VIBRATIONAL AND THERMAL STUDY OF HEXAAQUATRIS(MALONATO)DIEUROPIUM(III) DIHYDRATE

Brusau, E.V.; Pedregosa, J.C.; Narda, G.E.

Área de Química General e Inorgánica "Dr. G. F. Puelles", Facultad de Química, Bioquímica y Farmacia, Universidad Nacional de San Luis, Chacabuco y Pedernera, 5700 San Luis, Argentina.
FAX: +54(2652)430224; *E-mail: gnarda@unsl.edu.ar.

Ayala, E. P.; Oliveira, E.A.
Departamento de Física, Universidade Federal do Ceará, Fortaleza (CE), Brazil.

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Dedicated to Prof. Pedro J. Aymonino on the occasion of his 75th birthday

Abstract

The vibrational spectra (FTIR-Raman) of the hexaaquatris(malonato)dieuropium(III) dihydrate are reported and discussed. An assignment of H_2O, CH_2 and OCO modes in the complex is proposed on the basis of the structural data previously reported. Valuable information about the water librational modes has been obtained. The different types of interaction between the carboxylate groups of the malonate ions and Eu(III), four- and six-membered chelate rings and monodentate bridging interactions, have been also evidenced. The mechanism of the thermal dehydration is analysed and the results are in agreement with the crystal structure.

Resumen

En este trabajo se presentan y discuten los espectros vibracionales (FTIR-Raman) de hexacuotris(malonato)dieuropio(III) dihidrato. Se propone una asignación de los modos asociados a H_2O, CH_2 y OCO de acuerdo con los datos estructurales reportados en literatura. Fue posible obtener información valiosa sobre los modos libracionales de agua. Se evidenciaron también los diferentes tipos de interacción entre grupos carboxilato del malonato con el ion Eu(III), con presencia de anillos de cuatro y seis miembros e interacciones monodentadas. El mecanismo de la deshidratación térmica resultó consistente con las interacciones descriptas en la estructura cristalina.

Introduction

The binding of metal ions to the dicarboxylate residues has been a subject of interest because of the importance of such interactions in a wide variety of metalloproteins. Metal complexes containing malonate or α-substituted malonates have been taken as models for blood and bone calcium proteins that present the modified amino acid residues γ-carboxyglutamic acid and β-carboxyaspartic acid. In addition, some lanthanide (Ln(III)) dicarboxylates are applied as metal probe techniques [1-3].

Specific lanthanide dicarboxylates are also applied to other areas such as materials with attractive optical and magnetic properties [4-7] and recently, the study on the Ln-dicarboxylate complexes has been expanded to the design of new solid-state architectures which are characterized as organic/inorganic hybrids with polymeric layer structures [8-11].

The discovery of these interesting applications of Ln(III)-dicarboxylates has stimulated the enthusiasm of inorganic chemists in obtaining these complexes and studying the binding of metal ions and carboxylate groups. Within a general research program focused on understanding the factors that influence the way of binding and the formation and stability of polymeric structures with different dimensionality, e.g. Ca(II) and Cd(II) dicarboxylates, we have previously reported the structural, vibrational and thermal analysis of some metal-$OOC(CH_2)_nCOO$ complexes with $n = 1$-4 [12-15**]**.

Structural data of Eu(III) and Nd(III) malonates hydrates has been reported [16-18**]**. On the basis of these investigations, the lanthanide malonates, $M_2mal_3{\cdot}nH_2O$, can be divided into three different isostructural groups, one with $n = 8$ and M = Ce – Gd (referred as octahydrate type I), another with $n = 6$ and M = Ce – Eu, and a third type with $n = 8$ and M = Eu – Lu (referred as octahydrate type II). However, a novel malonato - gadolinium(III) complex with $n = 6$ was reported recently [19**]**. In spite of its structure being known, neither the complete vibrational assignment of the title compound nor its thermal analysis in air were found in the literature.

Then, in order to obtain a wider insight into metal dicarboxylate complexes properties, FTIR and Raman analysis and TGA-DTA measurements were carried out and the results are presented in connection with a brief description of the single-crystal X-ray study.

