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PREPARATION, CHARACTERIZATION AND THERMAL STUDIES OF SOME TRANSITION METAL TERNARY COMPLEXES

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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 in slightly acid medium. Their molecular masses were determined by acid-base titration against standard potassium hydroxide solution. Their molecular structures were found to be [M (HNTA)(glyH)(2H_2O)]. 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. IR spectra suggested the presence of intermolecular hydrogen bonding. This phenomenon was supported by mass spectra. The ionization constants of these complexes, as diprotic acids, were determined.

Keywords: *glycine, nitrilotriacetic acid, ternary complexes, thermogravimetric analysis*

Introduction

Many authors investigated coordination compounds due to their chemical, biological, environmental, ion-exchange and catalytic importance [1–5]. Recently, considerable attention has been devoted to the study of mixed-ligands complexes of metal(II) containing nitrogen donor ligands [6–9]. While structural analysis of ternary complexes containing amino acids or peptides is difficult, X-ray diffraction has been used to structurally characterize a limited number of ternary complexes containing NTA [10]. Only a few structures of the general form [M(NTA) (amino acid)] have been reported [11–13].

Ternary metal complexes have been recently studied due to their ability as metal systems for metal–protein complexes such as metallo-enzymes. They received particular attention and have been employed in mapping protein surfaces [14], as probes for biological redox centers [15] and in protein capture for both purification [16] and study [17, 18]. Study of the structure of model ternary complexes provides information about how biological systems achieve their specificity and stability, as well as strategies to improve these features for biotechnological applications.

Ternary metal complexes of nitrilotriacetic acid (NTA) have been widely adopted in biology and are gaining increasing uses in biotechnology, particularly in protein purification techniques known as immobilized metal ion affinity chromatography (IMAC) [19]. Nitrilotriacetic acid has gained, recently, popularity as metal chelator in IMAC. Other studies of mixed ligand NTA is characterization of thorium–ethylenediaminetetraacetic acid complex which was investigated by electro spray ionization-mass spectrometry (ESI-MS) [20].

The formation constants of the four ternary complexes of the present work were determined by Hopgood and Augelici [21] and were found to be 3.65, 4.95, 5.42 and 3.64 for the Co, Ni, Cu and Zn complexes, respectively.

In an effort to improve our understanding of the interaction between NTA, metal ions used in IMAC and glycine, the present study on the synthesis and the characterization of ternary complexes of Co(II), Ni(II), Cu(II) and Zn(II) with NTA as a primary ligand and the biologically important ligand glycine, as a secondary ligand is conducted.

Experimental

Materials

All chemicals used in the present study are reagent grade. Nitrilotriacetic acid, Merk product was used without further purification. Glycine, $CoCl_2\cdot6H_2O$, $NiSO_4\cdot7H_2O$, $CuSO_4\cdot5H_2O$ and $ZnSO_4\cdot7H_2O$, B.D.H. products were used.

Preparation of the (1:1:1) metal nitrilotriacetate glycine complexes

Two solutions were prepared, the first contains 10^{-3} mole of the metal salt; 23.793, 26.250, 24.968 or 24.968 mg of Co, Ni, Cu or Zn salts in 100 mL water

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and the second one containing a mixture of 10^{-3} mole glycine (7.511 mg) and 10^{-3} mole nitrilotriacetic acid (19.1 mg) in 100 mL water. The two solutions were mixed and heated nearly to boiling to ensure complete reaction. The solution was left on a water bath until the volume was reduced to about 50 mL. The solution was then left to cool to room temperature. Crystals of the 1:1:1 complexes were separated, filtered and washed with ethyl alcohol followed by ether and then kept in a vacuum desiccator over anhydrous $CaCl_2$.

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 discs in the range 400–4000 cm^{-1} and CsI technique in the range 200–500 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.

Solubility

The solubility of the prepared complexes was determined by shaking few mg of the complex with about 50 mL aliquots of distilled water in a water thermostat at 25°C±0.2 for about 3 h. The suspension was rapidly filtered and measured aliquots of the filtrate titrated against standard potassium hydroxide solution using phenolphthalein as indicator.

Potentiometric and conductometric measurements

Determination of the ionization constants 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 according to the method described by Albert and Serjeant [22].

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.

