2O)_2$], **c** [Cu(HNTA)(alaH)$(H_2O)_2$], **d** [Zn(HNTA)(alaH)$(H_2O)_2$]

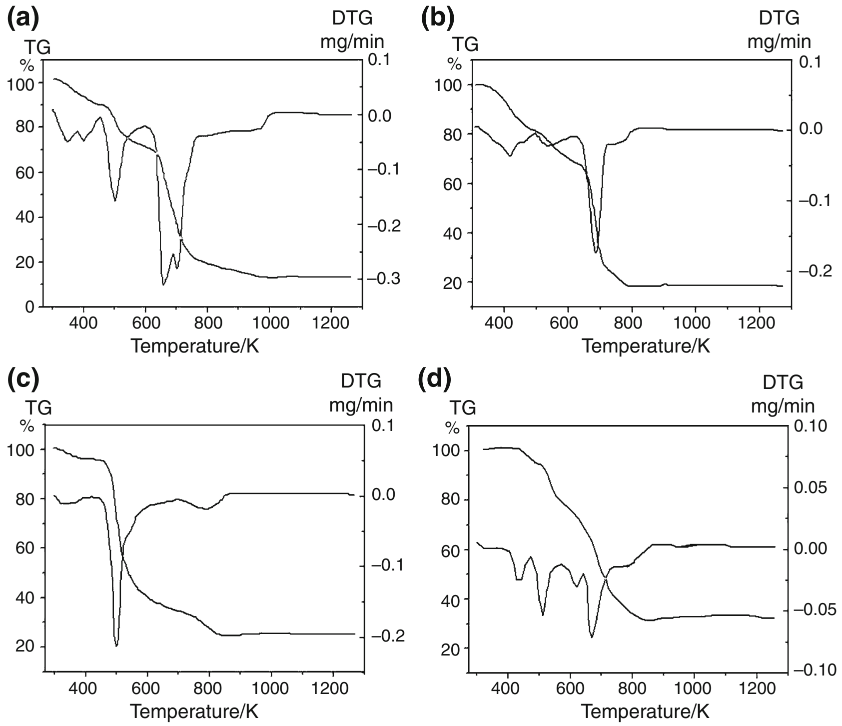

Fig. 4 TG and DTG of ternary complexes: **a** [Co(HNTA)(pheH)(H_2O)$_2$], **b** [Ni(HNTA)(pheH)(H_2O)$_2$], **c** [Cu(HNTA)(pheH)(H_2O)$_2$], **d** [Zn(HNTA)(pheH)(H_2O)$_2$]

transition with expected splitting of these states as a result of tetragonal distortion of the octahedral Cu(II) ion, d^9.

Mass spectra

The mass spectra of the eight complexes were recorded. All the spectra contain molecular ion peaks confirm the molecular mass of the complexes. The data are presented in Table 1.

Thermal analysis

Thermogravimetric analyses of our complexes were carried out under nitrogen atmosphere. The results are shown in Table 3 and Figs. 3, 4. Interpretation of the thermal mass losses shows that the complexes thermally decompose in the same patterns exhibited by the parent ligands. It was shown that H_3NTA thermally decompose in two overlapping steps [26], into glycine and maleic acid. Both thermal products, on further heating, decompose giving organic residue overlapping steps. The first mass loss in our complexes was found to be equivalent to the water molecules which supported our suggested structure for these prepared complexes and methyl alcohol or phenol with respect to aniline or phenylalanine [31] in which their decomposed temperatures are very close to the coordinate water temperature decomposition. It may be observed from (Table 3) that the final thermal decomposition residue is mixture of metal and metal oxide or metal oxide although thermal decomposition was made under nitrogen atmosphere [32].

Conclusions

The Co, Ni, Cu, and Zn nitrilotriacetic acid and aniline or phenylalanine ternary complexes prepared in slightly acidic medium have an octahedral structure of the general form [M(HNTA)(alaH)(H_2O)$_2$] and [M(HNTA)(PheH)(H_2O)$_2$], in which nitrilotriacetic acid acts as a tridentate ligand and alanine or phenylalanine acts as a monodentate ligand. Two coordinated water molecules are required to complete octahedral coordination. These complexes, thus, behave as dibasic acids.

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