Experimental

$[Eu_2(mal)_3(H_2O)_6]\ 2H_2O$ crystals were obtained by precipitation from solution at room temperature according to the procedure described in reference [16] for the octahydrates type I. Reagents of analytical grade were used in the synthesis.

Europium(III) oxide (0.5 mmol, Aldrich) was dissolved in 50-mL of water with the aid of hydrochloric acid (Merck) and then it was slowly added to a 50-mL aqueous solution containing 1.5 mmol of malonic acid (Sigma) under stirring. The pH of each solution was adjusted to about 5 by the addition of sodium hydroxide (Merck) before mixing. The resulting solution was left to evaporate slowly at room temperature under inert atmosphere. A large number of prismatic colorless single crystals was obtained after several days. They were filtered, washed with distilled water and dried at room temperature.

FTIR spectra were recorded on a Nicolet PROTÉGÉ 460 spectrometer in the 4000-225 cm^{-1} range with 32 scans, using the KBr pellet technique; spectral resolution was 4 cm^{-1}. Raman spectrum was scanned on a Raman Jobin-Yvon T64000 provided with a N_2 - cooled CCD and operating with an Ar laser. Two excitation wavelengths (488 and 514.5 nm) were used to avoid the strong europium luminiscence.

TGA-DTA curves were obtained with a Shimadzu TGA-50H/DTA-50 thermal analyzer apparatus using flowing air at 50 mL min^{-1} at a heating rate of 10°C min^{-1}. Appropriate combinations of X-ray powder diffraction and FTIR spectroscopy were used for further characterization of the pyrolysis residue.

X-ray powder diagrams were obtained with a Rigaku D-MAX-IIIC diffractometer using CuK_α radiation (Ni-filter) and NaCl and quartz as external calibration standards.

Results And Discussion

Structure Description

The powder X-ray pattern of $[Eu_2(mal)_3(H_2O)_6]\ 2H_2O$ shows an excellent agreement with that simulated by the Fullprof refinement program [20] on the basis of the single-crystal X-ray diffraction data reported previously in literature [16]. This fact allows us to conclude that the title compound crystallizes as the octahydrate type I. The crystals are orthorhombic, space group *Pbcn*. The structure is a three-dimensional europium malonate network. Figure 1 shows the Eu(III) coordination polyhedra. Each europium ion is coordinated by six carboxylate and three water oxygen atoms which form a monocapped square antiprism. There are two independent malonate ions in the structure, both non planar. One of them has one strict twofold symmetry and is bonded to four metal ions by six Eu – O bonds, *i.e.* two of its oxygens form two Eu – O bonds each. The other malonate ion forms a six-membered chelate ring, namely "malonate type" binding, with europium and one bridge Eu – OCO – Eu. One of the coordinated water molecules forms two hydrogen bonds to carboxylic oxygens and accepts one hydrogen bond from the uncoordinated (hydration) water molecule oxygen. The remaining coordinated water molecules each form one intralayer hydrogen bond to a carboxylic oxygen and one to the uncoordinated water molecule. The hydration water molecule is situated between the europium malonate layers. It is bonded to the coordinated water oxygens of one layer and to a carboxylic oxygen of an adjacent layer.

Vibrational Spectra

The vibrational study has been carried out taking into account the structural characteristics outlined above. The internal vibrations can be described by means of the following building units: carboxylate groups, methylene groups and water molecules. The interpretation of the FTIR and Raman spectra is supported by their comparison with the spectroscopic data of malonic acid and related compounds found in literature [21, 22].

