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Europium-151 Mössbauer Effect Study of Several Organoeuropium(II) Complexes

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The europium-151 Mössbauer spectra of several organoeuropium(II) compounds have been measured at 77 and 4.2 K. All the compounds give isomer shifts of ca. −12 to −13 mm/s, typical of ionic europium(II). For $(C_5Me_5)_2Eu$, $(C_5Me_5)_2Eu(THF)$, and $(C_5Me_5)_2Eu(THF)(Et_2O)$, broad absorptions were observed, arising from spherical paramagnetic relaxation at a rate comparable to the Mössbauer time scale of 9.7×10^{-9} s. The relaxation rates are 490, 450, and 420 MHz, respectively, at 4.2 K, and the values for $(C_5Me_5)_2Eu(THF)$ and $(C_5Me_5)_2Eu(THF)(Et_2O)$ increase to 635 and 650 MHz at 77 K as a result of greater coupling of the spin with the lattice vibrations. For $[(C_5Me_5)Eu(THF)_2(\mu\text{-}I)]_2$ the spectrum corresponds to a relaxation rate of 1710 MHz at 4.2 K. $[(C_5Me_5)_2Eu(THF)]_n$ shows a symmetric spectrum that is close to the fast relaxation limit with an estimated relaxation rate of 5580 MHz. $EuI_2(THF)_2$ shows a narrow line width spectrum with a quadrupole interaction of −12.9 mm/s and an asymmetric parameter of 0.58 at 4.2 K. The rate of paramagnetic relaxation correlates well with the inverse of the distance between Eu(II) ions, suggesting that the relaxation occurs via a spin-spin interaction. The magnetic susceptibility of $(C_5Me_5)_2Eu$, measured between 2 and 320 K, shows it to be paramagnetic in this temperature range with a moment of 6.99 μ_B and a Curie-Weiss temperature of 3.28 K.

Introduction

Europium-151 Mössbauer spectroscopy is well suited for the study of the oxidation state and the local environment of europium in solid compounds.[1] The isomer shift, relative to EuF_3, of europium(III) in organic compounds or coordination complexes is in the range 0-1 mm/s, whereas that of europium(II) ions is in the range −12 to −15 mm/s. Because the typical experimental line width for a europium-151 Mössbauer spectrum is 2.4 mm/s, the two oxidation states of europium are easily distinguished. The quadrupole interaction, which is determined by the symmetry of the environment of the europium, removes the degeneracy of both the ground and the excited states of the Mössbauer nucleus and gives rise to Mössbauer spectra composed of eight overlapping lines. In europium(III) coordination complexes, as in most europium(III) compounds,[1] the quadrupole interaction is small, typically less than 10 mm/s, and the observed spectrum is a broad line, from which it is difficult to obtain an accurate value of the quadrupole interaction. In order to observe a resolved quadrupolar hyperfine structure, quadrupole interactions of 20 mm/s or more are required. $EuRh_3B_2$, with a quadrupole interaction of 45 mm/s,[2,3] is one of the few examples of a compound that shows a well-resolved quadrupole interaction for europium.

Organoeuropium(II) compounds are rare,[4] but recently, a number of bis(pentamethylcyclopentadienyl) complexes of europium(II) have been synthesized.[5,6] The crystal structure of $(C_5Me_5)_2Eu$ consists of discrete monomeric units possessing a bent metallocene geometry.[5] The compound is monoclinic with four molecules per unit cell and a minimum europium-europium distance of 6.2 Å. By comparison with the X-ray crystal structure of $(C_5Me_5)_2Yb(THF)\cdot 0.5\text{toluene}$[6] and $(C_5Me_5)_2Sm(OC_5H_{10})$,[7] $(C_5Me_5)_2Eu(THF)$ is also expected to have a bent metallocene geometry.

The very distorted environment of the europium(II) ions in these compounds suggested the possible presence of a large quadrupole interaction and stimulated a preliminary study of $(C_5Me_5)_2Eu$ and $(C_5Me_5)_2Eu(THF)$ at 77 K using the europium-151 Mössbauer effect.[8] The results of this study confirmed the divalent nature of europium in these complexes, but showed very broad absorption lines that were attributed to the presence of slow paramagnetic relaxation of the $^8S_{7/2}$ electronic ground state of the Eu(II) ion, and were explained by a model using spherical relaxation of the hyperfine field. To confirm these results, and to obtain further information on the relaxation mechanism, we have studied the Mössbauer spectra of these two compounds and a number of related Eu(II) compounds at 77 and 4.2 K, and the results of this study are given in this paper.

