Mössbauer Spectroscopic Investigation of some Europium(III) Diketonates

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A study is described of some europium(III) diketonate complexes in the solid state. Mössbauer spectra, taken with a ^{151}Eu source in a Sm_2O_3 lattice, have been obtained over the temperature range 79—220 K. Measurements of relative intensities of europium(III) fluorescence following irradiation by near u.v. light are also reported. Isomer shifts are discussed in terms of the europium–oxygen bonding but no obvious correlation is apparent between fluorescence efficiency and overall covalency of the bonds revealed by the data. Intermolecular bonding in the complexes, as deduced from the temperature dependence of the Mössbauer resonant effect, is discussed; the results are consistent with available structural data.

LIGHT absorption and emission of europium(III) and terbium(III) complexes with β-diketones have received considerable attention in recent years. Irradiation in the near u.v. produces fluorescence characteristic of the metal ion and emission intensity appears to be very dependent on the nature of the complex. The observation [1] that certain of these chelates exhibit laser action has stimulated interest in energy-transfer mechanisms within the molecules. While significant progress [2] has been made towards an understanding of the mechanism of energy transfer, to date it has not been possible to relate structural features of the complexes with intensity of emission from the metal ion. The Mössbauer spectroscopic investigations and fluorescence intensity measurements reported here have been carried out as part of a search for such correlations in tris- and tetrakis-europium(III) diketonates.

EXPERIMENTAL

The preparation and purification of the β-diketonate complexes used in this work (see Table 1) are described elsewhere.[3]

The γ-ray source consisted of 10 mCi of ^{151}Sm incorporated in a Sm_2O_3 lattice (New England Nuclear Corp., Boston, Mass.). It was driven in the constant acceleration mode in a spectrometer, the essential components of which were obtained from 20th Century Electronics Limited, New Addington, England. The 21·6 keV γ-ray emission from the ^{151}Eu daughter was monitored by means of a thin Na(Tl)I crystal scintillator and spectral data were stored in a Laben 512 channel analyser operated in the multiscalar mode. Spectra were taken with both source and absorber at the same fixed temperature within the range 79—220 K. Absorber thicknesses were chosen so that the ^{151}Eu content was constant at 3·4 mg cm^{-2} in each sample.

TABLE 1

Diketone [a]	Abbreviation used	Europium chelate
Pentane-2,4-dione	Haa	$[Eu(aa)_3],3H_2O$
1,1,1,5,5,5-Hexafluoropentane-2,4-dione	Hhfa	$[Eu(hfa)_3],2H_2O$ $[Eu(hfa)_4][pip]$ [b]
1,1,1-Trifluoro-4-phenylbutane-2,4-dione	Hbta	$[Eu(bta)_3],2H_2O$ $[Eu(bta)_4][pip]$
1,Phenylbutane-1,3-dione	Hba	$[Eu(ba)_3],2H_2O$ $[Eu(ba)_4][pip]$
1,1,1-Trifluoropentane-2,4-dione	Htfa	$[Eu(tfa)_4][pip]$
1,3-Diphenylpropane-1,3-dione	Hdbm	$[Eu(dbm)_3]$ $[Eu_2(dbm)_5OH]$ $[Eu(dbm)_4][pip]$

[a] The ligand is considered to be derived from the diketone by removal of a hydrogen ion. [b] pip is the piperidinium ion.

The variable-temperature cryostat operating on a design principle described by Wiedemann [4] was obtained from 20th Century Electronics Ltd.

The velocity scale of the spectrometer was calibrated and frequently checked using the magnetic hyperfine spectrum from an enriched (90—95% ^{57}Fe) iron absorber 2 mg cm^{-2} in thickness (Radiochemical Centre Ltd., Amersham, England).

Relative fluorescence intensities were measured with an Aminco–Bowman spectrophotofluorimeter. The integrated fluorescence output in the wavelength range 570—630 nm was obtained from microcrystalline (pulverised) samples using frontal illumination-detection geometry. As a previous study [5] at this laboratory had shown that the intensity of fluorescence is dependent on the exciting wavelength within the range 250—400 nm, emission intensities were recorded at the wavelength of maximum excitation.

