Mössbauer studies of [151]Eu in europium oxalate, europium bissalen ammonium and europium benzoate

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Abstract Although a number of europium water insoluble chelates have been prepared for several decades, the covalent nature of these compounds has never been established in any quantitative fashion. Shifts in the I.R. bands and conductivity measurements of these salts were hitherto used to qualitatively compare their molecular nature. In this communique we have used temperature coefficients of [151]Eu Mössbauer spectra to determine the Debye temperatures (θ_D) of three europium chelates: namely europium oxalate, europium bissalen ammonium (recently reported) and europium benzoate and compared their θ_D with the measured θ_D of the known ionic EuF_3. Additionally, the mean square amplitude ($<x^2>$) of these four compounds was computed and plotted as a function of temperature giving in each case a reasonable linear plot. It was interesting to note that the θ_D of the most ionic EuF_3 was greatest (283 ± 10 K) followed by the oxalate (166 ± 15 K), then the europium bissalen ammonium (133 ± 5 K) and lastly the europium benzoate with a θ_D of (105 ± 5 K).

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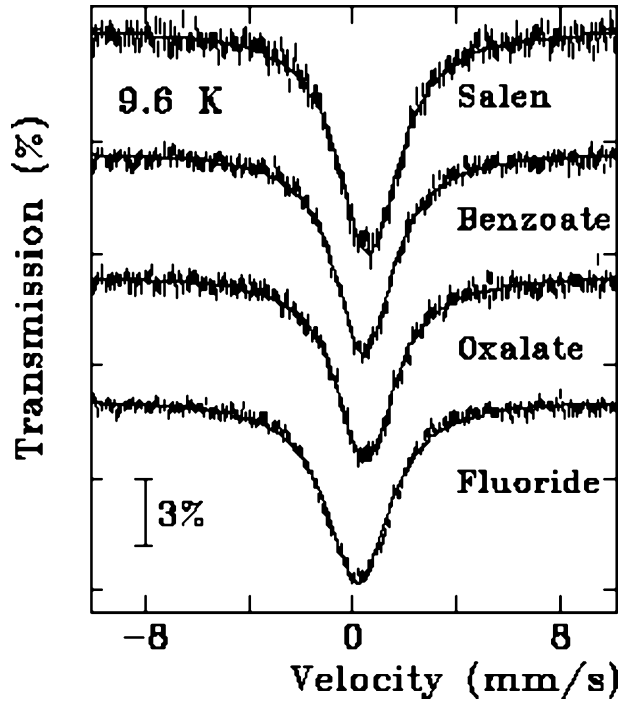Department of Physics, Morgan State University, Baltimore, MD 21251, USA

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Figure 1 Typical ^{151}Eu Mössbauer spectra of EuF$_3$ and complexes at 9.6 K.

1 Introduction

Quite recently, the properties of a new europium salen complex [NH$_4$Eu(salen)$_2$] were characterized and a Debye temperature value of 133 ± 5 K reported [1]. To determine what effect acid ligands would have, the studies of two more chelates, europium oxalate Eu$_2$ (C$_2$0$_4$)$_3$ and europium benzoate Eu (C$_6$H$_5$C00)$_3$ were made. For comparison, europium fluoride (EuF$_3$) was also studied as the prototype of the 'truly' ionic europium compound. This paper reports the results of the Mössbauer spectral studies of these compounds at various temperatures.

2 Experimental

The preparation of the Eu (salen)$_2$ NH$_4$ complex was recently reported [1] while the benzoate and oxalate salts were prepared by standard methods previously reported in the literature [2].

The Mössbauer spectra of each of the four compounds were measured at temperatures ranging from 10 to 295 K in the constant acceleration mode using the
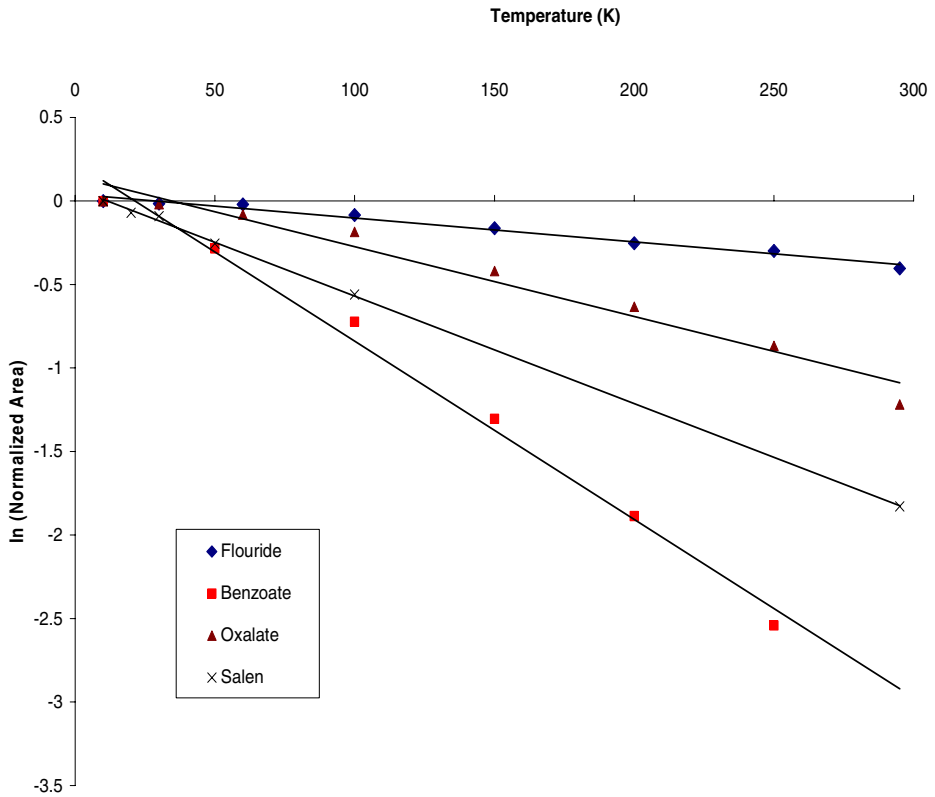
Figure 2 Plot of lnA vs. temperature.

