

Mössbauer spectroscopy of 151 europium dicarboxylates

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Abstract We have previously reported the stability of europium oxalate compared to ammonium europium bis-salen and europium benzoate. We now extend the dicarboxylic acid chain of the oxalate by introducing additional-CH₂-groups in the dicarboxylate ligands by using malonate, succinate, glutarate and adipate. Additionally, we have examined the effect of alterations in the succinate dianion by introducing functional groups such as [C = C] in the case of the maleide and -OH group in the case of the malide. This study is an attempt to further characterize these compounds. Infrared spectra were used to characterize bridging and chelating dicarboxylates

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while Mössbauer spectroscopy measurements were used to gain better insight into the structure of heterocyclic “cages” containing two Eu^{3+} ions and two dianions.

Keywords Europium dicarboxylates · Mössbauer spectroscopy · Infrared

1 Introduction

A number of rare earth ion complexes with dianion carboxylic acids [1–5] have been reported over several decades; they continue to be of interest because these metal coordination polymers provides a link between synthetic chemistry and materials science. The study is fascinating and intriguing because the actual complex formed depends on such factors as lanthanide ion, the pH, the dicarboxylic ion, and other modes of preparation like the temperature of the solution. Further their practical utility in fluorescence, electrical and magnetic technology makes them very desirable material.

To date their study and characterization have been primarily by single crystal x-ray diffraction, infrared and Raman vibrational studies and thermal gravimetry.

We have prepared the much studied Eu^{3+} –malonate complex by a different method to give $\text{Eu}_2(\text{mal})_3 \cdot 6\text{H}_2\text{O}$ units where mal is the malonate dianion $(\text{OOC}(\text{CH}_2)\text{COO})^{-2}$. Additionally we have prepared similarly other Eu^{3+} complexes, namely europium succinate pentahydrate europium malide hydrate, europium maleide hexahydrate, europium glutarate tetrahydrate and europium adipate hexahydrate.

These white salts were characterized by infra-red spectra to substantiate bridging and chelating dicarboxylic dianions in these polymers while Mössbauer measurements were used to get better insight into the heterocyclic “cages” containing the 2 Eu^{3+} ion and the two dianions.

The Mössbauer spectra validated not only trivalent europium ions in the complexes but also the lattice dynamic calculations of the Debye temperatures (θ_D) reflected the order of stability of the heterocyclic rings in these polymeric coordination compounds.