RESULTS AND DISCUSSION

The Mössbauer spectra, all of which consisted of a single broad absorption line devoid of any resolved fine structure, were computer fitted with a single Lorentzian curve from which line positions, widths, and intensities were obtained. A sample spectrum, with computed curve, is shown in the Figure.

In the absence of a generally satisfactory reference substance, isomer shifts are reported relative to the zero velocity position of the source. A sample of Eu_2O_3 freshly prepared by ignition of $Eu(NO_3)_3,6H_2O$ and another of $EuF_3,0{\cdot}5H_2O$ obtained from aqueous chloride solution by precipitation with hydrofluoric acid had isomer shifts of 0·23 and −0·78 mm s^{-1} respectively when measured relative to this reference. Isomer shifts and line widths from the Mössbauer spectra over the temperature range studied are presented in Table 2. It can be seen that all the shifts recorded are positive with respect to the predominantly ionic $EuF_3,0{\cdot}5H_2O$ but decidedly more negative than Eu_2O_3. Isomer shifts and line widths for each complex are also seen not to vary significantly over the range of temperatures studied.

Relative intensities of fluorescence are presented in

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[1] A. Lempicki and H. Samelson, *Phys. Letters*, 1963, **4**, 113.

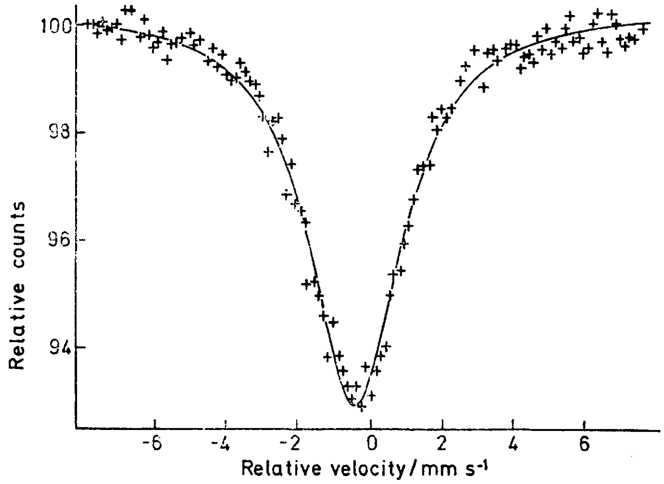
[2] A. P. B. Sinha in 'Spectroscopy in Inorganic Chemistry,' eds. C. N. R. Rao and J. R. Ferraro, Academic Press, London, 1971, vol. 11, p. 255.

[3] S. J. Lyle and A. D. Witts, *Inorg. Chim. Acta*, 1971, **5**, 481.

[4] W. Wiedemann, W. A. Mundt, and D. Kullman, *Cryogenics*, 1965, **5**, 94.

[5] S. J. Lyle, J. E. Newbery, and A. D. Witts, *J.C.S. Dalton*, 1972, 1726.

Table 3. Although a high degree of precision cannot be expected in these measurements, reproducibility was good (5—10%) and there is reasonable agreement with the limited data available for comparison in the literature[6,7] (Table 3). It can be seen that the intensity varies widely from substance to substance. As has generally been recognised for some time, tetrakis-complexes are more efficient emitters than the corresponding hydrated tris-complexes. Co-ordinated water in tris-complexes may be responsible for the dissipation of energy through vibrational deactivation, but the results for [Eu(dbm)$_3$] and perhaps [Eu$_2$(dbm)$_5$OH] would suggest that other factors, probably stereochemical in origin, are more fundamental in this context. It is notable also that fluorescence output for tetrakis-complexes is higher for those which contain aromatic groups.



Mössbauer spectrum of [Eu(ba)$_4$][pip] at 86·5 K

Metal–ligand bonds in these complexes are predominantly ionic in character and hence variation in isomer shifts may be expected to be rather limited. However, since it has been suggested[8] that the degree of covalency of the bonds in question may affect the efficiency of the intramolecular energy-transfer leading to europium fluorescence, an examination of isomer shifts is relevant in this context.