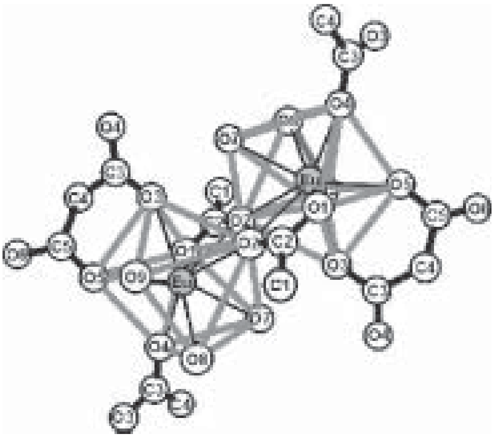

Figure 1: *Coordination polyhedra of Eu(III) in* $[Eu_2(mal)_3(H_2O)_6]\ 2H_2O$

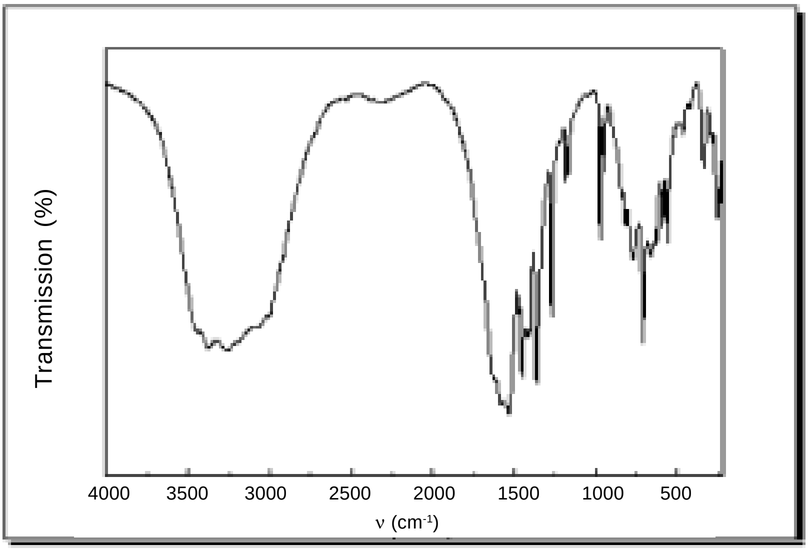

Figure 2: *FTIR spectrum of* $[Eu_2(mal)_3(H_2O)_6]\ 2H_2O$

Figure 2 and Figure 3 show the FTIR and Raman spectra respectively. The proposed assignment is detailed in Table 1. The features of the principal modes assigned to H_2O and OCO groups are discussed below.

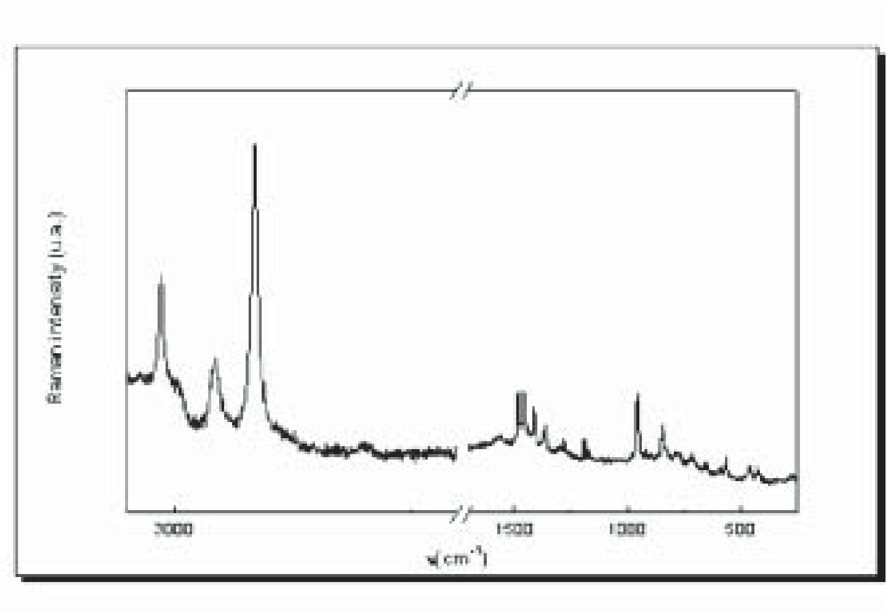

Figure 3: *Raman spectrum of* $[Eu_2(mal)_3(H_2O)_6]\ 2H_2O$

Table 1. *Assignment of the FTIR-Raman spectra of $[Eu_2(mal)_3(H_2O)_6]$ ’•$2H_2O$ (values in cm^{-1})*