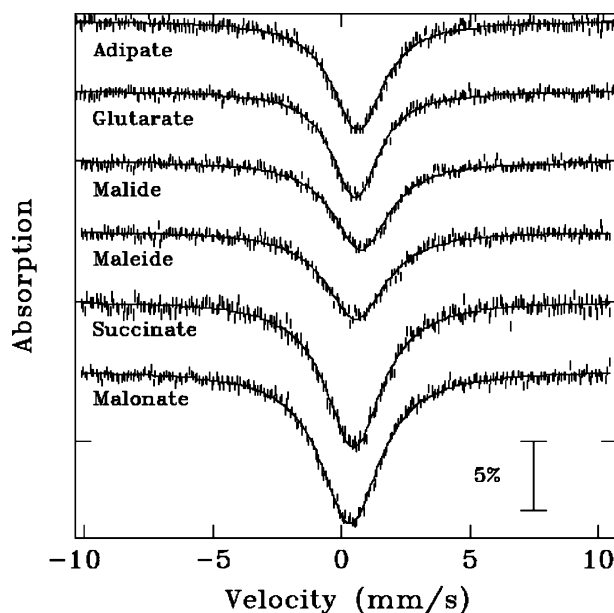
2 Experimental methods

Six europium dicarboxylates salts, europium (III) malonate hexahydrate $\text{Eu}_2[\text{OOC}(\text{CH}_2)\text{COO}]_3 \cdot 6\text{H}_2\text{O}$, europium (III) malide hydrate $\text{Eu}_2[\text{OOC}(\text{CHOH}-\text{CH}_2)\text{COO}]_3 \cdot \times \text{H}_2\text{O}$, europium (III) maleide hexahydrate $\text{Eu}_2[\text{OOC}(\text{CH}=\text{CH}-\text{COO})_3 \cdot 6\text{H}_2\text{O}$, europium (III) succinate pentahydrate $\text{Eu}_2[\text{OOC}(\text{CH}_2)_2-\text{COO}]_3 \cdot 5\text{H}_2\text{O}$ europium (III) glutarate tetrahydrate $\text{Eu}_2[\text{OO}(\text{CH}_2)_3\text{COO}]_3 \cdot 4\text{H}_2\text{O}$ and europium (III) adipate hexahydrate $\text{Eu}_2[\text{OOC}(\text{CH}_2)_4\text{COO}]_3 \cdot 6\text{H}_2\text{O}$ were each prepared in hot solutions by dissolving 0.71 mmol Eu_2O_3 in slight excess 0.1 M HCl and adjust the pH between 2–3 by adding MNH_3 . 2.13 mmol of each dicarboxylic acid respectively in 10 ml deionized H_2O was added slowly with stirring to the europium chloride solution, and the pH adjusted with NH_3 to between 4.5 and 5.5. The solution was allowed to stand, cool, filtered and dried overnight in a desiccator.

Table 1 IR spectra of Eu malonate hexahydrate

* Brusau, E.V., Pedregosa, J.C., Narda, G.E. Vibrational and thermal study of hexaaqua-tris(malonato)dieuropium(III) malonate *J. Argentine Chem. Soc.* **2004**, 92(1), 43–52

IR Spectrum of europium malonate		
This work	Reference*	Assignment
3,310–3,200 (s, br)	3,375 (m, br)	ν -OH
1,695 (m)	1,690 (sh, ov)	δ -H ₂ O
1,556 (s)	1,550 (s)	ν_{as} -OCO
1,450 (m)	1,450 (m)	δ -CH ₂
1,378 (s)	1,365 (s)	ν_s -OCO
1,279 (m)	1,275 (m)	ρ_w -CH ₂
1,195 (w)	1,185 (m)	ν_{as} -CC
987 (w)		
967 (m)	975 (m)	ν_s -CC
943 (w)	950 (m)	ν_s -CC
800 (w)	820 (m)	δ -OCO
709 (m)	710 (m)	ρ_w -OCO

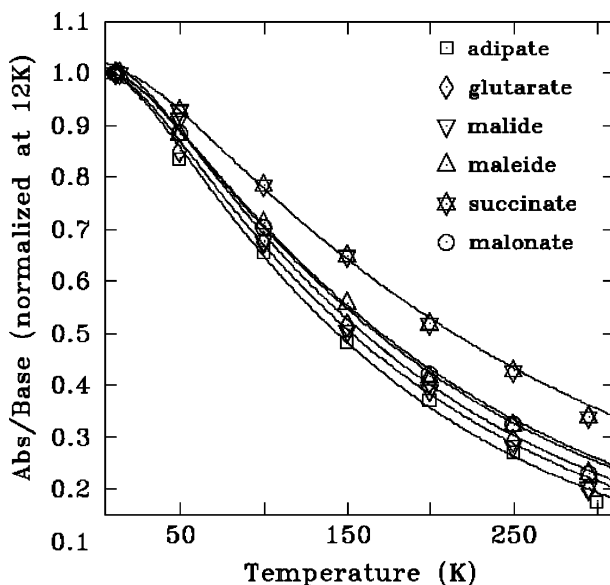
Fig. 1 Mössbauer spectra of europium 151 dicarboxylates

IR spectra were performed on neat solids in a diamond ART cell of a Thermo-Nicolet Avertat 380 FT. Spectra were taken of each complex and corresponding dicarboxylate acid.