The large shift observed in going from europium(III) to europium(II) would suggest that if 4*f* orbitals participate, even only in a limited way, in bond formation, measurable effects could be expected. However, in view of the number of *s*, *p*, *d*, and *f* orbitals theoretically available, it is not essential for *f* orbitals to be involved at all. The relatively few *X*-ray diffraction studies of tris-(hydrated) and tetrakis-diketonates reported so far have revealed[9-14] in all instances a co-ordination of 8

TABLE 2

Mössbauer spectral data

Chelate complex	T/K	Isomer shift mm s^{-1}	Line width mm s^{-1}
[Eu(ba)$_4$][pip]	86·5	−0·43(4) [a]	3·0(1) [a]
	96·5	−0·45(4)	3·1(1)
	105·5	−0·46(4)	3·0(1)
	121·0	−0·44(4)	3·1(1)
	140·1	−0·47(4)	3·1(1)
	178·5	−0·40(6)	3·0(2)
	218·5	−0·45(12)	
[Eu(bta)$_4$][pip]	85·2	−0·49(3)	3·2(1)
	118·4	−0·52(5)	3·2(1)
	144·5	−0·48(6)	3·1(2)
	180·0	−0·44(8)	3·1(3)
	180·5	−0·39(9)	2·9(3)
[Eu(bta)$_3$],2H$_2$O	84·2	−0·44(3)	2·6(1)
	118·8	−0·43(3)	2·5(1)
	144·5	−0·40(4)	2·6(1)
	180·0	−0·45(6)	2·6(2)
	218·8	−0·44(9)	2·8(3)
[Eu(hfa)$_4$][pip]	82·3	−0·55(3)	2·4(1)
	118·6	−0·56(4)	2·4(1)
	119·2	−0·57(3)	2·5(1)
	145·2	−0·55(4)	2·2(1)
	155·2	−0·55(5)	2·3(1)
	180·7	−0·58(6)	2·4(2)
[Eu(hfa)$_3$],2H$_2$O	79·5	−0·38(4)	2·9(1)
	117·6	−0·41(4)	3·1(1)
	143·5	−0·37(5)	2·8(1)
	178·8	−0·43(8)	3·2(2)
[Eu(aa)$_3$],3H$_2$O	79·3	−0·37(3)	3·1(1)
	119·0	−0·36(4)	2·8(1)
	143·5	−0·33(4)	2·8(1)
	173·0	−0·37(5)	3·0(2)
[Eu(dbm)$_4$][pip]	79·2	−0·38(4)	3·0(1)
	99·0	−0·44(3)	3·0(1)
	118·0	−0·45(5)	3·0(1)
	139·7	−0·40(7)	3·1(2)
	168·5	−0·35(11)	3·3(3)
[Eu$_2$(dbm)$_5$OH]	83·6	−0·29(3)	3·2(1)
	116·5	−0·28(4)	3·1(1)
	143·5	−0·32(5)	3·0(1)
	160·3	−0·35(5)	3·2(2)
	185·5	−0·35(6)	2·8(2)
	203·0	−0·28(8)	3·1(3)

[a] Figures quoted in parentheses are the uncertainty in the last digit and take into account estimated spectrometer errors and curve fitting errors.

TABLE 3

Relative fluorescence intensity for the complexes

Chelate complex	Measured fluorescence intensity relative to [Eu(tfa)$_4$][pip]	Fluorescence intensity data from other work	
[Eu(aa)$_3$],3H$_2$O	0		
[Eu(hfa)$_3$],2H$_2$O	6		
[Eu(hfa)$_4$][pip]	13		
[Eu(bta)$_3$],2H$_2$O	18	0·2 [6]	
[Eu(bta)$_4$][pip]	62	0·6 [6]	0·6 [7]
[Eu(ba)$_3$],2H$_2$O	6		
[Eu(ba)$_4$][pip]	62		
[Eu(tfa)$_4$][pip]	100		0·9 [7]
[Eu(dbm)$_3$]	7		
[Eu$_2$(dbm)$_5$OH]	5		
[Eu(dbm)$_4$][pip]	85		

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[6] R. G. Charles and E. P. Riedel, *J. Inorg. Nuclear Chem.*, 1966, **28**, 3005.

