Mössbauer Effect Studies of Europium-151 Complexes

S. Kumar and G. N. Rao

Department of Physics, Indian Institute of Technology, Kanpur 208016/India

O. K. Medhi, U. Agarwala

Dept. of Chemistry, Indian Institute of Technology, Kanpur 208016/India

(Z. Naturforsch. **29 a**, 1778–1781 [1974]; received July 27, 1974)

The Mössbauer effect in a number of europium (III) complexes with ligands having nitrogen or oxygen as donor atoms has been studied at room temperature. A comparison of the resonance effects indicates significant differences between several of the complexes. High resonance effects are correlated with the polymeric nature of the complexes. The isomer shifts of the complexes have also been interpreted on the basis of the participation of 6s or/and 4f or 5p orbitals in the bond formation.

Introduction

In general, it has been found that the bonding in the rare earth compounds is mostly ionic[1]. One can have a fairly good idea through Mössbauer studies about the nature of bonding in various compounds. Thus, Deeney, et al.[2, 3] have reported a partial covalent character in the bonds of certain europium complexes. They suggested that the possible mechanism by which the covalent bonding in the compounds arises could be through a partial transfer of electron density from the ligand of 4f orbitals whereby the electronic configuration of Eu^{+3} changes to $4f^{6+x}\,5s^2\,5p^6$, where $0 < x < 1$. However, Targin and Eisenstein[4] proposed that the isomer shifts of most of the Eu^{+3} complexes could be explained on the basis of non-zero density of 6s electrons at the europium nucleus and the partially covalent bond involving the participation of 5d and 6s orbitals. Besides, Mössbauer studies have been carried out only on a few europium compounds[2–8]. It will, therefore, be interesting to study the Mössbauer effect of some of those europium complexes in which the metal ion is in different environments and also in various oxidation states. Such studies will tell us about the nature of the bonding in the europium complexes.

In this paper we report on Mössbauer studies of some Eu^{+3} complexes with ligands containing oxygen or nitrogen as donor atoms. An attempt has been made to interpret the data on the basis of 4f or 6s orbital participation in forming covalent bonds. The resonance effects in these complexes have also been studied in order to investigate the extent of polymerism in the complexes.

Experimental

All the reagents used were either chemically pure or Analar grade.

a) *Preparation of the Complexes*

The complexes given in Table 1 have been prepared by standard methods given in the literature[9–17]. The purity of the samples was determined by chemical analyses.

b) *Mössbauer Studies*

The details of the Mössbauer spectrometer have been discussed elsewhere[18]. An ND 512 multichannel analyzer was used in the multiscaling mode for data acquisition. The spectrometer was operated in the sinusoidal velocity mode. The folding point was determined accurately to a fraction of a channel corresponding to the maximum velocity. The zero of the spectrometer was obtained with the help of the accurately measured drive-frequency, and the memory advance frequency. In the spectrometer used by us, both these frequencies were derived from the same crystal oscillator. Thus, the zero of the spectrometer was fixed without any external calibration standards. In all our measurements the zero of the spectrometer was also checked independently with standard absorbers. Standard spectra of the enriched iron were obtained both before and after the spectrum of each europium compound was taken up.

A 10 mc Sm-151 source in the form of Samarium oxide procured from Harwell was used for all measurements. The 21.6 keV γ-rays of Eu-151 were

Reprint requests to Dr. U. Agarwala, Dept. of Chemistry, Indian Institute of Technology, *Kanpur 208016/India.*

Dieses Werk wurde im Jahr 2013 vom Verlag Zeitschrift für Naturforschung in Zusammenarbeit mit der Max-Planck-Gesellschaft zur Förderung der Wissenschaften e.V. digitalisiert und unter folgender Lizenz veröffentlicht: Creative Commons Namensnennung-Keine Bearbeitung 3.0 Deutschland Lizenz.

This work has been digitalized and published in 2013 by Verlag Zeitschrift für Naturforschung in cooperation with the Max Planck Society for the Advancement of Science under a Creative Commons Attribution-NoDerivs 3.0 Germany License.