21.6 keV gamma ray from a 100 mCi ^{151}SmF$_3$ source. The velocity was calibrated with iron foil at room temperature, and all Eu spectra reported with EuF$_3$ as the standard at room temperature. A Wissel Mössbauer system was used and spectra fitted using a least square analysis program.
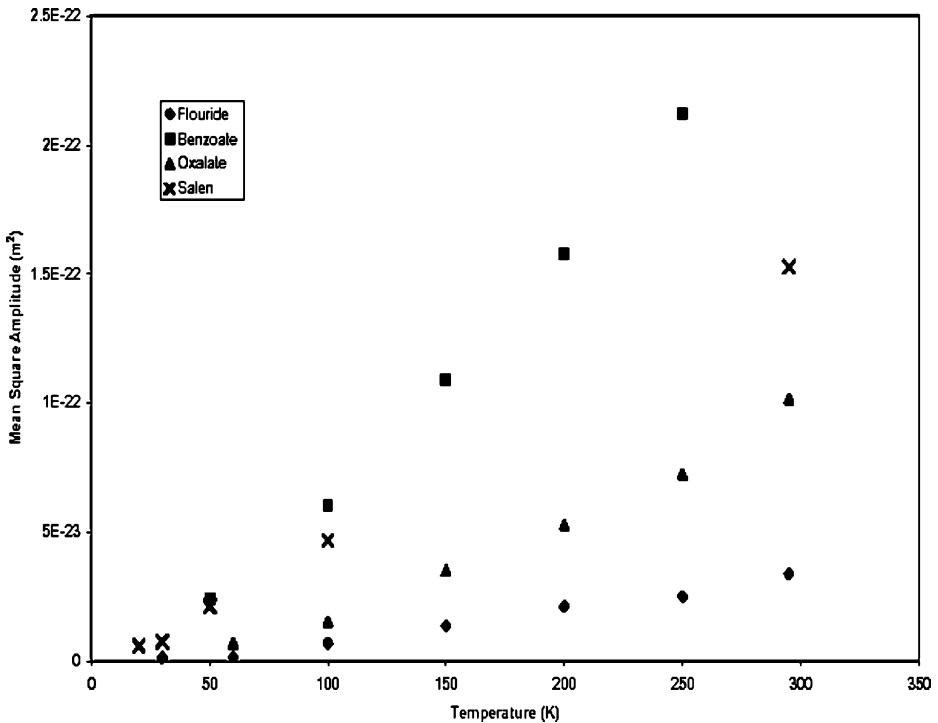
3 Results and discussion

Figure 1 shows the similar gross features of the spectra of the Eu compounds at 9.6 K, the chelates exhibiting among the narrowest of line width shown by Eu^{3+} compounds to date and the positive isomer shifts with respect to EuF$_3$ confirming trivalent europium [3, 4].

The Debye temperature of the fluoride was 283 ± 10 K whereas the oxalate and the benzoate were 166 ± 15 K and 105 ± 5 K, respectively. Further intermolecular and intramolecular bond strength information was extracted from computation of the mean square amplitude of these compounds.

Of paramount interest was a plot of the natural logarithm of the normalized area versus temperature, Figure 2. The Debye temperature from these plots gave the θ_D's reported in Table I. The obviously most ionic compound, EuF$_3$, gave the

Table I Debye temperatures (θ_D) of Eu compounds

Substance	$\theta_D(K)$
EuF$_3$	283 ± 10
Eu$_2$ (C$_2$O$_4$)$_3$	166 ± 15
Eu NH$_4$ (salen)$_2$	133 ± 5
Eu (benzoate)$_3$	105 ± 5

Figure 3 Mean square amplitude vs. temperature.

highest θ_D of 283 K and the least stable or most covalent chelate, the benzoate, recorded 105 K. One can contribute this high covalency as due to the bulk of the benzoate bidentate ligand unabling to bond to the Eu^{3+} ion as firmly as the less bulky oxalate chelate or the more highly symmetrical salen group. The strong ionic Eu-F bonds yielded the smallest mean square amplitude $\langle x^2 \rangle$ at any given temperature, for example 100 K for these four compounds and was greatest for the bulky benzoate, most unstable of these compounds $\langle x^2 \rangle$ was 6.04×10^{-23} m^2.

Recall that the recoil-free fraction f is given by the total area under the resonance curve. It has been shown that the recoil-free (f) is related to the mean square amplitude (x^2) by $f = \exp(-k^2\langle x^2 \rangle)$ where k is the wave vector of the gamma radiation.

$$\lambda = hc/E_\gamma$$

and $<x^2>$ is the mean square amplitude of vibration parallel to the gamma ray propagation axis. Figure 3 shows a plot of the mean square amplitude versus temperature for europium fluoride, oxalate, salen adduct and the benzoate. The graph shows a positive slope for $<x^2>$ versus temperature reflecting an increase in the vibration amplitude with increasing temperature. Moreover, for a given temperature $<x^2>$ is least for the fluoride, followed by the oxalate, then the salen complex and the benzoate.

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