Results and discussion

Elemental analysis and physical properties

Elemental analyses and physical and chemical properties of the four complexes are given in Table 1 The four

Table 1 Elemental analysis, physical and chemical properties of the acid complexes

		Co(HNTA)(glyH)$(H_2O)_2$	Ni(HNTA)(glyH)$(H_2O)_2$	Cu(HNTA)(glyH)$(H_2O)_2$	Zn(HNTA)(glyH)$(H_2O)_2$
Metal/%	Cal.	16.400	16.360	17.400	17.810
	Found	16.000	16.000	17.000	17.400
C/%	Cal.	26.740	26.780	26.460	26.300
	Found	27.000	26.700	26.470	26.280
H/%	Cal.	4.460	4.460	4.400	4.380
	Found	4.180	4.270	4.460	4.690
N/%	Cal.	7.800	7.810	7.700	7.670
	Found	7.240	7.230	7.690	7.500
Solubility in H_2O/g L^{-1}		3.657	5.256	2.468	19.754
Decomposition temperature/°C		245.0	260.0	265.0	210.0
Molecular mass		359.0	358.5	363.5	365.0
Magnetic susceptibility/B.M.		5.384	3.342	1.883	diamagnetic
Conductivity of 10^{-3} M solution/mS		3.000	2.800	3.100	2.600
Colour		pink	green	blue	colourless
Ionization constants/	pka_1	2.407	2.489	2.499	2.257
	pka_2	4.423	6.810	5.326	5.172

complexes prepared have some common features such as low solubility in water, thermal decomposition before melting, effervescence and evolution of carbon dioxide on reaction with sodium bicarbonate. Use was made from their quantitative reaction with sodium hydroxide in determining their molecular masses. The molecular masses of the four complexes suggest the presence of two water molecules. If these two molecules are crystal water, the complex should have a tetrahedral structure, Fig. 1a, while if the two water molecules are coordinated to the central atom, then the complex should have an octahedral structure, Fig. 1b. On comparing the 10 Dq values of the complexes of this study which were found to be 20400, 12615 and 12200 cm^{-1} with 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.

The pH values at which all the complexes under study were crystallized ranged from 3 to 4.5. In this pH range $HNTA^{2-}$ and glyH predominate. This is shown in the distribution curves of the two ligands concerned, Fig. 2 $HNTA^{2-}$ has three coordination sites while glycine coordinates in slightly acid medium via its carboxylic oxygen after being converted into the zwitter ion form ($H_3N^+CH_2COO^-$). The structure of the 1:1:1 complex is thus as shown in Fig. 1b.

Different tools were utilized to support the above conclusions regarding the octahedral structure of these complexes. These tools are thermal analysis, IR and mass spectra and conductivity measurements.

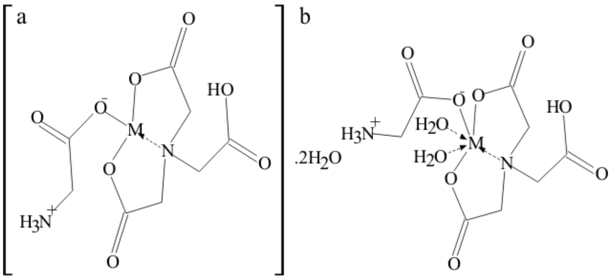

Fig. 1 The two expected structures of the four complexes; a – tetrahedral structure, b – octahedral structure

