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Spectroscopic and Thermal Behaviour of Complex Compounds Useful for Magnesium Supplementation

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SUMMARY. We present the synthesis of three Mg(II) complexes potentially useful for magnesium supplementation in human and veterinary medicine: magnesium chloro-aspartate, $Mg(C_4H_6O_4N)Cl.3H_2O$; magnesium citrate, $[Mg(H_2O)_6][MgC_6H_5O_7(H_2O)]_2.5H_2O$, and magnesium orotate, $[Mg(C_5H_3O_4N_2)_2].8H_2O$. These compounds were characterized by IR and Raman spectroscopy and their thermal behaviour was investigated by means of thermogravimetric measurements and differential thermal analysis, working in oxygen atmosphere.

RESUMEN. "Comportamiento Espectroscópico y Térmico de Compuestos Complejos Utiles para la Suplementación de Magnesio". Se presenta la síntesis de tres complejos de Mg(II) potencialmente útiles para la suplementación de este elemento en medicina humana y veterinaria: cloro-aspartato de magnesio, $Mg(C_4H_6O_4N)Cl.3H_2O$; citrato de magnesio, $[Mg(H_2O)_6][MgC_6H_5O_7(H_2O)]_2.5H_2O$; y orotato de magnesio, $[Mg(C_5H_3O_4N_2)_2].8H_2O$. Estos compuestos se caracterizaron a través de sus espectros de IR y Raman y su comportamiento térmico fue investigado por termogravimetría y análisis térmico diferencial, trabajando en corriente de oxígeno.

INTRODUCTION

Magnesium is the second most common intracellular electrolyte and the fourth most abundant cation in the human body [1,2]. Although it cannot be considered as a trace metal for the higher organisms, in recent years a number of disorders and diseases clearly related to hypomagnesemia could be established [3,4]. On the other hand, in certain geographic regions the low levels of Mg(II) generate a series of well known disorders in ruminants and other animals [5,6].

These situations prompted the search of systems adequate for magnesium supplementation in both human and veterinary medicine, and magnesium therapy has become an important issue in contemporary medicine and pharmacology [3,7].

One of the most relevant questions arising in this context is to find optimal routes for magnesium administration. This implies a selection of complex compounds or salts which lead to a rapid and efficient resorption of Mg(II) without upsetting the pH or the ionic equilibria in body fluids. Possible side effects arising from the anionic and/or ligand components of the proposed systems should also be minimized.

Different Mg(II) complexes have been proposed in recent years for the supplementation of this element [3,7]. One of them, magnesium-L-hydrogenaspartate chloride trihydrate, Mg(L-HAsp) $Cl.3H_2O$, which allows oral administration, has awaken great medical interest because it presents a potentially broad range of therapeutic activity [7,8].

As part of a research project devoted to the physicochemical characterization of new inorganic medicines we have initiated some work

KEY WORDS: Mg(II) complexes, Mg-supplementation, IR and Raman spectra, Thermal Behaviour.
PALABRAS CLAVE: Complejos de Mg(II), Suplementación de Mg, Espectros de IR y Raman, Comportamiento Térmico.

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with systems potentially useful for Mg(II) supplementation. In this paper, we present the results obtained with the above mentioned aspartate complex, as well as with recently characterized Mg(II) complexes of citric and orotic acid.

EXPERIMENTAL

Synthesis of the complexes

1. Mg(L-HAsp)Cl.3H$_2$O. This compound can be obtained from aqueous solutions containing the components Mg^{2+}, HAsp- and Cl- in the molar ratio 1:1:1 [7, 9]. In our preparations we used MgO as the magnesium source and HCl as the chloride source. In a typical synthesis procedure 2.015 g of MgO together with 6.65 g of L-aspartic acid were suspended in a small volume of distilled water and immediately 4.15 ml of concentrated HCl were dropwise added. After completion of the acid addition a clear solution is obtained. The isolation of the complex compound can be achieved by spray-drying of these solutions [7, 9]. On the other hand, we have found that the complex can also be easily precipitated by addition of an excess of methanol to the aqueous solution. In this last case, the precipitated complex was kept in contact with the hydroalcoholic solution during one or two days and then filtered off. After washing with cold metha-nol, it was dried in vacuum over H_2SO_4.