Zum 01.01.2015 ist eine Anpassung der Lizenzbedingungen (Entfall der Creative Commons Lizenzbedingung „Keine Bearbeitung") beabsichtigt, um eine Nachnutzung auch im Rahmen zukünftiger wissenschaftlicher Nutzungsformen zu ermöglichen.

On 01.01.2015 it is planned to change the License Conditions (the removal of the Creative Commons License condition "no derivative works"). This is to allow reuse in the area of future scientific usage.

Table 1. Mössbauer data of the Eu^{+3} complexes.

Compound	Eu-Thickness (mg/cm^2)	Linewidth $^+$ (mm/sec)	δ * (mm/sec)	Resonance effect	$\sqrt{M}$
Eu_2O_3	20.0	3.4	$+0.07 \pm 0.05$	40.8	18.7
$Eu(HCO_2)_3 \cdot 2\,H_2O$	15.0	2.74	-0.6 ± 0.05	28.8	18
$Eu(CH_3CO_2)_3 \cdot 2\,H_2O$	12.3	2.61	-0.5 ± 0.02	7.8	19.1
$Eu(CCl_3CO_2)_3 \cdot 2\,H_2O$	1.8	3.05	-0.38 ± 0.02	9.1	26
$Eu(p\text{-}O_2N-C_6H_4CO_2)_3 \cdot 2\,H_2O$	1.8	2.50	-0.1 ± 0.02	10.0	26.2
$Eu(C_6H_5CO_2)_3 \cdot 2\,H_2O$	2.2	2.69	-0.1 ± 0.02	8.1	23.4
$Eu(OX)_3 \cdot 10\,H_2O$	8.3	2.58	-0.56 ± 0.02	14.9	24.4
$Na[Eu(phth)_2]4\,H_2O$	5.0	2.68	-0.54 ± 0.02	10.7	24
$Eu(HSal)_3 \cdot 2\,H_2O$	9.3	3.03	-0.3 ± 0.02	24.2	24.4
$EuCl_3 \cdot 6\,H_2O$	15.0	2.77	-0.5 ± 0.02	12.5	19.1
$Eu(NO_3)_3 \cdot 6\,H_2O$	10.3	2.64	-0.15 ± 0.02	26.4	21.1
$Eu(phen)_2 \cdot Cl_3 \cdot H_2O$	2.7	3.01	-0.29 ± 0.02	18.0	25.2
$Eu(dip)_2Cl_3 \cdot H_2O$	2.2	3.02	-0.33 ± 0.02	9.0	24.7

HSal = Salicylate; Ox = Oxalate; phth = Phthalate; phen = 1,10-phenanthroline; M = Molecular weight of the compound; dip = dipyridyl; δ = Isomer shift; + = ± 0.05 mm/sec; * With respect to source.

detected in a 2 mm thick NaI(Tl) crystal coupled to a RCA 6342 photomultiplier and an ORTEC Model 410 linear amplifier. The resonance effect (dip multiplied by experimental line width) observed for the europium oxide absorber was approximately 40%.

Accurately weighed absorbers were sandwitched between two cellulose tapes and were fixed in a standard geometry in a lead block. The errors were obtained from the uncertainty in locating the peak positions. In general, we have given high estimates of the errors.

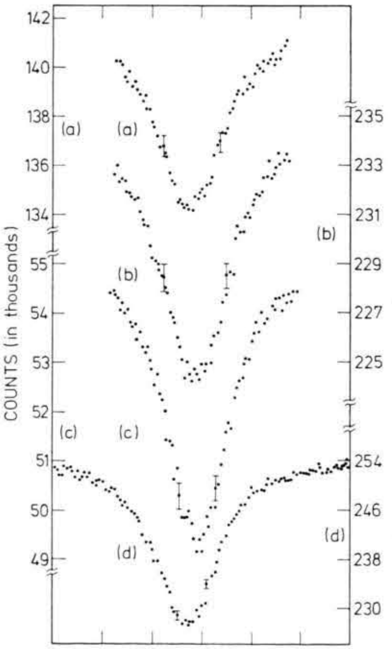

Fig. 1. Mössbauer spectra of (a) $EuCl_3 \cdot 6\,H_2O$, (b) $Eu(phen)_2Cl_3 \cdot H_2O$, (c) $Eu(NO_3)_3 \cdot 6\,H_2O$ and (d) $Eu(HCOO)_3 \cdot 2\,H_2O$ at room temperature (300 °K) with a Sm-151 source in the form of Sm_2O_3.