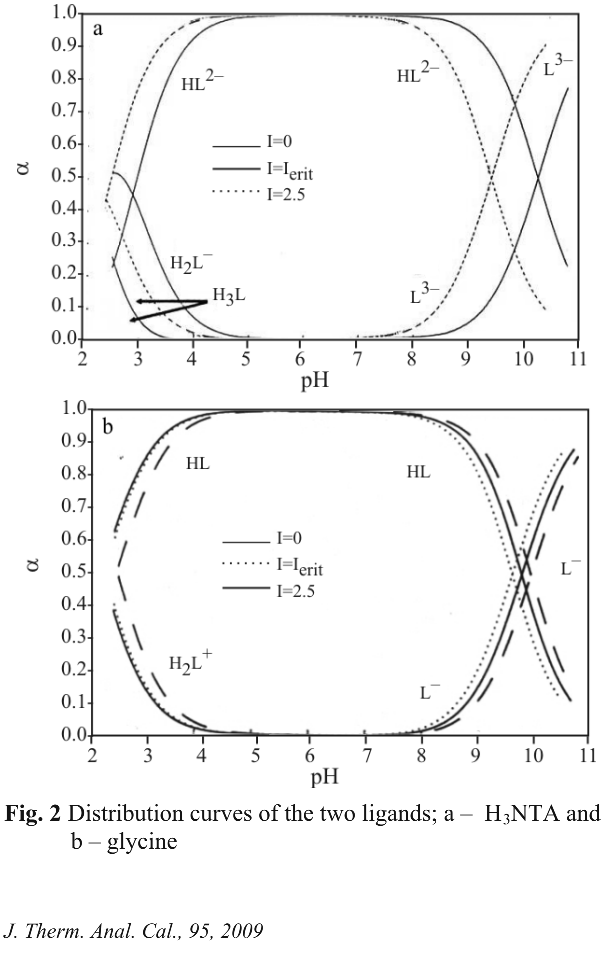

Fig. 2 Distribution curves of the two ligands; a – H_3NTA and b – glycine

Thermal analysis

Thermogravimetric analysis of the four complexes were carried out Figs 3–6. The results are shown in Table 2. Interpretation of the thermal mass losses shows that the complexes thermally decompose, in the same pattern

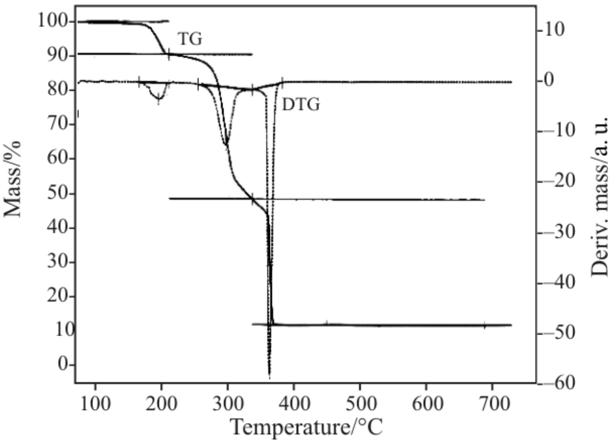

Fig. 3 TG and DTG of cobalt complex

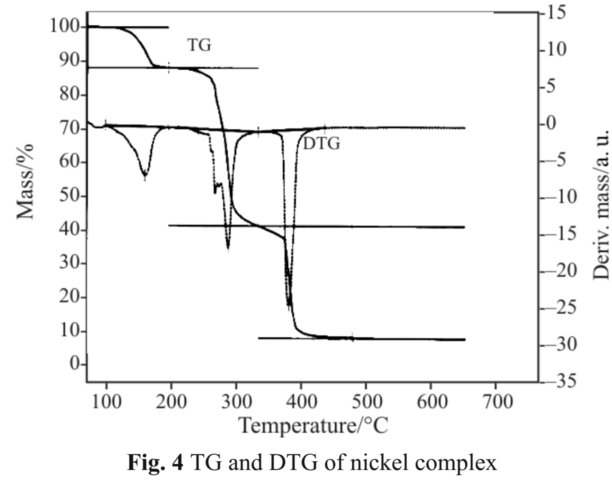

Fig. 4 TG and DTG of nickel complex

Table 2 Temperature values for the decomposition along with the species lost in each step

Complex	Temperature/°C	Mol. mass	Mass loss/%		Significance
			Cal.	Found	
$Co(HNTA)(Hgly)(2H_2O)$	177	358.900	10.000	11.509	$2H_2O$
	370		74.100	76.665	2glycine+maleic acid
	Above 370		16.430	11.826	mixture Co and CoO
$Ni(HNTA)(Hgly)(2H_2O)$	210	358.700	10.020	9.434	$2H_2O$
	379		74.090	78.124	2glycine+maleic acid
	379		46.400	12.442	mixture Ni and NiO
$Cu(HNTA)(Hgly)(2H_2O)$	206	363.500	9.900	10.308	$2H_2O$
	570		73.100	71.879	2glycine+maleic acid
	Above 570		17.460	17.813	residue Cu
$Zn(HNTA)(Hgly)(2H_2O)$	206	650.000	30.410	30.609	$2H_2O$+glycine
	650		52.320	52.520	glycine+maleic acid
	Above 650		17.800	16.871	residue Zn

exhibited by the parent ligands. It was shown that H_3NTA thermally decompose in two overlapping steps, [23] into glycine and maleic acid. Both thermal products, on further heating, decompose giving CH_3NH_2, CO_2, C_2H_4, C_2H_2 and CO. The first mass loss in the four complexes was found to be equivalent to two water molecules which supported our suggested structure for these prepared complexes.