Experimental Section

The synthesis and subsequent manipulations of the complexes under study were conducted with the rigorous exclusion of air and water by using Schlenk-line and glovebox (Vacuum/Atmospheres HE-553 Dri-Lab) techniques. Solvents were dried as previously described.[9] KC_5Me_5,[9] NaC_5H_5,[10] $(C_5Me_5)_2Eu$,[5] $(C_5Me_5)_2Eu(THF)$,[6] and $(C_5Me_5)_2Eu(THF)(Et_2O)$[6] were obtained by following published literature procedures. Europium was obtained from Research Chemicals of Phoenix, AZ. $EuI_2(THF)_2$[11] $[(C_5H_5)_2Eu(THF)]_n$,[12,13] and $[(C_5Me_5)Eu(THF)_2(\mu\text{-}I)]_2$[9] were obtained by modifications of literature procedures as described below. Complexometric metal analysis was performed as previously described.[14]

$EuI_2(THF)_2$. In an inert-atmosphere glovebox, diiodoethane (2.67 g, 9.5 mmol) was added to europium metal (10.48 g, 60 mmol) in a 500-mL round-bottom flask containing a Teflon-coated stir bar. THF (50 mL) was added, and the reaction was stirred for approximately 48 h. The solution was centrifuged to remove the excess metal, and the resulting yellow-purple solution was dried by rotary evaporation to yield $EuI_2(THF)_2$ (4.97 g, 95%) as a greenish yellow powder. Anal. Calcd for $EuC_8H_{16}I_2O_2$: Eu, 27.63. Found: Eu, 27.5.

$[(C_5H_5)_2Eu(THF)]_n$. In the glovebox, NaC_5H_5 (0.131 g, 1.48 mol) was added to a stirred solution of $EuI_2(THF)_2$ (0.406 g, 0.74 mmol) in 8 mL of THF. The solution immediately became light yellow and was stirred for 3 h. The solution was centrifuged, and the slightly cloudy yellow solution was discarded. The solid consisted of two layers: a light yellow layer on the bottom and a white layer on the top. The solids were resuspended in THF (10 mL) and centrifuged eight times, after which the cloudiness of the solution had disappeared and only the light yellow

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layer of solid remained. The light yellow solid was dried by rotary evaporation, leaving $[(C_5H_5)_2Eu(THF)]_n$ (0.23 g, 90%) as a light yellow free-flowing powder. Anal. Calcd for $EuC_{14}H_{18}O$: Eu, 42.90. Found: Eu, 41.2.

$[(C_5Me_5)Eu(THF)_2(\mu\text{-}I)]_2$. In the glovebox, KC_5Me_5 (0.244 g, 1.40 mmol) dissolved in 5 mL of THF was added to a stirred solution of $EuI_2(THF)_2$ (0.749 g, 1.36 mmol) in 15 mL of THF in a 50-mL Erlenmeyer flask. The solution immediately turned orange-yellow and formed light-colored solids. After the reaction had been stirred for 2 h, the solution was centrifuged to remove KI as a white solid, leaving a bright orange solution. Solvent was removed from the solution by rotary evaporation, and the yellow-orange solid was washed with 30 mL of toluene to remove any $(C_5Me_5)_2Eu(THF)$ present. The remaining bright orange-yellow powder was dissolved in THF (2 × 10 mL) and centrifuged to remove any trace amounts of KI still present. The solvent was then removed by rotary evaporation to yield $[(C_5Me_5)Eu(THF)_2(\mu\text{-}I)]_2$ (0.65 g, 85.6%) as a fluorescent yellow-green microcrystalline powder. This powder crystallized from THF/hexane at ambient temperature in the $P2_1/n$ space group with unit cell parameters a = 12.692 (7) Å, b = 13.445 (5) Å, c = 13.847 (7) A, and β = 112.32 (4)°. The complex is isostructural with $[(C_5Me_5)Sm(THF)_2(\mu\text{-}I)]_2$.[9]

Magnetic susceptibility results were obtained by using a standard Faraday magnetic susceptibility balance that was calibrated with $HgCo(NCS)_4$. The sample was loaded under an inert atmosphere and gave identical results upon warming from 2.2 K to room temperature.

Mössbauer spectra were measured at 77 and 4.2 K in an Oxford Instruments liquid pool cryostat with the source and absorber at the same temperature. The source was samarium-151 in a SmF_3 matrix and the γ-rays were detected with a Harshaw scintillation counter. The velocity scale was calibrated with room-temperature α-iron foil, and the zero velocity was determined at room temperature with EuF_3, which is the isomer shift reference for all results reported herein. The spectrometer used a symmetric triangular velocity scan generated by a Wissel GmbH System MS I drive, with 1024 channels used for data accumulation. Samples were sealed inside lead or Teflon rings with tape and contained 30–40 mg of natural Eu/cm^2. All absorbers were prepared in an inert-atmosphere glovebox under nitrogen and were transferred under nitrogen.