FTIR	*Raman*	Assignment
3440 (m, br)		ν (OH) W
3375 (m, br)		ν (OH) W
3260 (m, br)		ν (OH) W
3180 (m, br)	3120 (w)	ν (OH) W
3070 (m, br)	3075 (m)	ν (OH) W
3010 (m, ov)	3015 (s)	ν_{as} (CH)
2995 (m, ov)	2995 (m)	ν_{as} (CH)
	2955 (m)	ν_{as} (CH)
2915 (m, ov)	2915 (vs)	ν_s (CH)
1690 (sh, ov)		$\delta(H_2O)$
1625 (s)	1635 (w)	ν_{as} (OCO)
1585 (s)	1580 (vw)	ν_{as} (OCO)
1550 (s)	1560 (vw)	ν_{as} (OCO)
1535 (vs)		ν_{as} (OCO)
1475 (m)	1480 (m)	δ (CH_2)
1450 (s)	1455 (m)	δ (CH_2)
		δ (CH_2)
1415 (m)	1410 (m)	δ (CH_2)
1365 (s)	1365 (m)	ν_s (OCO)
	1300 (vw)	ρ_w (CH_2)
1275 (m)	1275 (w)	ρ_w (CH_2)
	1270 (vw)	ρ_w (CH_2)
1185 (m)	1190 (w)	ν_{as} (CC)
1170 (m)	1170 (vw)	ν_{as} (CC)
975 (m)	980 (vw)	ν_s (CC)
950 (m)	955 (m)	ν_s (CC)
	920 (vw) 900 (vw)	ν_s (CC)
845 (m)	845 (m)	δ (CC)
820 (m)	825 (vw)	δ (OCO)
775 (m)	775 (m)	ρ_r (H_2O)
710 (m)	715 (w)	ρ_w (OCO)
665 (m)	655 (vw)	ρ_r (H_2O)
645 (m)		π (OCO)

Table 1 continuing

625 (m)		ρ_r (H_2O)
595 (m)	595 (vw)	ρ_r (H_2O)
560 (m)	565 (w)	ρ_w (H_2O) + δ (CCO)
465 (w)	460 (vw)	Lattice modes no associated with water molecules
	430 (vw)	
420 (w)	420 (vw)	
	405 (vw)	
	385 (vw)	
340 (m)		
255 (m)	280 (vw)	ν (M-O)
250 (vw)	250 (m)	
245 (m)	240 (vw)	

***Key to Table 1:* vs**: *very strong* **s**: *strong* **m**: *medium* **w**: *weak* **vw**: *very weak* **ov**: *overlap* **br**: *broad* ν_{as}: *asymmetric stretching;* ν_s: *symmetric stretching;* **δ:** *deformation;* ρ_w: *wagging mode;* ρ_r: *rocking mode;* **π** : *out of plane deformation*

Water Modes

The assignment of these modes, particularly the librational ones, was performed considering the spectra of partial and completely dehydrated samples. These samples were obtained by thermal treatment of the original compound at selected temperatures (the thermal diagram was taken into account for the selection). Figure 4 shows the FTIR spectra of the dehydration course in the IR range of ν(O-H) modes (3a), δ(H_2O) mode (3b) and the zone of water librational modes (3c). The spectrum of the sample heating at 200ºC was removed in Figure 3c for a better viewing since it is similar to that obtained at 250 ºC.

The ν(O-H) can be identified in the 3500-3000 cm^{-1} IR zone with one markedly asymmetric, broad band which involves several components. This fact suggests the presence of different kinds of water molecules in the structure. The frequency values are lower than those expected for free water stretching vibrations owing not only to coordination but also to the presence of hydrogen bonds in the lattice. Some ν(O-H) signals were identified in the Raman spectrum. The strong europium luminiscence does not allow us to record the complete region of the ν(O-H) modes. Deformation modes are not observed in the FTIR spectrum but the progressive thinness of the ν_{as}(OCO) bands on thermal dehydration might reveals that δ(H_2O) bands are overlapped by the former ones. Thus, the shoulder that appears at 1690 cm^{-1} in the spectrum of the sample treated at 200ºC in Figure 3b can be assigned to δ(H_2O).