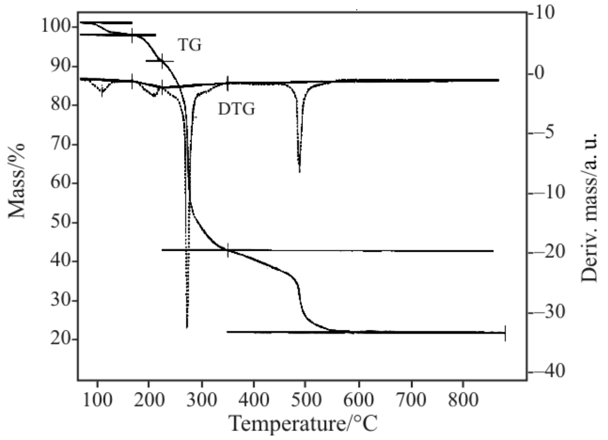

Fig. 5 TG and DTG of copper complex

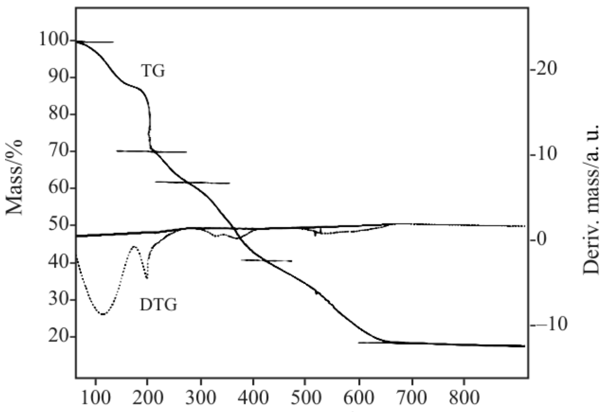

Fig. 6 TG and DTG of zinc complex

It may be observed from Table 2 that the final thermal decomposition residue is the metal alone as in case of Cu and Zn complexes. It may be noted that thermal decomposition was made under nitrogen atmosphere and that almost all gaseous products were reducing gases, (CO, C_2H_4 and C_2H_2). In case of Co and Ni complexes the percentage of the residue is less than the calculated value corresponding to the full decomposition to the metal so there must be some oxide left.

IR spectra

IR spectra of the two ligands and those for the four complexes are given in Figs 7 and 8. Assignments of the frequencies of the vibrational bands are given in Table 3. It may be observed that one can discuss the structure of these complexes in the light of the infrared spectra obtained for the carboxylate group both in nitrilotriacetic acid and in metal complexes. For the four complexes, two very strong bands are observed in the region 1739–1560 cm^{-1}. The first band is observed at 1734, 1739, 1737 and 1731 cm^{-1} for Co, Ni, Cu and Zn complexes, respectively. This

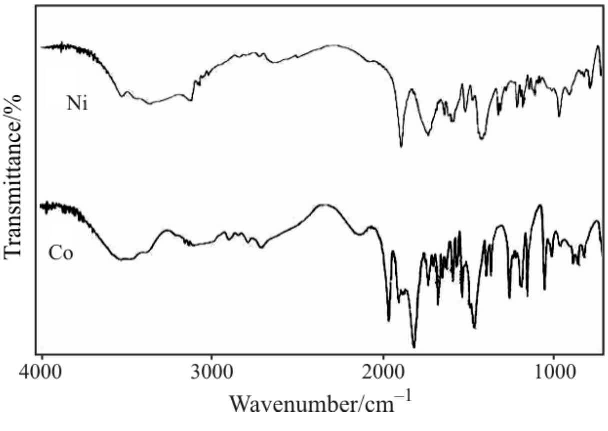

Fig. 7 IR spectra of cobalt and nickel complexes

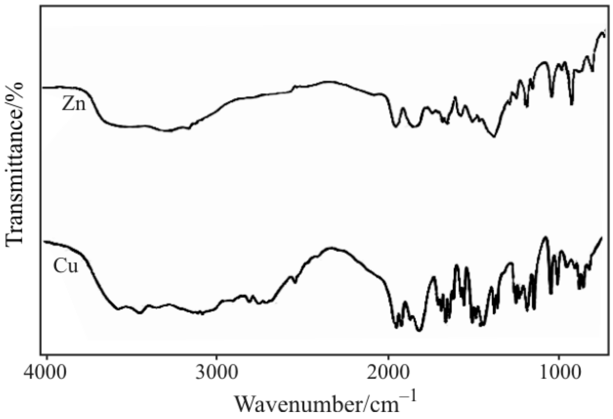

Fig. 8 IR spectra of copper and zinc complexes

band is also observed at 1730 cm^{-1} in the spectrum of the free acid where the absorption band of the free carboxylic acid group is expected [24, 25]. The other band which appeared as very strong absorption at 1671, 1560, 1593 and 1614 cm^{-1} for the Co, Ni, Cu and Zn complexes, respectively is not observed in the spectrum of the free H_3NTA and can be assigned to stretching vibration ν_{CO} of the coordinated carboxylate group, COOM [26]. From these observations, it is clear that in these four complexes, one or more of the free carboxyl groups do not coordinate with the central metal ion and remain as free carboxylic acid and the suggested structure, [M(HNTA) (glyH)], is justified.