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[11] M. A. Porai-Koshits, L. A. Aslanov, L. A. Butman, A. L. Il'inskii, and E. F. Koritny, *Acta Cryst.*, 1969, **A25**, S165.

[12] L. A. Aslanov, A. L. Il'inskii, I. I. Lazarev, and M. A. Porai-Koshits, *J. Struct. Chem.*, 1969, **10**, 321.

[13] A. L. Il'inskii, M. A. Porai-Koshits, L. A. Aslanov, and P. I. Lazarev, *J. Struct. Chem.*, 1972, **13**, 254.

[14] J. H. Burns and M. D. Danford, *Inorg. Chem.*, 1969, **8**, 1780.

oxygen atoms around each europium(III). Kettle and Smith[15] have identified certain stereochemical arrangements around a lanthanoid(III) ion indicative of *f* orbital involvement. One such arrangement having point group symmetry denoted by D_{4h} bears some relation to the tetragonal antiprismatic arrangements found for $[Eu(aa)_3],3H_2O$[9-11] and $[Eu(ba)_4][pip]$.[11-13] According to Brecher *et al.*[16] d^5p^3 and d^4sp^3 hybrid orbitals on europium would lead to Archimedean antiprismatic arrangements. The latter can also give rise to a tetragonal dodecahedron which has been found for example in $[CsEu(hfa)_4]$.[14] $\Delta R/R$, Where ΔR is the difference between the excited- and ground-state nuclear charge radii, is positive for ^{151}Eu. Hence an increase in electron density at the nucleus produces a positive isomer shift. Some 6*s* electron participation in the bonding of the complexes is suggested from the isomer shift values in Table 2, since these are all positive relative to the predominantly ionic $EuF_3,0{\cdot}5H_2O$. A d^4sp^3 orbital system is thereby favoured for all the diketonates examined.

π-Bonding was not considered by Kettle and Smith,[15] nor did Brecher *et al.*[16] invoke it in their discussion. In the context of ligand–metal ion energy transfer, orbital overlap of a π-type in a given molecular geometry may have an important bearing on the efficiency of energy transfer. It has to be remembered, however, that the ligand orbital possessing the necessary energy is an excited state. An electron in a ligand π^* orbital having the correct symmetry for overlap with a 4*f* orbital may provide the necessary condition for transfer. Isomer shifts from Mössbauer spectroscopic studies would not reflect the consequences of such overlap since the molecules are in the electronic ground state during measurement. The isomer shifts nevertheless indicate that there is some covalency in the Eu–O bonds but the former are not related in any simple way to the fluorescence efficiency.

A consequence of the requirement for adequate overlap of specific metal–ligand orbitals is the need for a suitable stereochemistry for the europium(III) ion. Mössbauer spectra can yield relevant information from electric quadrupole effects but, using the 21·6 keV resonance of ^{151}Eu, conditions are generally unfavourable on account of the close spacing of the spectral lines in relation to the natural line width. Individual component lines are not resolved but the overall width of the spectral envelope can give a measure of the quadrupole splitting present. For most of the complexes listed in Table 2 an overall 'line width' of *ca.* 3·0 mm s^{-1} is obtained and these are seen not to be temperature dependent within experimental error. The values for $[Eu(bta)_3],2H_2O$ and $[Eu(hfa)_4][pip]$ are however significantly narrower. The theoretical minimum width is 1·3 mm s^{-1} [17] and the broadening observed will arise from the source (a constant contribution) and the absorber. By way of comparison, a sample of Eu_2O_3 of comparable thickness had a line width of 3·6 mm s^{-1} as against 3·1 mm s^{-1} for $EuF_3,0{\cdot}5H_2O$.