The names of the complexes, their respective sample thicknesses, linewidths, resonance effects and the isomer shifts are given in Table 1. Some of the sample spectra obtained are given in Figure 1.

Results and Discussion

a) *Resonance Effect*

The resonance effect in the complexes were calculated from the area under the resonance absorption curve which has been shown to be preferable to the method in which the effect is calculated by computing the percentage decrease in count rate [19]. It is clear from the data that there does not exist an inverse relationship between the resonance effect and the molecular mass [2, 5]. When the resonance effects in the carboxylate complexes were compared, it is noteworthy that for the formate and the salicylate complexes these values are nearly three times greater than those of most of the other carboxylate complexes. It appears that the intermolecular forces in these complexes are larger than those in other carboxylate complexes. These forces may occur as a result of bridging carboxylate groups as in the aminopoly-carboxylate complexes [3]. Or, there may be a strong intermolecular hydrogen bonding, especially in the salicylate complex. Similarly, the comparatively large resonance effect in the oxalate complex may be explained on the basis of the intermolecular bonding through carboxylate groups.

The magnitude of the resonance effect for the 1,10-phenanthroline complex indicates its polymeric nature. 1,10-phenanthroline is a big molecule and the polymeric nature of the complex may be due to steric factors which may prevent the ligands to form a monomeric species. Or, it may be due to strong intermolecular hydrogen bonding through water molecules.

The high resonance effect of the nitrate complex is interesting. As indicated by its isomer shift, the forces between the nitrate ion and the europium ion are electrostatic. Therefore, the polymerism in the nitrate complex should be due to strong intermolecular hydrogen bonding.

No doubt the resonance effects indicate the polymeric nature of some of the complexes, but additional structural work has to be done to establish the nature of the intermolecular forces and also to know why a particular carboxylic acid forms a polymeric species while the others form complexes having limited or practically no intermolecular forces. It is possible that steric hindrance and the size of the chelate ring are two of the many factors in forming the polymeric species.

b) *Isomer Shift*

The isomer shift is given by

$$\delta = \tfrac{2}{5}\, Z\, e^2 \left[\,|\Psi(0)|_a^2 - |\Psi(0)|_s^2\right] \Delta\langle R^2\rangle$$

where $|\Psi(0)|_a^2$ and $|\Psi(0)|_s^2$ indicate the densities at the absorber and source nuclei respectively and $\Delta\langle R^2\rangle = \langle R^2_{\text{ex}}\rangle - \langle R_{\text{g}}^2\rangle$, Since the $\Delta\langle R^2\rangle$ term is positive in europium, a decrease in the isomer shift will indicate a decrease in $|\Psi(0)|_a^2$ relative to the source. This change in electron density at the nuclei depends on two factors: (a) shielding by the electrons in the 4f or 5p orbitals [4] and (b) increasing participation of the 6s orbital [2].

The isomer shifts are in the range of -0.1 to -0.6 mm/sec. Since the removal of one electron from the 4f orbital ($\text{Eu}^{+2} \rightarrow \text{Eu}^{+3}$) corresponds to a shift of 15 mm/sec, the maximum degree of covalency in the complexes is estimated to be about 4%. This agrees well with the reported values [2, 4, 20].

The isomer shift for $\text{EuCl}_3 \cdot 6\,\text{H}_2\text{O}$ is much smaller than that for $\text{Eu(NO}_3)_3 \cdot 6\,\text{H}_2\text{O}$. It indicates a larger shielding of the s electrons by the 4f or 5p orbital electrons in the chloride complex as compared to that in the nitrate complex. It has been shown by X-ray diffraction that in the chloride complex there is a direct metal to chlorine bond [21]. Thus, the larger electron density of the 4f orbital in the chloride complex may be due to the donation of the p_π electrons of chloride to the 4f orbitals of europium. The donation by the halide may also consist in a partial displacement of the 5p electron density to the unfilled 4f orbitals, followed by the transfer of electron density of the p_π orbitals of the chloride ion to the 5p orbitals of the metal. In both cases the effect on the isomer shift will be the same. Such a π-electron donating property of the chloride ion is well known in the literature [22]. In the nitrate complex no such donation of electrons from the nitrate ions is possible. As a result of this, the isomer shift in the nitrate complex is larger than that in the chloride complex.