The ν_{MO} frequencies of copper and nickel complexes with glycine as a ligand are at 360, 290 cm^{-1}, respectively [27]. In the prepared complexes these two bands appeared at 343 and 285 cm^{-1}. Thus one may assign the bands at 279 cm^{-1} for the copper complex and at 274 cm^{-1} for the nickel complex to the M–O vibrational frequencies between these two metals and oxygen of nitrilotriacetic acid. In a similar way, the M–N frequencies for Cu and Ni glycinate, in basic medium, were found at 439 cm^{-1} [27]. In the present study the bands at 469 and 403 cm^{-1} may be assigned to the vibrational frequencies of Cu–N and Ni–N bands. By analogy the M–O and M–N bands for the Co and Zn complexes are those at 365 and 565 cm^{-1} for cobalt and at 257 and 593 cm^{-1} for zinc.

The infrared spectra of the four complexes exhibit a crowded region between 3600–2900 cm^{-1}, where H_2O, –OH and –NH are expected to absorb. The broad band in the range 3300–3400 cm^{-1} appearing in all the spectra of the four complexes is assigned to the probable intermolecular hydrogen bonding (O…H–O, O…H–N, O–H…N) which explains the low solubility of these complexes in water (Table 2). Such probable hydrogen bonding is shown in Fig. 9. Intermolecular hydrogen bonding will result into the formation of different structures including mononuclear or polynuclear molecules, one dimensional chain, two dimensional and three dimensional networks.

Mass spectra

The mass spectra of the four complexes were recorded. It may be observed that all the spectra contain molecular ion beams exceeding the molecular masses of the complexes, Table 3. Such a phenomenon strongly supports our assumption that all these complexes contain intermolecular hydrogen bonds, Fig. 9.

Ionization constants

Potentiometric titrations of the four acid complexes were carried out for the determination of ionization constant of such complexes. The metal salt, nitrilotriacetic acid and glycine were mixed in 1:1:1 molar ratio in about 20 mL bidistilled water then the solution was warmed

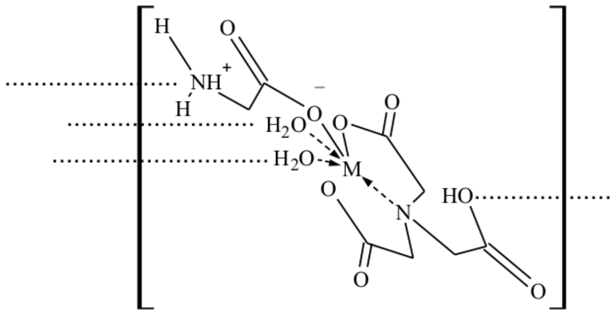

Fig. 9 Probale H-bond sites in the ternary complexes

Table 3 Assignments of the IR bands in cm^{-1} and *m/e* values of the mass spectra exceeding the molecular masses of the prepared complexes

Complex	ν_{OOH}	ν_{OOM}	$\nu_{M–O}$	$\nu_{M–N}$	*m/e*
Co(HNTA)(Hgly)($2H_2O$)	1734	1671 1490	365	565	497
Ni(HNTA)(Hgly)($2H_2O$)	1739	1560 1460	285	403	512, 408
Cu(HNTA)(Hgly)($2H_2O$)	1737	1593 1450	343	469	491
Zn(HNTA)(Hgly)($2H_2O$)	1730	1614 1435	257	593	378, 428, 505

to ensure that the reaction is complete. The volume was then made up to 50 mL by distilled water to give $5\cdot10^{-3}$ M solutions, the temperature was adjusted to 25°C±0.2 and the solution titrated potentiometrically against potassium hydroxide solution. As expected the four prepared complexes showed two ionization constants. The obtained results confirm our assumption. These results are shown in Table 1.

Conclusions

The Co, Ni, Cu and Zn nitrilotriacetic acid and glycine ternary complexes prepared in slightly acidic medium has an octahedral structure of the general form M (HNTA) (HGly) ($2H_2O$) in which nitrilotriacetic acid acts as a tridentate ligand and glycine acts as a monodentate ligand. Two coordinated water molecules are required to complete octahedral coordination. These complexes, thus, behave as dibasic acids. Intermolecular hydrogen bonding between the suggested octahedral units leads to the formation of a polymeric structure.

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