2. [Mg(H$_2$O)$_6$][MgC$_6$H$_5$O$_7$(H$_2$O)]$_2$.5H$_2$O. An aqueous solution (30 ml) containing $Mg(CH_3COO)_2.4H_2O$ and citric acid in the molar ratio 3:2, was slowly heated up to 85 °C on a water bath, and an excess of propanol was added in order to produce two phases. Crystals of the complex grew in the liquid interface and finally deposited in the bottom of the vessel [10]. We have made experiences using 1-propanol and 2-propanol as the layering solvent and found that with 2-propanol crystallization occurs faster and crystalline quality is improved.

3. [Mg(C$_5$H$_3$O$_4$N$_2$)$_2$].8H$_2$O. A suspension of 0.031 g of $Mg(OH)_2$ in 40 ml of water is slowly neutralized with 0.186 g of orotic acid (6-uracilic acid) at room temperature. The obtained clear solution was concentrated in vacuum, and the complex crystallizes after cooling [8, 11]. It is filtered off, washed with small portions of water and dried in air.

Spectroscopic measurements

Infrared spectra were recorded with a Perkin Elmer 580 B spectrophotometer, using the KBr pellet technique. Raman spectra were obtained with a Bruker IFS 66 FTIR instrument provided with a FRA 106 Raman accessory. The samples were excited with the 1064 nm line of a solid state Nd:YAG laser.

Thermal analysis

Thermogravimetric (TG) and differential thermal analysis (DTA) were performed on a Shimadzu thermoanalytical system (models TG-50 and DTA-50, respectively), working with Pt crucibles in an oxygen flow (60 ml/min) and at a heating rate of 5 °C/min. Sample quantities ranged between 10 and 15 mg. Al_2O_3 was used as a DTA standard.

RESULTS AND DISCUSSION

Vibrational spectra

Mg(L-HAsp)Cl.3H$_2$O

The three compounds were characterized by means of their IR spectra and assignments compatible with the structural characteristics are proposed. When possible, in certain spectral ranges the assignments were additionally supported by Raman data.

The structure of the Mg(II)-L-hydrogenaspartate chloride trihydrate has been recently solved [9]. It is formed by polycationic layers of composition $[Mg(L\text{-}HAsp)(H_2O)_2]_n^+$ and intercalated H_2O molecules and Cl^- ions. In the complex units the Mg(II) ions present octahedral coordination, with $HAsp^-$ acting as bidentate ligands, through their carboxylate groups, two H_2O molecules and two carbonyl oxygen atoms from neighboring complexes. The amino group is protonated and has not contact with the metal cation [3, 9].

As expected, both the spry-dried and the precipitated samples are completely X-ray amorphous [9]. This behaviour is also reflected in the quality of the spectral information. The IR spectra of these products show rather broad and ill defined bands whereas their Raman spectra presented only very weak and undefined signals. Notwithstanding, the middle part of the IR spectrum, depicted in Fig. 1, can be used for the characterization of the compound.

The proposed assignment of the complete spectrum is shown in Table 1. This assignment is based on some general literature references [12-15] and on the results of some recent investigations of other amino acid complexes [16, 17].