Two different methods were used in the analysis of the europium-151 Mössbauer spectra. The first method assumed rapid paramagnetic relaxation on the Mössbauer time scale of 9.7×10^{-9} s, and the spectra were fitted by varying the isomer shift, the quadrupole interaction, the line width, and the total absorption area with a fixed asymmetry parameter, η, for a total of four variables, by using the nonlinear least-squares method of Stone.[15] The function fitted was a pure quadrupole-split spectrum calculated for a $^5/_2$–$^7/_2$ transition with a ratio of $Q(^7/_2)/Q(^5/_2)$ of 1.31. The optimum value for η was found by a series of fits with different η values.

The second method fits the spectrum to a spherical relaxation profile[16,17] by varying the isomer shift, the total absorption area, and the relaxation rate with a fixed line width and effective hyperfine field, for a total of three variables. As expected, there was a high correlation between the line width, effective hyperfine field, and the relaxation rate. Hence, in all the spherical relaxation fits, the line width was fixed at 2.4 mm/s, a reasonable value for europium-151 and consistent with the calibration of the spectrometer. Further, in the spherical relaxation fits, the quadrupole interaction was fixed at zero, a valid assumption because, as mentioned above and discussed below, the quadrupole interaction is negligible when compared to the paramagnetic hyperfine interaction and consequent relaxation broadening of the spectrum. Furthermore, the introduction of a quadrupole interaction would require an assumption about the asymmetry parameter and would lead to a model that is much more complex than is needed to give satisfactory fits to the experimental spectra.

Results

The observed Mössbauer spectra for the organoeuropium(II) complexes may be divided into two groups. In the first group, the spectra of $EuI_2(THF)_2$, $[(C_5H_5)_2Eu(THF)]_n$, and $[(C_5Me_5)Eu(THF)_2(\mu\text{-}I)]_2$ are narrow, as illustrated in Figure 1, for spectra obtained at 4.2 K. The spectra are virtually identical at 77 K. In the second group, the spectra of $(C_5Me_5)_2Eu$, $(C_5Me_5)_2Eu(THF)$, and $(C_5Me_5)_2Eu(THF)(Et_2O)$ are broad, as shown in Figure 2. All of the spectra measured in this study show two components, a major component centered at ca. −13 mm/s and a minor component centered near zero mm/s. The major component is attributed to europium(II) and is of interest in this work. The minor component, which ranges from 2 to 12% of the total absorption area, is an impurity resulting from the oxidation of the extremely air- and moisture-sensitive europium(II) complexes. Exposure of the samples to traces of oxygen resulted in an increase in the area of this component at the expense of the europium(II) component. The europium(III) component has been fit with a single Lorentzian line in all cases and will not be discussed further here.

Table I. Europium-151 Mössbauer Spectral Hyperfine Parameters[a]

compd	T, K	δ,[b] mm s^{-1}	e^2qQ, mm s^{-1}	η	Γ, mm s^{-1}
$EuI_2(THF)_2$	77	−12.3 (1)	−12.3 (6)	0.53 (5)	3.01 (7)
	4.2	−12.2 (1)	−12.9 (5)	0.58 (5)	3.21 (4)
$[(C_5H_5)_2Eu(THF)]_n$	77	−13.2 (1)	±6.0 (6)	1.00 (5)	2.83 (14)
	4.2	−13.2 (1)	±6.2 (4)	1.00 (5)	2.59 (8)
$[(C_5Me_5)Eu(THF)_2$-$(\mu\text{-}I)]_2$	77	−12.7 (1)	±12.0	1.00	4.0 (2)
	4.2	−12.73 (3)	±13.0	1.00	3.0 (1)

[a] Fits obtained by assuming rapid paramagnetic relaxation on the Mössbauer time scale. δ is the isomer shift, e^2qQ, the quadrupole interaction, η, the asymmetry parameter, and Γ, the full width at half-maximum. [b] Relative to room-temperature EuF_3.

Table II. Europium-151 Mössbauer Spectral Parameters As Obtained from a Spherical Relaxation Model

compd	T, K	δ,[a] mm s^{-1}	λ, MHz	H, kOe
$(C_5Me_5)_2Eu$	77	−12.9 (1)	450 (30)	−330 (10)
	4.2	−12.7 (1)	490 (30)	−330 (10)
$(C_5Me_5)_2Eu(THF)$	77	−13.4 (1)	635 (40)	−330 (10)
	4.2	−12.8 (1)	450 (30)	−330 (10)
$(C_5Me_5)_2Eu(THF)(Et_2O)$	77	−13.3 (1)	650 (45)	−330 (10)
	4.2	−12.9 (1)	420 (30)	−330 (10)
$[(C_5Me_5)Eu(THF)_2(\mu\text{-}I)]_2$	77	−12.7 (1)	1490 (50)	−340 (10)
	4.2	−12.7 (1)	1710 (50)	−340 (10)
$[(C_5H_5)_2Eu(THF)]_n$	77	−13.4 (1)	5550 (340)	−330 (10)
	4.2	−13.1 (1)	5580 (340)	−330 (10)

[a] Relative to room-temperature EuF_3.