The isomer shift differences in $\text{Eu(phen)}_2\text{Cl}_3\text{H}_2\text{O}$ and $\text{Eu(dip)}_2\text{Cl}_3 \cdot \text{H}_2\text{O}$ may also be explained on the basis of a higher double bond character (back-donation) of the Eu-N bond in the 1,10-phenanthroline complex relative to that in the dipyridyl complex. In these complexes the back donation of the electrons is from the 4f or the 5p orbitals of the metal ion to the antibonding orbitals of the 1,10-phenanthroline and dipyridyl molecules. It is well known that 1,10-phenanthroline is a stronger π-acceptor than dipyridyl [23]. The higher double bond character of the M-N bond in the 1,10-phenanthroline complex is also reflected by the shift in the position of the band arising due to ν(M-N) towards higher wave numbers in its i.r. spectrum [24]. Thus, 1,10-phenanthroline, being a stronger π-acceptor, polarizes the 4f or 5p electron density more towards itself as compared to that in the dipyridyl complex. This will result in a weaker shielding of the s electrons in the 1,10-phenanthroline complex, an effect which is clearly shown by the values of their isomer shifts.

In $\text{Eu(H Sal)}_3 \cdot 2\,\text{H}_2\text{O}$, the phenyl ring can participate more in the delocalization than in $\text{Na Eu[(phth)}_2] \cdot 4\,\text{H}_2\text{O}$. Therefore, it can be safely assumed that the spin density of the unpaired electrons, formally restricted to the 4f orbitals of the metal, actually moves out into the π-system of the ligand. This type of sharing of the electrons is known for the transition metal acetylacetonates. Thus, the larger sharing of the 4f or 5p electron in the delocalization process in the complex, $\text{Eu(HSal)}_3 \cdot 2\,\text{H}_2\text{O}$, as compared to the phthalate complex will decrease the shielding of the s-electron by the 4f or 5p electrons. This will result in a relatively larger isomer shift as compared to the phthalate complex.

The above isomer shifts are explained by involving the electrons in the 4f or 5p orbitals. However, these isomer shifts can not be explained by invoking the participation of the 6s orbitals. Besides, 6s orbitals can not participate in the π-bond formation due to symmetry reasons.

In the complexes of the type $Eu(RCO_2)_3 \cdot 2\,H_2O$ the isomer shift increases as: $R = H < CH_3 < Cl_3C < C_6H_5 \approx p\text{-}O_2N - C_6H_4$. It appears that in order to explain the isomer shifts in the series the participation of both the 6s orbital and the 4f or 5p orbital is necessary. The higher value of the isomer shift of the acetate complex as compared to that of the formate complex is due to the higher donation of σ electrons of the acetate ion to the 6s orbital of the metal. This higher donation is due to a positive inductive $(+I)$ effect of the CH_3 group compared to H. This effect will make a higher electron density at the europium nucleus in the case of acetate, and thereby a larger isomer shift will result. A second factor which might affect the isomer shift in these complexes may be that the π-electron density of the COO^- group is also participating in the metal 4f or 5p orbitals. If the effect due to sesond factor is larger than that of the first one, shielding will be greater which will make the isomer shift smaller and vice versa. The strong $-I$ effect of the Cl_3C-group in the europium trichloracetate complex will make the 6s electron density comparatively smaller than that in acetate complex. This should produce a lower isomer shift in the trichloracetate complex. But at the same time the π-electron density will participate relatively less in the 4f or 5p orbitals which will tend to produce a larger isomer shift. It appears that in the trichloracetate complex, it is the second factor which dominates, thus producing a larger isomer shift. This increase in the ionic character of the metal oxygen bond in the lanthanides with the successive replacement of protons of the CH_3 group by the chlorine atoms, was also found in the isotropic proton shifts of the NMR data[25].