Detailed structural information is at present only available for $[Eu(aa)_3],3H_2O$[9-11] and $[Eu(ba)_4][pip]$.[11-13] There is greater departure from the ideal square antiprism arrangement in the former compared to the latter. This does not, however, produce a change in line width so that the narrowing in $[Eu(bta)_3],2H_2O$ and $[Eu(hfa)_4][pip]$ may be indicative of a higher degree of symmetry at the europium(III) site than with the square antiprism or similar arrangements.

Recent measurements on europium-doped terbium complexes have suggested[18,19] that intermolecular energy transfer can occur by means of exciton migration; the efficiency of such processes may depend on the extent of intermolecular interactions in the lattice.[19] The recoil-free fraction, f', as a function of temperature, T, yields information on such lattice properties. f' Can be obtained from the absorption H, the ratio of the peak at maximum absorption to the off-resonance baseline count in the Mössbauer spectrum. As the source and sample were held at the same temperature over the range of temperatures studied the resonant emission will be temperature dependent. However, separate measurements with an absorber at constant temperature revealed that the variation thus introduced was small compared with the change in resonant absorption in the chelates. Straight lines could readily be fitted to plots of $\ln H$ against T. The slope, G, from such a plot is then related[20] to θ, the Debye temperature, when $T \geqslant \theta/2$ by

$$G \approx -3E^2/Mc^2k\theta^2$$

where E is the γ-ray energy, M the molecular weight, c the velocity of light, and k the Boltzmann constant. In the absence of a reliable value for the recoil-free fraction from the source, a quantity $G' = (GM)^{-\frac{1}{2}}$ was calculated and values are given in Table 4.

TABLE 4

Data relating to the recoil-free fraction of the diketonates

Chelate complex	M	G'
$[Eu(aa)_3],3H_2O$	503	0·395
$[Eu(hfa)_3],2H_2O$	809	0·252
$[Eu(hfa)_4][pip]$	1066	0·263
$[Eu(bta)_3],2H_2O$	833	0·263
$[Eu(bta)_4][pip]$	1098	0·245
$[Eu(ba)_4][pip]$	882	0·287
$[Eu(dbm)_4][pip]$	1130	0·214
$[Eu_2(dbm)_5OH]$	1436	0·221

Taking G' to be approximately proportional to θ, $[Eu(aa)_3],3H_2O$ has the most rigid lattice. This can be ascribed to the role played by the third water molecule in providing cross-linking of chains of molecules.[10] Likewise hydrogen bonding between the nitrogen of the piperidinium ion and an oxygen atom

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[15] S. F. A. Kettle and A. J. Smith, *J. Chem. Soc.* (*A*), 1967, 688.

[16] C. Brecher, H. Samelson, and A. Lempicki, *J. Chem. Phys.*, 1965, **42**, 1081.

[17] 'Mössbauer Effect Data Index for 1970,' eds. J. G. Stevens and V. E. Stevens, Interscience, New York, 1972.

[18] M. Kleinerman, *J. Luminescence*, 1970, **1**, **2**, 481.

[19] J. S. Curran and T. M. Shepherd, *J.C.S. Faraday II*, 1973, 126.

[20] V. I. Goldanskii and E. F. Makarov, in 'Chemical Applications of Mössbauer Spectroscopy,' eds. V. I. Goldanskii and R. H. Herber, Academic Press, New York, 1968.

of a ligand in [Eu(ba)$_4$][pip] [13] would account for the observed G' value which is larger than that for other tetrakis-complexes (Table 4). This suggests weaker cation–anion bonding in the latter substances some of which, however, show high fluorescence efficiency (Table 3). In general a simple correlation between G' and relative fluorescence efficiency is not observed for the substances listed in Table 4. It would appear that no obvious single property of the solid chelate is responsible for the observed fluorescence. Thus, isomer shift measurements clearly show that overall covalency in the metal–oxygen bond plays at best a very limited role and from the above discussion a similar conclusion can be drawn with regard to bonds linking europium chelate groups in the lattice.

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