The spectra for $EuI_2(THF)_2$, $[(C_5H_5)_2Eu(THF)]_n$, and $[(C_5Me_5)Eu(THF)_2(\mu\text{-}I)]_2$ were fit initially with a quadrupole interaction under the assumption of fast paramagnetic relaxation. The resulting hyperfine parameters are given in Table I. For $EuI_2(THF)_2$ the spectra at 77 and 4.2 K show a clear asymmetry, and, as illustrated in Figure 3, the fits show a well-defined minimum in χ^2 as η is varied, indicating the hyperfine parameters to be clearly defined for this spectrum. For $[(C_5H_5)_2Eu(THF)]_n$ the fit shown in Figure 1B is clearly satisfactory, but the minimum of χ^2 as a function of η is more shallow than that for $EuI_2(THF)_2$, implying that the hyperfine parameters are less well defined in this case. The best fit indicates the presence of a small quadrupole interaction of ca. ±6 mm/s. The sign of this quadrupole interaction is undetermined because a symmetric spectrum with an asymmetry parameter of 1 is insensitive to the sign of the quadrupole interaction.[1]

The fit for $[(C_5Me_5)Eu(THF)_2(\mu\text{-}I)]_2$, obtained by assuming rapid paramagnetic relaxation, is poor at both 77 and 4.2 K, as is illustrated in Figure 1C. For this compound no reasonable combination of quadrupole interaction, asymmetry parameter, and line width would reproduce the observed line shape, and as a result, the hyperfine parameters obtained for this compound are given in Table I for comparison purposes only. In this case, the assumption of rapid paramagnetic relaxation on the Mössbauer time scale is apparently not valid. To check this conclusion, we have fit the spectra of $[(C_5Me_5)Eu(THF)_2(\mu\text{-}I)]_2$ with a relaxation profile. The results of these fits are excellent, as is illustrated in Figure 1D. The resulting hyperfine parameters are given in Table II. The significance of this result is discussed in detail below.

The Mössbuaer spectra of the second group of compounds, $(C_5Me_5)_2Eu$, $(C_5Me_5)_2Eu(THF)$, and $(C_5Me_5)_2Eu(THF)(Et_2O)$, are broad at both 77 and 4.2 K, as is illustrated in Figure 2. The

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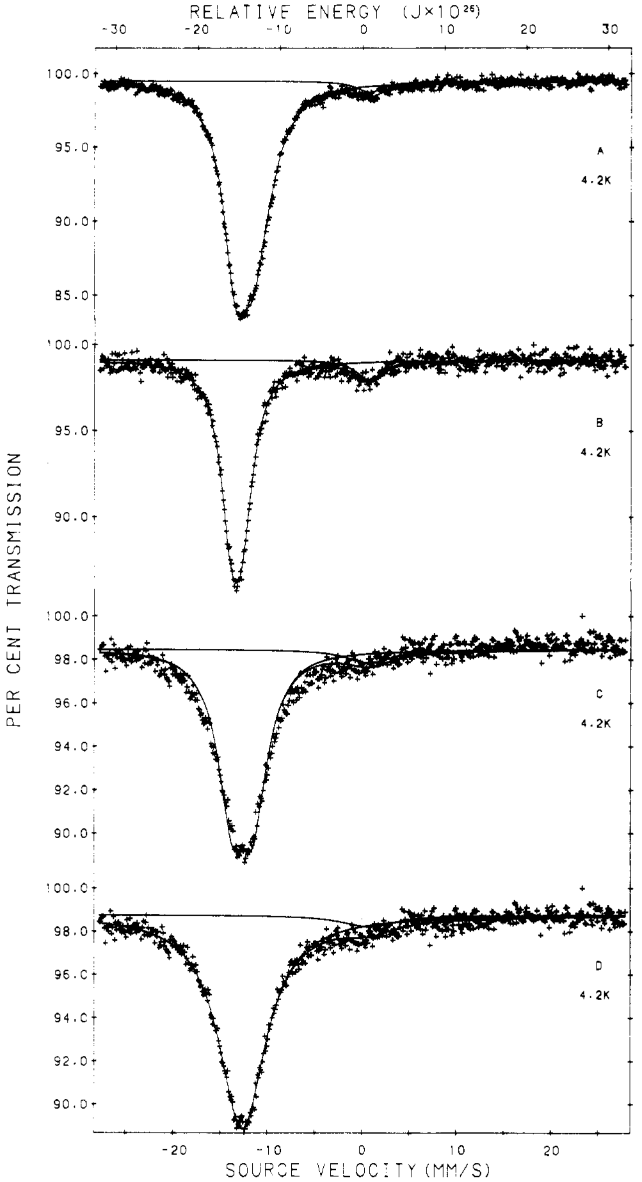

Figure 1. Europium-151 Mössbauer spectra of $EuI_2(THF)_2$ (A), $[(C_5H_5)_2Eu(THF)]_n$ (B), and $[(C_5Me_5)Eu(THF)_2(\mu\text{-}I)]_2$ (C, D) obtained at 4.2 K. The fits shown in (A–C) are the results of a least-squares fit with a quadrupole interaction. In (D) the solid line is a fit with a spherical relaxation profile.