It is interesting to note the high covalency as well as high resonance effect in the formate complex. It is very difficult to pin point any definite reason for this peculair behaviour but, as mentioned, it may be possible that by some mechanism, p_π donation of the COO^- group to the metal 4f or 5p orbitals in the formate complex is enhanced as compared to other carboxylate complexes providing a higher covalency in the M-O bond of the formate complex.

In the benzoate and p-nitrobenzoate complex possibly it is due to the resonance of the π-electrons of the phenyl ring with the p_π electrons of the COO^- group by which the π electron on the oxygen atoms will be less available for participation in the 4f or 5p orbitals. This will increase the value of $|\Psi(0)|_a^2$ compared to the other carboxylates. Similar isomer shifts in the benzoic acid and p-nitrobenzoic acid complexes suggest practically no effect on the nature of M-O bond by the NO_2 group in the para position.

Acknowledgement

One of the authors (OKM) thanks the Council of Scientific and Industrial Research, New Delhi (India) for financial assistance.

[1] C. S. G. Phillips and R. J. P. Williams, Inorganic Chemistry, Volume II, Oxford University Press, London 1966.

[2] F. A. Deeney, J. A. Delaney, and V. P. Ruddy, J. Inorg. Nucl. Chem. **30**, 1175 [1968].

[3] F. A. Deeney, J. A. Delaney, and V. P. Ruddy, Phys. Lett. **A 25**, 370 [1967].

[4] M. F. Taragin and J. C. Eisenstein, J. Inorg. Nucl. Chem. **35**, 3815 [1973].

[5] J. L. Mackey and N. N. Greenwood, J. Inorg. Nucl. Chem. **34**, 1529 [1972].

[6] G. Gerth, P. Kienle, and K. Luchner, Phys. Lett. **A 27**, 557 [1968].

[7] O. Berkooz, J. Phys. Chem. Solids **30**, 1763 [1969].

[8] S. Hüfner, P. Kienle, D. Quitmann, and P. Brix, Z. Phys. **187**, 67 [1965].

[9] P. B. Sarkar, Bull. Soc. Chim. (France) **4**, 1390 [1926].

[10] J. R. Witt and E. I. Onstott, J. Inorg. Nucl. Chem. **24**, 637 [1962].

[11] W. W. Wendlandt, Anal. Chem. **30(1)**, 58 [1958].

[12] R. G. Charles, J. Inorg. Nucl. Chem. **27**, 1489 [1965].

[13] F. A. Hart and F. P. Laming, J. Inorg. Nucl. Chem. **27**, 1605, 1825 [1965].

[14] J. K. Marsh, J. Chem. Soc. **1941**, 561.

[15] S. P. Sinha, Chr. K. Jørgensen, and R. Pappalardo, Z. Naturforsch. **19 a**, 434 [1964].

[16] N. A. Kazanskaya, V. L. Ermolaev, A. V. Moshinskaya, A. A. Petrov, and Yu. I. Kheruze, Optica Spektroskopiya **28(6)**, 1150 [1970].

[17] S. P. Sinha, Europium, Springer-Verlag New York Inc. New York 1967.

[18] A. K. Gupta, K. R. Sarma, J. J. Huntzikar, and G. N. Rao, Rev. Sci. Instruments, in press.

[19] G. Lang, Nucl. Inst. Methods **24**, 425 [1963].

[20] A. Z. Hrynkiewicz, D. S. Kulgawczuk, A. M. Pustówka, I. Stronski, and K. Tomala, J. Inorg. Nucl. Chem. **33(3)**, 3707 [1970].

[21] N. K. Bel'skii and Yu. T. Struchkov, Kristallografiya **10**(1), 21 [1965].

[22] F. A. Cotton and G. Willkinson, Advanced Inorganic Chemistry, Second Revised Edition, John Wiley, New York 1966, pp. 256, 708.

[23] B. R. James and R. J. P. Williams, J. Chem. Soc. **1961**, 2007.

[24] J. R. Ferraro, L. J. Basile, and D. L. Kovacic, Inorg. Chem. **5**, 391 [1966].

[25] C. R. Kanekar, M. M. Dhingra, and N. V. Thakur, J. Inorg. Nucl. Chem. **34**, 3257 [1972].