A Mössbauer Spectroscopic Study of the Iodides of Europium †

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The enthalpy of formation of europium(III) iodide from its elements at 298 K has been estimated to be −534 kJ mol^{-1} lending encouragement to attempts at the preparation of this substance. Accordingly some reactions which might be expected to lead to its formation have been examined. Thermal decomposition of europium(III) iodide nonahydrate in a closed system gives europium(II) iodide monohydrate and then the impure anhydrous di-iodide. Displacement of water by ammonium iodide in an open system under vacuum leads only to anhydrous europium(II) iodide and heating the latter with excess iodine does not unequivocally yield any anhydrous tri-iodide. A linear relation is observed between the Mössbauer spectroscopic isomer shift and ionicity for the anhydrous europium(II) halides.

Published data on the products of interaction between europium and iodine, either under hydrous or anhydrous conditions, are meagre when compared to the body of information relating to products of this metal with the other halogens. Anhydrous europium(II) iodide and hydrated europium(III) iodides have been described and characterised but although reference is made to anhydrous europium(III) iodide in the literature its preparation and properties have not been recorded.[1–7] In this paper, the results of some attempts to prepare and characterise anhydrous europium(III) iodide are set out. Thermodynamic data which lend encouragement to the search for suitable reaction conditions are presented. In the course of the work, a study of the thermal decomposition of europium(III) iodide nonahydrate and of the dehydration of this substance in the presence of ammonium iodide have been carried out. Europium-151 Mössbauer spectroscopy was used to monitor reaction mixtures and isolated products as the chemical isomer shifts for the +2 and +3 oxidation states are unequivocal.

Experimental

Reagents.—Europium(III) oxide (99.9% Eu_2O_3) was supplied by Rare Earth Products Ltd. Other chemicals were of reagent grade and supplied by Fisons Scientific Apparatus Ltd.

Chemical Analysis.—Reaction products were analysed for iodine by titration with standard mercury(II) nitrate as described by White[8] and for europium by titration with standard ethylenediaminetetra-acetic acid.[9]

(*i*) *Preparation and Thermal Decomposition of Hydrated Europium*(III) *Iodide.*—Europium(III) iodide nonahydrate was prepared by the method described by Kwestroo and van Hal[10] from europium(III) oxide and concentrated hydriodic acid (HI + water) (Found: Eu, 21.7; I, 54.9. $EuI_3 \cdot 4H_2O$ requires Eu, 21.9; I, 54.8%). The hydrated europium(III) iodide (100 mg) was placed in a Pyrex reactor tube [13 cm long, 2.5 cm (internal diameter)] and sealed in a dry nitrogen atmosphere. The tube was heated in a tubular furnace for 1 h at a predetermined temperature (368, 398, 423, 445, or 573 K) and then cooled rapidly to ambient temperatures.

(*ii*) *Dehydration of Hydrated Europium*(III) *Iodide in the Presence of Ammonium Iodide.*—Europium(III) oxide (300 mg) was dissolved in concentrated hydriodic acid in the presence of ammonium iodide in the approximate molar ratio 1 : 20 : 10 respectively. The solution was concentrated by heating in air below 423 K until a pasty slurry resulted. This was transferred to a silica crucible inside a tubular reaction vessel [13 cm long by 2.5 cm (internal diameter)] which was attached to a vacuum line and evacuated to 10^{-3} Torr. The contents were heated at 353 K for 30 min, 373 K for 1 h, 403 K for 1.5 h, and then at a final temperature selected from 573, 673, 723, and 773 K (all under vacuum) for 8 h.

(*iii*) *The Anhydrous Europium*(II) *Iodide–Iodine System.*—Anhydrous europium(II) iodide was prepared as described under (*ii*) employing a final heating temperature of 673 K. Europium(II) iodide (*ca.* 300 mg) was ground together with a ten-fold excess of iodine (by weight) in the argon-filled glove box. The reactants were then sealed in the tubular reaction vessel [as under (*ii*)] in dry argon and heated at 383 K. Reaction times between 24 and 168 h were employed. The resulting mixtures were analysed chemically for europium compounds after removal of excess iodine. Removal was accomplished in one of two ways. (*a*) Excess iodine was separated by vacuum sublimation at 423 K or (*b*) water-saturated benzene was added to the reaction mixture and the excess iodine extracted into the benzene. The extraction was repeated with portions (50 cm^3) of benzene until all free iodine was removed.

(*iv*) *Preparation of Europium*(III) *Iodide Oxide.*—Europium(III) iodide oxide was prepared by a method similar to that of Bärnighausen.[11] Anhydrous europium(II) iodide (250 mg) prepared as under (*ii*) was heated in a stream of moist air at 373 K until evolution of iodine ceased. The sample was then evacuated to <10^{-3} Torr, heated at 473 K for 2 h, and finally annealed under vacuum at 800 K for a further 4 h.

Apparatus and Application.—Differential thermal analyses were performed using a model 671-B differential thermal analyser (Stanton-Redcroft, London). A sample (2—5 mg) of europium(III) iodide nonahydrate was encapsulated in an aluminium sample holder in an argon-filled glove box. A reference sample of europium(III) oxide was made up in a similar manner. The encapsulated samples were placed on separate thermocouple junctions inside the furnace of the analyser and the temperature raised at rates of either 5 K min^{-1} or 10 K min^{-1}.