Librational modes which usually present low intensity and are overlapped with other modes, are spread out in the 800-500 cm^{-1} range of vibrational frequencies. Several bands associated to these modes are observed in both Raman and IR spectra supporting the presence of water molecules differently involved in the structure. They were assigned taking into account the nature of the modes and water molecules interactions in the structure. The IR bands associated to these modes are marked in Figure 3c where it can be seen that they disappear with increasing temperature. The frequency values of these modes are lower than those observed for i.e. diaquamalonatocalcium(II) [12] in response to the different masses of the respective cations, since these values depend on the inverse of the inertial moment.

OCO Group Modes. ν_{as}(OCO) stretching modes are present in the FTIR and Raman spectra as broad, asymmetric bands with various components included, whereas the ν_s(OCO) mode exhibits no splitting. The splitting of the former mode can be explained in terms of the different types of interaction between the carboxylate groups of the malonate ions and Eu(III), four- and six-membered chelate rings and monodentate bridging interactions.

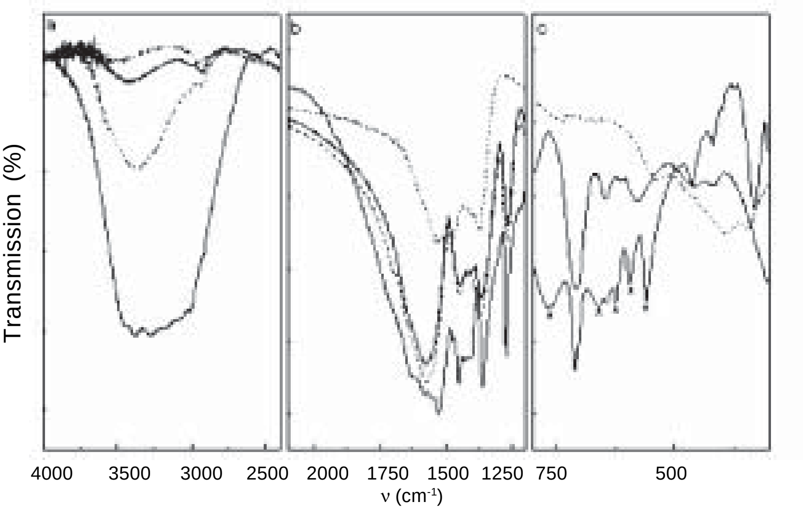

Figure 4 : *FTIR spectra of the dehydration course of* $[Eu_2(mal)_3(H_2O)_6]$ *'•2H₂O*
━━━ *Room temperature* — - — *200 ºC* ——— *250 ºC* _ _ _ _ *350 ºC*
**Librational modes of water*