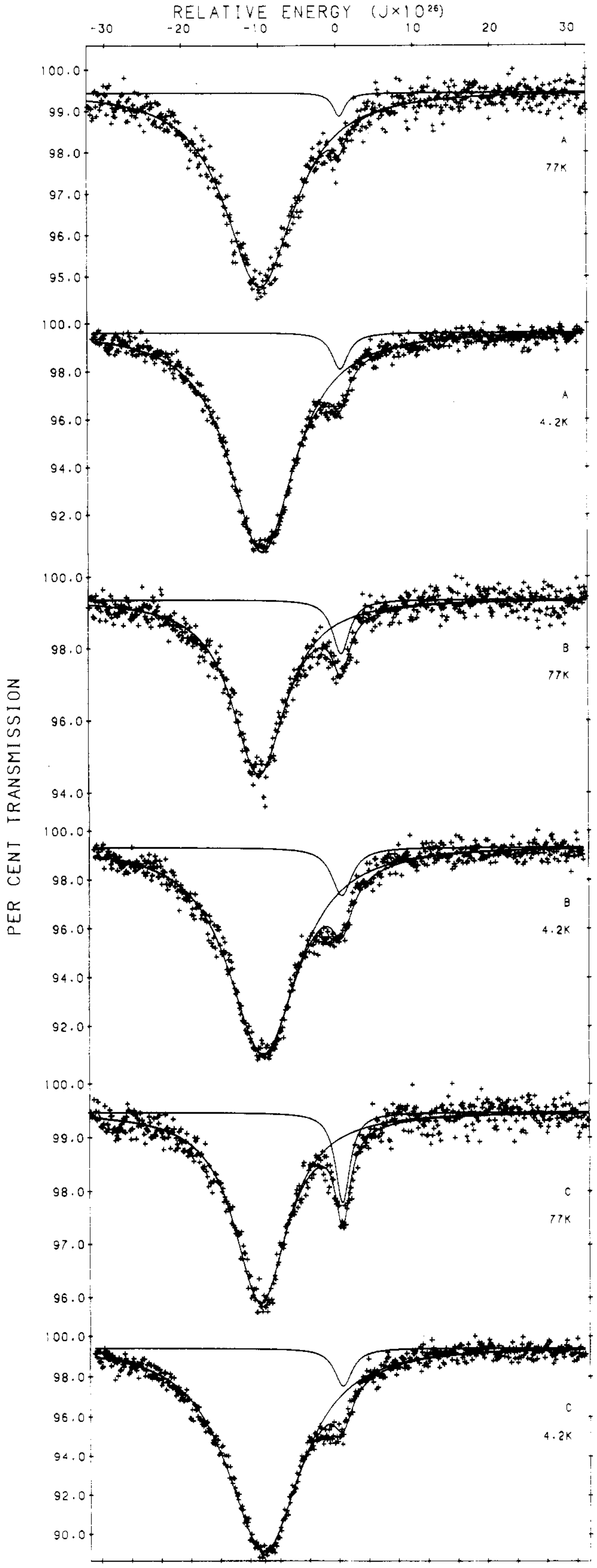

Figure 2. Europium-151 Mössbauer spectra of $(C_5Me_5)_2Eu$ (A), $(C_5Me_5)_2Eu(THF)$ (B), and $(C_5Me_5)_2Eu(THF)(Et_2O)$ (C) obtained at 4.2 and 77 K. The solid lines are the result of a least-squares fit with a relaxation profile.

single broad absorption line centered at ca. −13 mm/s indicates europium(II). However, as discussed[8] in our preliminary paper, several explanations for these broad absorptions, with line widths of ca. 10–14 mm/s, were examined, and no combination of a quadrupole interaction, with an asymmetry parameter close to 1, as required to account for the symmetric absorption, and a reasonable linewidth of ca. 3 mm/s or less, could reproduce the observed spectra. The possibility of a distribution of quadrupole interactions and/or isomer shifts was rejected because there is no structural basis for such a distribution in these complexes.[5] However, broad line shapes in Mössbauer spectra are often due to slow relaxation, and in these paramagnetic compounds, slow paramagnetic relaxation on the europium-151 Mössbauer time scale of 9.7×10^{-9} s is quite possible. Furthermore, as can be seen in Figure 2, the line width of the complete absorption band increases from ca. 11 mm/s at 77 K to 15 mm/s at 4.2 K for both $(C_5Me_5)_2Eu(THF)$ and $(C_5Me_5)_2Eu(THF)(Et_2O)$. Such behavior is consistent with the temperature dependence of slow paramagnetic relaxation.