The very strong and broad band located be-

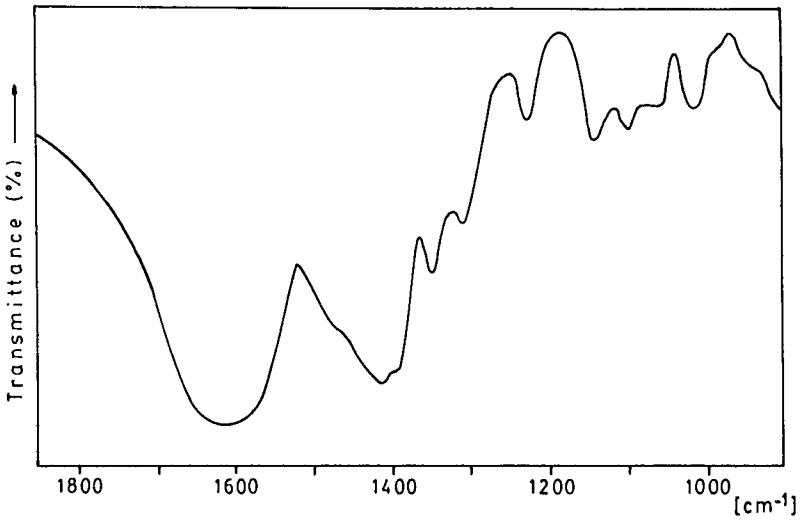

Figure 1. Infrared spectrum of $Mg(HAsp)Cl.3H_2O$ between 1850 and 900 cm^{-1}.

Band position (cm^{-1})	Assignment
3400 vs, br; 3240 sh	ν(O-H), ν(N-H)
1620 vs, br; 1580 sh	ν(C=O)
1500 sh; 1420 vs; 1400 sh	ν(C-O)
1351 m	CH_2-wag + ν(C-CO_2)
1314 w; 1233 s	δ(CH) + δ(CH_2)
1144 s	ν(C-CO_2)
1102 m	
1063 m; 1012 s	ν(C-N)
905 sh; 855 w; 816 w	
665 s	CO_2-rock + NH_3^+-rock
534 m, br	ρ(H_2O)
368 s, br	ν(Mg-O)

Table 1. Assignment of the IR spectrum of $Mg(HAsp)Cl.3H_2O$. *vs:* very strong; *s:* strong; *m:* medium; *w:*weak; *br:* broad; *sh:* shoulder.

tween 3600 and 3150 cm^{-1} includes the stretching vibrations of the water molecules and of the protonated amine residue, $-NH_3^+$. Their bending vibrations are overlapped by the strong and broad carboxylate bands centered at 1620 and 1420 cm^{-1}.

In the low frequency region we have tentatively assigned one rocking vibration of the bounded water molecules (534 cm^{-1}). In aquo complexes of divalent cations this band is usually found in this spectral range [18] whereas in $[Mg(H_2O)_6]^{2+}$ it lies at 460 cm^{-1}. In this region we have also assigned the 368 cm^{-1} to one of the Mg-O stretching motions.

$[Mg(H_2O)_6][MgC_6H_5O_7(H_2O)]_2.5H_2O$

In the case of the Mg(II) complex of citric acid, and as shown by the chemical analysis and by the thermal behaviour, we could isolate a pentahydrate, instead the dihydrate originally described in the literature. The crystallographic study of this complex, which belongs to the monoclinic $P2_1/n$ space group with Z = 2, showed that the Mg(II) cations are only partially present as a true citrate complex [10]. The constitution can be described by the formula $[Mg(H_2O)_6]^{2+}$. $2[MgC_6H_5O_7(H_2O)]^-.nH_2O$[7] because each citrate chelates to one Mg(II) ion as a tridentate ligand, through one end car-

boxylate group, the central carboxylate group and the hydroxyl oxygen and bridges two other magnesium atoms with its remaining carboxyl group. This leads to an extended chelated strip with double bridging between magnesium ions and the remaining Mg(II) ion is present as an hexaaquo complex which is hydrogen bonded to the chelated strips[10].