The Mössbauer spectra of each of the compounds using the same europium sample size were measured at temperatures ranging from 10 to 300 K in constant acceleration mode using the 21.6 keV gamma ray from a 100 mCi $^{151}\text{SmF}_3$ source. The velocity was calibrated with iron foil at room temperature, and all Eu spectra are reported with EuF_3 as the standard at room temperature. A Wissel Mössbauer system was used and spectra were fitted using a conventional non-linear least-squares minimization routine to a single broadened Lorentzian line.

Table 2 Mössbauer parameters of Eu(III) dicarboxylates in this work at 10 K

Dicarboxylic acid	Formula	Θ_D (K)	Linewidth (mm/s at base)	Absorption (% at base)
Malonate	C ₃ H ₄ O ₄	149 (1)	1.24 (3)	4.3
Succinate	C ₄ H ₆ O ₄	169 (1)	1.34 (2)	10.4
Glutarate	C ₅ H ₈ O ₄	141 (2)	1.10 (2)	7.6
Adipate	C ₆ H ₁₀ O ₄	137 (2)	1.19 (2)	7.8
Malcide	C ₄ H ₄ O ₄	150 (1)	1.44 (3)	6.3
Malide	C ₄ H ₆ O ₅	143 (3)	135 (3)	6.3

Fig. 2 Plot of $\ln A$ with temperature of $\text{Eu}_2[\text{dicarboxylates}]_3 \cdot n\text{H}_2\text{O}$ 

3 Results and discussion

In this study, we have further characterized and extended the series of europium dicarboxylic acids by infrared and Mössbauer spectroscopy. These compounds, we have alluded, are extremely important in their ability to fluoresce.

Using the infra-red spectra of europium malonate as a prototype we established bridging as well as coordinating carboxylic group to the europium (III) ions in these polymeric compounds as seen from Table 1. Note that the spectrum in the work is in good agreement with that previously reported by Brusau and company.

This type of behavior shown in Table 1 was repetitive as observed from the spectra of complex and corresponding ligand

Figure 1 exemplifies typical Mössbauer spectra of europium dicarboxylates hydrates studied with a percent effect greater than 5% in each case. The gross features are the same with line width approximately twice the natural line width (0.65 mm/s) of Eu-151 as seen in Table 2. No asymmetry due to electric field gradient contributions was detected in any of the spectra.

Figure 2 gives a plot of the normalized area of the spectra of the complexes versus temperature; Debye temperatures were obtained by fitting the temperature

dependence of the spectral area. To avoid restrictions imposed by using the high temperature limiting form for the f -factor, the complete form of the Lamb–Mössbauer factor within the Debye approximation was solved by numerical integration so that data taken over the entire temperature range (10 to 300 K) could be used in our analysis.

Note that the europium succinate complex with the larger bridging heterocyclic ring (14 atoms) has the higher Debye temperature (169 K) compared to the malonate (12 membered bridging ring) (149 K); it is not surprising that the larger succinate ring with less strain is more stable than the 12 membered malonate bridges. The malide and the maleide complexes have the same number of carbon atoms in the heterocyclic bridges as the succinate but do also contain other functional OH group in the case of the malide and cis carbon-carbon double bond in the case of the maleide complex. The reactive functional group do introduce additional strains in the heterocyclic ring in these complexes resulting in a lower Debye temperature for the maleide ($\theta_D = 150$ K) and (143 K) for the malide in which intramolecular hydrogen bonding is evident. However as the ring size increased to glutarate ($\theta_D = 141$ K) and adipate ($\theta_D = 137$ K) the heterocyclic rings became less stable due to steric effects (“bundling”). Previously we [5] have used the Debye temperature to establish the order of stability for a series of similar europium complexes; it is reasonable to say here, also, that the numerical order of the Debye temperature for these europium dicarboxylic hydrates do support the thermodynamic stability of these complexes.

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