The paramagnetic nature of these compounds is confirmed by a study of the magnetic susceptibility of $(C_5Me_5)_2Eu$ from 2 to 320 K, as is shown in Figure 4. The inverse susceptibility decreases linearly with temperature and gives a Curie–Weiss temperature of 3.28 K and an effective magnetic moment of $6.99\mu_B$, if a diamagnetic correction of -240×10^{-6} cgsu is used. Above

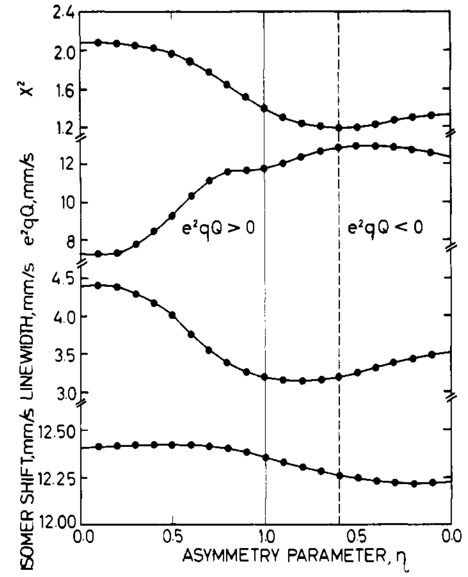

Figure 3. The variation of the isomer shift, line width, quadrupole interaction, and χ^2 with the asymmetry parameter for the Mössbauer spectrum of $EuI_2(THF)_2$ obtained at 4.2 K.

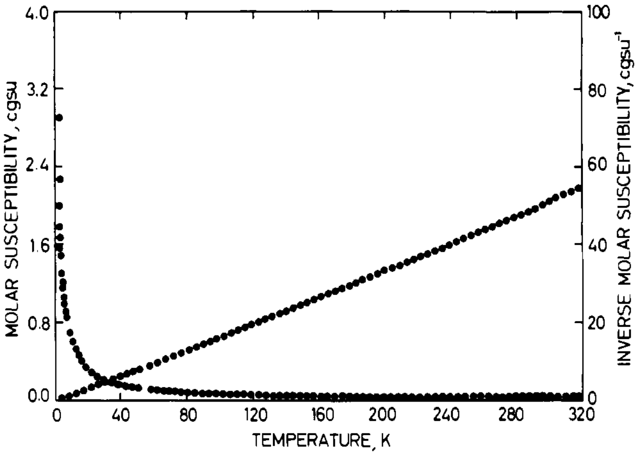

Figure 4. Molar and inverse molar magnetic susceptibility of $(C_5Me_5)_2Eu$ measured between 2.2 and 320 K at various applied fields.

ca. 5 K the molar magnetic susceptibility is independent of the applied magnetic field. However, below ca. 5 K there is a very small field dependence to the magnetic susceptibility, as is illustrated in Figure 5. The results of these measurements indicate that $(C_5Me_5)_2Eu$ is paramagnetic over the temperature range of our Mössbauer studies. However, the positive Curie–Weiss temperature and the field dependence of the molar susceptibility below 5 K may indicate the presence of a very small ferromagnetic component to the susceptibility at very low temperatures. Although we have not studied the magnetic properties of the remaining compounds in detail, similar paramagnetic behavior would be expected. Indeed, it is reported that $(C_5Me_5)_2Eu(THF)(Et_2O)$ is paramagnetic from 5 to 50 K.[6]

In order to try to understand the broad Mössbauer absorption profiles shown in Figure 2, two relaxation models were tried. The first model assumed uniaxial relaxation of the effective hyperfine field corresponding to a random field reversal,[18] as might be expected for the monoclinic structure of these compounds.[5] No satisfactory fit could be obtained with this model, and a visual examination of the fit revealed that the theoretical line profile was too triangular and gives more structure than is observed in the experimental spectra. This is the case even if an anomalously large line width of 5 mm/s is used for the theoretical line profile. The second relaxation model assumes a spherical relaxation of the hyperfine field,[16] which, as shown by Litterst et al.,[17] leads to a broader line shape than does uniaxial relaxation. The solid lines in Figure 2 are the results of fits with this spherical relaxation model. While the spectra were being fitted, it became apparent that the line width, the effective hyperfine field, and the relaxation rate were highly correlated. Hence, the line width was held constant at 2.4 mm/s in all these fits. This value is reasonable for the spectrometer, because the line width observed for EuF_3 is 2.2 mm/s at 300 K and 2.7 mm/s at 77 K. Furthermore, such a small value for the line width is a strong constraint on the model because all other models we have tried required a line width of more than 5 mm/s to come even close to a fit. Even with a constant line width, the relaxation rate and the hyperfine field could not be varied simultaneously without obtaining unrealistic parameters. Consequently, we have fit the relaxation rate for various fixed values of the hyperfine field and selected the best fit on the basis of MISFIT.[19] The hyperfine field was varied between −300 and −340 kOe, values that are reasonable for the rather isolated europium(II) ions in these complexes.[1,5] Because the sign of the hyperfine field is undetermined, we assume that the field is negative, as is expected[1] for the core field of the europium(II) ion. Figure 6 shows the change in the isomer shift, the relaxation rate, and MISFIT[19] as a function of the hyperfine field for the