The IR spectrum of this compound, in the spectral range between 1850 and 250 cm^{-1}, is shown in Fig. 2 and the assignments proposed for the most important and characteristic vibrational modes is given in Table 2. As in the former case, the same is based on some general references [12-14] complemented with more specific data, obtained partially from recent studies of our laboratory [19-22]. Some general comments on these assignments, and some additional data

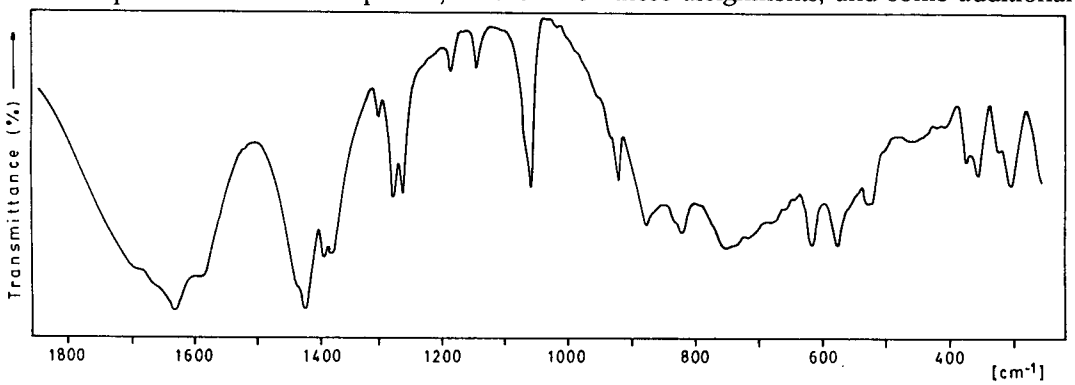

Figure 2. Infrared spectrum of the Mg-citrate complex between 1850 and 250 cm^{-1}.

Band position (cm^{-1})	Assignment
3490-3210 vs, br	ν(O-H)
1694 sh	
1632 vs	ν(C=O) + ν_{as}(COO$^-$) + δ(H_2O)
1591 sh	
1436 sh	δ_{scis}(CH_2)
1426 vs	
1396 m	ν_s(COO$^-$) + δ(C-OH) + δ_w(CH_2)
1383 m	
1308 w	
1288 m/1269 m	τ(CH_2) + ν(C-OH)$_{carb.}$
1194 w, 1153 w	
1076 sh/1068 s	ν(CCO)$_{out\ phase}$
964 sh, 941 sh	
929 w/884 w	ν(C-C)
839 sh	ρ(CH_2)
828 w	ν(CCO)$_{in\ phase}$
763 w, 750 w	ρ(H_2O)
724 vw, 680 vw, 663 vw	
618 m/579 m	δ(COO$^-$)
529 m	ρ(H_2O)
458 vw, 426 vw, 411 w	
380 w/ 363 m	
333 sh/ 313 m	ν(Mg-O)

Table 2. Assignment of the IR spectrum of the Mg-citrate complex. *vs:* very strong; *s:* strong; *m:* medium; *w:* weak; *vw:* very weak; *sh:* shoulder; *br:* broad.

provided by the Raman measurements are given, as follows:

a) In the high frequency region the IR spectrum only shows a very strong and broad band, mainly related to O-H stretching vibrations. In the Raman spectrum this region shows a very much better resolution. To a medium intensity doublet with components at 3391 and 3204 cm^{-1}, assign-able to ν(OH) stretchings of the water molecules, follows a strong and well defined line at 2995 cm^{-1} assignable to the acid (OH) stretching. The CH_2-stretching modes are also seen as well defined and strong lines located at 2977, 2944 and 2913 cm^{-1}.

b) The IR multiplet in the 1600 cm^{-1} region is originated by superposition of different modes as shown in Table 2. In this region the Raman spectrum shows only a weak line, at 1639 cm^{-1}, assignable to the antisymmetric stretching of the carboxylate anions. Therefore, the IR shoulder at 1694 cm^{-1} can be assigned to the ν(C=O) mode of the non-ionized carboxylate group.

c) The second IR multiplet, centered around 1400 cm^{-1} also includes a number of different motions. The symmetric stretching of the carboxylate anion could be identified in the Raman spectrum as a very strong line, at 1431 cm^{-1}.