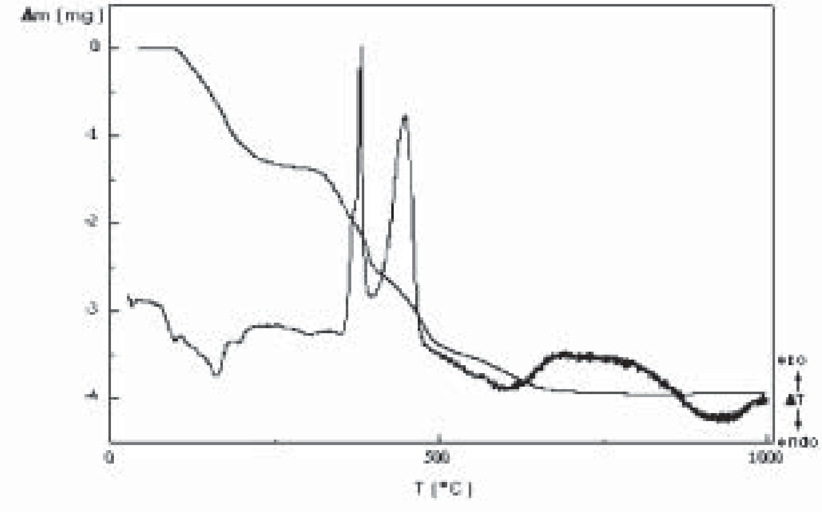

Figure 5: *TGA-DTA curves of* $[Eu_2(mal)_3(H_2O)_6]$ *2H₂O*

The ν_{as}(OCO) mode appears in a 1625-1550 cm^{-1} range being the band at the highest frequency expected in compounds where the "malonate" binding mode is present [23]. Taking into account the spectroscopic criterion to select the vibrational modes associated to the different metal-carboxylate interactions [24], the resulting $\Delta\nu$ from the FTIR spectrum are 265 cm^{-1} and 190 cm^{-1} and correspond to the presence of six- and four-membered chelate rings respectively. Robinson and Uttley [25] have characterized unidentate and bidentate modes of binding by OCO group frequencies. They found that ν_{as}(OCO) and $\Delta\nu$ values are closer to those in the free ion (i.e. sodium malonate: ν_{as}(OCO) 1600, 1562 cm^{-1} and ν_s(OCO) 1390, 1370 cm^{-1} [26]) for chelate four-membered ring coordination, while $\Delta\nu$ values for six-membered ring coordination are much larger, and ν_{as}(OCO) bands appear at higher frequencies. This systematic was observed for several M(III) malonate complexes [27-31].

The presence of malonic acid or bimalonate ion is discarded because no evidence of IR carbonyl (ν(C=O) 1735, 1705 cm^{-1} [26]) absorption is present.

No significant differences are observed in frequency values of equivalent IR and Raman bands in our spectra, in disagreement with the prediction for a centrosymmetric space group. This behavior could probably be ascribed to unimportant coupling effects between different oscillators in the unit cell.

Thermal Behavior

The TGA-DTA curves of hexaaquatris(malonato)dieuropium(III) dihydrate are shown in Figure 5. Dehydration proceeds via three stages associated with DTA endothermic peaks at 99, 162 and 195°C. The first signal corresponds to the loss of the two hydration water molecules. The experimental weight loss in the TGA curve is 4.75% (theoretical, 4.77%). The second stage is assigned to the departure of four water molecules with an experimental weight loss of 9.59% (theoretical, 9.55%). Two water molecules are eliminated in the further step with an experimental weight loss of 4.53% (theoretical, 4.77%). The second loss can be associated with coordinated water molecules which exhibit two H-bonds according to the structural description while the third one corresponds to those with stronger H-bond interactions.

On further heating, decomposition of the anhydrous compound occurs via three steps related with DTA exothermic peaks at 370, 381, 447 and 660°C. The complete weight loss for this process is 34.42% (theoretical, 34.23%). The final product, stable up to 1000°C, has been confirmed by XRD as europium(III) oxide (cubic) (JCPDS card 43-1008) [32]. Nagase et al. [33] have observed that in the decomposition course of the $Eu_2mal_3\ 6\ H_2O$, none of the weight loss values could be assigned to a distinct product possibly owing to side reactions; besides, their identification is difficult because they result amorphous to X-rays.

Conclusions

This work reports the vibrational and thermal behavior of $[Eu_2(mal)_3(H_2O)_6]\ 2H_2O$ obtained from solution at room temperature. A complete assignment of the FTIR and Raman signals was performed for malonate and water modes, particularly the librational contribution. The results were consistent with the reported structural data. The splitting of the ν_{as}(OCO) mode can be explained in terms of the different types of interaction between the carboxylate groups of the malonate ions and Eu(III), four- and six-membered chelate rings and monodentate bridging interactions. Higher frequencies for the ν_{as}(OCO) mode seem to be a common feature for metal malonates where the "malonate" binding mode is present.

The shift to lower frequencies of water stretching modes indicates the presence of strong hydrogen bonds in the lattice.

Dehydration process confirms the different nature of the interactions of water molecules in the lattice: hydration water, coordinated water molecules which exhibit two H-bonds and those ones with stronger H-bonds. Thus, vibrational and thermal information is in complete agreement with the structural description.

Acknowledgments

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