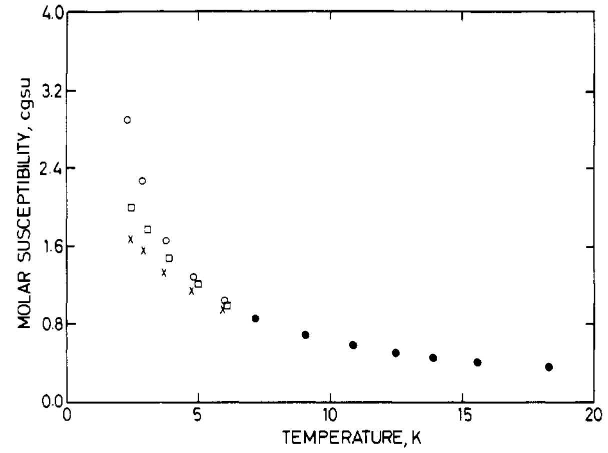

Figure 5. Molar magnetic susceptibility of $(C_5Me_5)_2Eu$ measured between 2.2 and 20 K at an applied field of 5.2 kG (○), 15.8 kG (□), and 19.5 kG (×). The remaining points are the average obtained at the three fields.

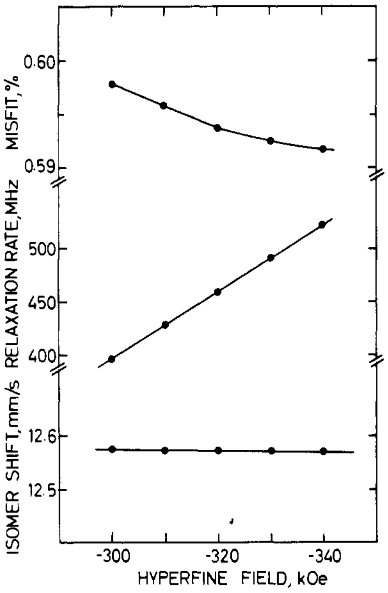

Figure 6. Variation of the isomer shift, relaxation rate, and MISFIT with the hyperfine field for the Mössbauer spectrum of $(C_5Me_5)_2Eu$ obtained at 4.2 K.

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Mössbauer spectrum of $(C_5Me_5)_2Eu$ obtained at 4.2 K. No values of the hyperfine field below −340 kOe were tried because, in these compounds, the only significant contribution to the hyperfine field is the core polarization term. The parameters obtained from the best fits are presented in Table II. This table also includes equivalent spherical relaxation fits for $[(C_5Me_5)Eu(THF)_2(\mu\text{-}I)]_2$ and $[(C_5H_5)_2Eu(THF)]_n$.

Discussion

Isomer Shifts. The isomer shifts of all the compounds studied lie in the range expected for Eu(II) compounds,[1] and only two compounds, $(C_5Me_5)_2Eu(THF)$ and $(C_5Me_5)_2Eu(THF)(Et_2O)$, show any significant change in isomer shift between 4.2 and 77 K. Because in these experiments the source and absorber were held at the same temperature, second-order Doppler shifts are expected to be small, and the isomer shift changes observed for $(C_5Me_5)_2Eu(THF)$ and $(C_5Me_5)_2Eu(THF)(Et_2O)$ with temperature must reflect significant changes in the lattice dynamics for these compounds between 4.2 and 77 K. At 4.2 K the isomer shifts of the pentamethylcyclopentadienyl compounds are virtually identical, whereas $EuI_2(THF)_2$ has a slightly more positive shift, which is close to that reported[20] for EuI_2 at 77 K. The cyclopentadienyl polymer, $[(C_5H_5)_2Eu(THF)]_n$, has a more negative isomer shift, which is close to that found[21] for EuF_2. It will be noted that ligands such as the cyclopentadienyl ion, which might be expected to show strong covalent donation, do not give isomer shifts significantly different from the more ionic halide ligands, suggesting that the europium–ligand bonds are essentially ionic. Further discussion of the small differences in the isomer shifts in these compounds must, however, await the development of a suitable theory and more detailed structural information, a situation that is also found for many europium(III) compounds.[1,22]

Quadrupole Interactions. Except for $EuI_2(THF)_2$ and $[(C_5H_5)_2Eu(THF)]_n$, the quadrupole interactions in the compounds studied appear to be insignificant or cannot be observed because of the relaxation broadening of the europium-151 Mössbauer spectra. Even for $EuI_2(THF)$ and $[(C_5H_5)_2Eu(THF)]_n$ the quadrupole interactions of −12.9 and ±6.2 mm/s observed at 4.2 K are small and result only in broadening of the absorption spectrum, as is seen in Figure 1. Because Eu(II) has a $^8S_{7/2}$ ground state, any electric field gradient must arise exclusively from a lattice term due to an asymmetric distribution of charge outside the europium ion. Even though coordination geometry may be quite irregular in these two compounds, it appears that the magnitude of the lattice contribution to the electric field gradient is rather small, as might be expected for a highly ionic system with relatively long metal–ligand distances.