d) The IR vibrations at 1076/1068 cm^{-1} which are often referred to as $C\text{-}O^-$ motions of deprotonated alcohols, can be better described as an out-of-phase $C\text{-}C\text{-}^-$ vibration of the secondary alcohol [14]. The corresponding in-phase vibration is found at 828 cm^{-1}. The first of these modes is also found, as a medium intensity line at 1069 cm^{-1}, in the Raman spectrum.

e) Assignments in the spectral range below 1000 cm^{-1} are very difficult as important coupling between skeletal and other modes can be expected. Notwith-standing, in this region we have assigned again two rocking modes of the complexed water molecules, one of which (529 cm^{-1}) is close to that identified in the aspartato complex (see above).

f) We have also assigned one of the Mg-O motions to the 333/313 doublet. Another band probably related to such type of vibrations may be the 380/363 doublet, although free citric acid shows a very intense IR band exactly at 384 cm^{-1}.

$[Mg(C_5H_3O_4N_2)_2].8H_2O$

This orotic acid compound can also not be considered as a true Mg(II) complex. It crystallizes in the monoclinic space group $P2_1/c$ with Z = 2 and is constituted by a $[Mg(H_2O)_6]^{2+}$ cation associated with two hydrated monodeprotonated orotate anions only through hydrogen bonds [11].

Also in this case the assignment of the vibrational spectra was based on a number of selected literature data [23-26] together with those obtained from the general references [12-14].

A comparison of the IR spectra of the free ligand with that of the Mg(II) compound shows some band displacements and intensity changes as well as an interesting simplification of the spectrum in the medium spectral range for the complex.

The IR spectrum in the most interesting and characteristic region, between 1800 and 700 cm^{-1}, is shown in Fig. 3 and the assignment of the most important bands is presented in Table 3.

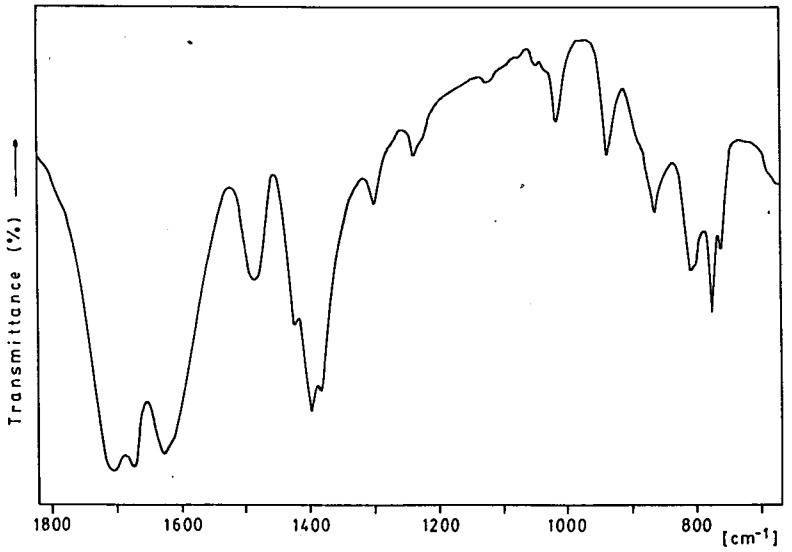

Figure 3. Infrared spectrum of the Mg-orotate complex between 1800 and 700 cm^{-1}.

Band position (cm^{-1})	Assignment
3558 sh	
3415 vs,br	ν(O–H)water
3228 vs,br	ν(N–H)
3120 w	ν(N–H)
3017 w, 2821 w	
1707 vs	$\nu(C_{(1)}=O) + \nu(C_{(4)}=O)$
1675 s	$\nu_{as}(COO^-)$
1629 vs	ν(C=C) + $\delta(H_2O)$
1486 s	δ(NH)
1424 w	δ(NH)
1399 vs, 1384 sh	$\nu_s(COO^-)$
1298 w, 1236 w, 1225 sh, 1119 w	
1013 m, 935 m, 863 m	
804 m, 773 s	π(NH)
759 w	
662 w, 644 w, 599 w	
557 w	$\rho(H_2O)$
541 m, 488 w, 442 s, 370 w	
335 vw	ν(Mg-O)

Table 3. Assignment of the IR spectrum of the Mg-orotate complex. *vs:* very strong; *s:* strong; *m:* medium; *w:* weak; *vw:* very weak; *sh:* shoulder; *br:* broad.

The most relevant aspects of this assignment are commented as follows:

a) The stretchings of the two (N-H) groups could be clearly identified. In the free acid they are located at 3170 and 3111 cm^{-1}, respectively.

b) The assignment of the three carbonyl bands is rather difficult as observed also in other similar cases [23-26]. We have tentatively assigned the 1707 cm^{-1} band to the two ring C=O carbonyl groups and those at 1675 cm^{-1} to the antisymmetric stretching mode of the deprotonated acid carbonyl, although surely important coupling between these three units exists. In the Raman spectrum only one medium intensity line, located at 1720 cm^{-1}, is observed in this region.

c) The strongest Raman line is found at 1668 cm^{-1} and can undoubtedly be assigned to the stretching of the C(5)=C(6) bond which is expected as a very intense Raman mode [14,26,27]. In the IR spectrum this band is found at 1629 cm^{-1}, strongly overlapped with the bending vibration of the water molecules. In the IR spectrum of the ligand this vibration is placed at 1666 cm^{-1} (1661 cm^{-1} in the Raman spectrum).

d) The IR spectrum of the ligand shows the typical ν(OH) band at 2835 cm^{-1}, the ν(C=O) stretching as a shoulder at 1730 cm^{-1}, whereas the ν(C-(OH)) and δ(C-OH) modes appear overlapped at 1423 cm^{-1}. In the Mg(II) salt these bands are absent and a new one, located at 1399 cm^{-1} (with a weak shoulder at 1384 cm^{-1}) is found. This band is clearly assignable to the $\nu_s(COO^-)$ stretching of the deprotonated acid group. In the Raman spectrum this mode is found as a strong band at 1383 cm^{-1}.

e) Four deformational modes related to the N-H groups could also be identified in the salt (1486, 1424, 804 and 773 cm^{-1}). In the Raman spectrum these vibrations were placed at 1477 (w), 1423 (s), 802 (vw) and 784 (s) cm^{-1}. All these bands are found at slightly higher values in the IR spectrum of the free acid (1516, 1438, 824, 783 cm^{-1}).

f) In the region between 1400 and 850 cm^{-1} in which the compound shows only a number of relatively weak or medium intensity bands (cf. Fig. 3), the free acid presents a series of strong bands (1340, 1279, 1236, 1013, 925, 893 and 854 cm^{-1}).

g) Only a very weak IR feature assign-able to a Mg-O motion could be identified at 335 cm^{-1}, i.e. in a similar region as that found in the case of the citrate complex. Besides, only one rocking mode of the ligated water molecules could be identified with certainty, although some of the weak features seen between 662 and 599 cm^{-1} could also be related to such type of vibrations.

Thermal behaviour

The thermograms of the three investigated compounds are depicted in Fig. 4. In all cases MgO was found as the final pyrolysis residue, as confirmed by its typical IR spectrum [28].

In the case of the hydrogen aspartato complex, and due to the fact that the unique proton, located on the ammino group, is engaged in hydrogen bonding with the chloride ion [9], one may expect that HCl may be eliminated at relatively low temperatures and this expectation is apparently fulfilled as seen from the experimental results (weight loss up to 210 °C was of 14.5%, and the expected value for the release of one HCl molecules is = 14.85%). The three water molecules are given off in the next step and in a rather narrow temperature range (210-330 °C), taking into account its very different structural characteristics. These two processes are accompanied by two rather weak DTA endothermic signals, located at 183 and 256 °C. The final degradation of the solid, which extends up to 650 °C, occurs in two successive steps and is related to three relatively important exothermic DTA signals (416, 470 and 523 °C). For the final degradation a mass loss of 46.80% is expected, in excellent agreement with the value of 46.70% observed experimentally.