Paramagnetic Relaxation. The most interesting feature of the spectra reported here is the observation of slow paramagnetic relaxation, with the relaxation rate changing considerably from compound to compound. In the absence of paramagnetic relaxation the Mössbauer spectrum would be split by the magnetic field due to the paramagnetic europium(II) ion.[1] However, paramagnetic relaxation produces a continuous reorientation of this magnetic field, and if the process is rapid on the Mössbauer time scale, the nucleus experiences a time-averaged field of zero and yields an unsplit absorption spectrum. In the case of slow relaxation a broadening of the Mössbauer absorption is observed. For the solid-state compounds studied here the predominant mechanism that produces the relaxation of the paramagnetic field is either spin–spin coupling with other magnetic ions or spin–lattice coupling of the magnetic ions via the lattice vibrations. Spin–spin interactions will depend on the distance between paramagnetic ions and will decrease as their separation increases. Spin–lattice interactions depend strongly on the nature of the electronic ground state of the paramagnetic species. Ions with orbitally degenerate ground states have several low-lying excited states with different magnetic moments and direct, Raman, or Orbach processes[23] can couple lattice vibrations to electronic excitations and lead to rapid reorientation of the magnetic moment. However, europium(II) has an orbitally nondegenerate $^8S_{7/2}$ ground state with no low-lying electronic excited states, and spin–lattice relaxation is consequently much slower. This effect is clearly observed for the $^8S_{7/2}$ ground state of the gadolinium(III) ion, whose relaxation times are estimated to be 10^{-8} to 10^{-9} s, some 4 or 5 orders of magnitude greater than those for the other lanthanide ions.[23]

The estimated europium(II) relaxation rates given in Table II are very close to the values quoted for the Gd(III) ion with the identical ground state. Only two compounds, $(C_5Me_5)_2Eu(THF)$ and $(C_5Me_5)_2Eu(THF)(Et_2O)$, show a significant decrease in relaxation rate on cooling from 77 to 4.2 K. Because the interionic distances, and hence the spin–spin interactions, are not expected to change greatly upon cooling, we attribute this decrease in relaxation rate to a slowing of the spin–lattice relaxation. It is important to note that it is just these two compounds which show a significant change in isomer shift upon cooling, attributed to a second-order Doppler effect, thus reflecting a change in the lattice dynamics between 77 and 4.2 K.

Spin–spin relaxation, if present, would be expected to show some dependence upon the Eu–Eu distances, and the data available strongly support this. In $(C_5Me_5)_2Eu$ the Eu–Eu distance is 6.2 Å, and in $(C_5Me_5)_2Eu(THF)$ the Eu–Eu distance may be estimated to be 6.4 Å through a comparison with the structure[7] of $(C_5Me_5)_2Sm(OC_5H_{10})$. The Eu–Eu distance is presumably similar in $(C_5Me_5)_2Eu(THF)(Et_2O)$. These three compounds have similar relaxation rates, whereas in the iodo-bridged dimer, $[(C_5Me_5)Eu(THF)_2(\mu\text{-}I)]_2$, which relaxes much faster, the Eu–Eu distance is only 4.8 Å. The polymeric species $[(C_5H_5)_2Eu(THF)]_n$, which, as discussed above, is close to the fast relaxation limit, must have a short Eu–Eu distance as a consequence of its polymeric structure. $EuI_2(THF)_2$, which also behaves as a rapidly relaxing system, must equally have short Eu–Eu distances, because a coordination number of 4, required for a monomeric $EuI_2(THF)_2$ unit, is most improbable for the large Eu(II) ion, and the presence of bridging ligands between Eu atoms is most likely.

The results of the relaxation analysis are thus in good agreement with what is known of the electronic and molecular structure of these compounds and suggest that variable-temperature Mössbauer spectroscopy is a useful method for studying paramagnetic relaxation in these solids. The success of the spherical relaxation model rather than the uniaxial model may be attributed to the $^8S_{7/2}$ ground state and to the absence of any axial constraint, as shown by the absence of large quadrupole interactions.

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Registry No. $(C_5Me_5)_2Eu$, 101200-04-8; $(C_5Me_5)_2Eu(THF)$, 74282-45-4; $(C_5Me_5)_2Eu(THF)(Et_2O)$, 74282-44-3; $[(C_5Me_5)Eu(THF)_2(\mu\text{-}I)]_2$, 124020-96-8; $(C_5H_5)_2Eu(THF)$, 104764-84-3; $EuI_2(THF)_2$, 123882-26-8.

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