Interestingly, also in the case of the citrato compound all the thirteen present water molecules are given off in one unique step and in a temperature range extending up to 220 °C (expected loss = 34.15%, found = 34.00%) in a process which is also related to a single, but broad, endothermic DTA signal found at 150 °C. The final degradation, which starts immediately after the end of the dehydration process, appears as very complex and implies, at least, three more steps, associated with a number of DTA-signals at 280 (very weak, endo), 317 (weak, exo), 368 (very weak, endo), 435 (weak, exo) and 489/517/530 °C (strong exo). The total observed mass loss of 82.43% is in very good agreement with the theoretically expected one of 82.36%, according to the following equation:

$$[Mg(H_2O)_6][MgC_6H_5O_7(H_2O)]_2.5H_2O \rightarrow$$
$$\rightarrow 3\ MgO + \text{volatile products}$$

The TG and DTA traces of the orotato compound appears as specially complex. Water is given off in three well defined steps. The first two molecules, which are lost at relatively low temperature (up to 106 °C), are surely the interstitial mole-cules bound to the anions. The six remaining molecules, coordinated to the Mg(II) cation, are lost in two additional steps (106-250 and 250-326 °C). These dehydration processes are accompanied by a series of endothermic DTA signals located at 82, 110, 158, 212, 237 and 330 °C.

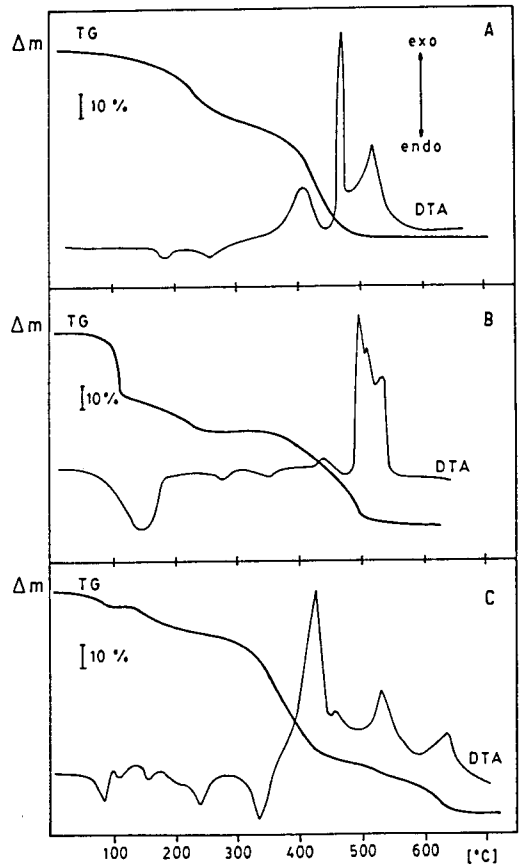

Figure 4. Thermograms of the investigated compounds: $Mg(HAsp)Cl.3H_2O$ (**A**); Mg-citrate (**B**); Mg-orotate (**C**).

After the release of water a rapid, but complex, degradation process of the remaining material is observed. It shows at least, three steps: 1) between 326 and 470 °C (with the strongest DTA signal at 426 °C and two weaker features at 365 and 460 °C); 2) between 470 and 553 °C (exothermic DTA signal at 530 °C) and 3) between 553 and 654 °C (with DTA signals at 597 and 643 °C). After this last mentioned temperature, weight constancy is attained. The total observed mass loss was of 91.30%, in excellent agreement with the calculated value of 91.57%.

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