A 50 mCi samarium-151 source incorporated in an anhydrous samarium(III) fluoride matrix (supplied by the Radiochemical Centre Ltd., Amersham) was driven in the constant acceleration mode in the Mössbauer spectrometer. A thin Na(Tl)I crystal scintillation detector was set to count the 21.6 keV γ-rays from the excited europium-151. Spectral data

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† *Non-S.I. units employed*: 1 Torr = (101 325/760) Pa; 1 Ci = 3.7 × 10^{10} Bq; 1 eV ≈ 1.60 × 10^{-19} J.

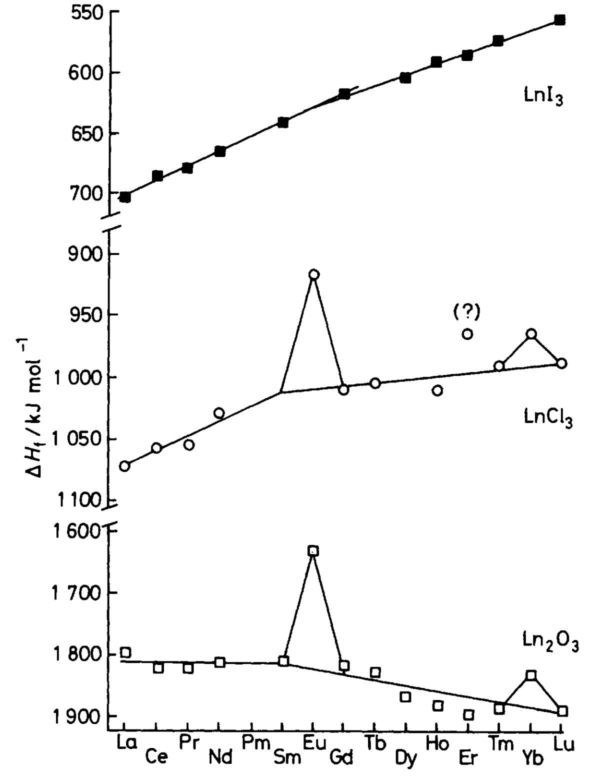

Figure 1. Heats of formation (ref. 3 and ' Handbook of Chemistry and Physics,' 56th edn., C.R.C. Press, Florida, 1975) from the elements at 298 K

were collected by a Brandenburg 4000 series multichannel analyser (Brandenburg Ltd., Thornton Heath, Surrey). Both source and absorber, held at a common temperature, were placed in a continuous-flow variable temperature cryostat cooled by means of liquid nitrogen. The cryostat was a modification of that described by Wiedemann *et al.*[12] Instead of operating with the vibrator and drive-rod assembly located in a horizontal geometry, the cryostat was altered to allow the vibrator and drive-rod to move in a vertical plane.[13] The Mössbauer spectra, which were all recorded at 78 K, were fitted to Lorentzian lineshapes using a least-squares fitting program based on that devised by Stone.[14] Isomer shifts (δ) were measured relative to monoclinic europium(III) oxide; the errors recorded are standard deviations.

Due to the oxygen- and water-sensitive nature of some of the substances studied, it was necessary to handle them in an argon-filled glove-box (Lintott Engineering Ltd., Horsham, Sussex).

Results and Discussion

When the heats of formation (all at 298 K in the subsequent discussion) ΔH_f of the lanthanoid(III) chlorides and oxides are plotted against atomic number, in each series, all, with the exception of europium and to a lesser extent ytterbium, lie on a smooth curve. Gschneidner[3] has attributed these deviations to the special stability of the half-filled and filled $4f$ electron sub-shell possessed by europium(II) and ytterbium(II) respectively. The stabilisation energies amount to some 96 kJ mol^{-1} for europium and 38 kJ mol^{-1} for ytterbium. Similarly, an estimate of ΔH_f for anhydrous europium(III) iodide may be made from ΔH_f for the known lanthanoid(III) iodides plotted against atomic number as in Figure 1. By interpolation, ΔH_f for europium(III) iodide is -630 kJ mol^{-1} and correcting for the unfavourable contribution assumed to be 96 kJ mol^{-1} this still leaves a substantially large ΔH_f of -534 kJ mol^{-1}. Taking this value for ΔH_f (EuI_3) and -670 kJ mol^{-1} for ΔH_f (EuI_2), the enthalpy change associated with the disproportionation reaction [equation (1)] would be 942 kJ mol^{-1} (the corresponding value for the chloride analogue is 577 kJ mol^{-1}).

$$3EuI_2(s) \longrightarrow Eu(s) + 2EuI_3(s) \qquad (1)$$

Johnson[15] has shown that for the chlorides the entropy contribution to the change in Gibbs free energy, ΔG_f, may be neglected since $\Delta G_f = \Delta H_f \pm 8$ kJ mol^{-1}. Assuming that the entropy component of ΔG_f for each of the iodides is also negligibly small, it may be concluded that both europium(II) halides are stable to disproportionation to the metal and europium(III) halide, but europium(II) iodide is less likely to undergo such a reaction than the chloride. However, the large estimated ΔH_f (EuI_3) points to its possible existence and lends encouragement to attempt its preparation. On the other hand, for the reaction shown by equation (2) $\Delta H = -136$ kJ and

$$EuI_3 \longrightarrow EuI_2 + \tfrac{1}{2}I_2 \qquad (2)$$

with ΔS almost certainly positive the reverse reaction looks decidedly less promising.

Europium iodide oxide was prepared so that its Mössbauer chemical isomer shift could be compared with those of other europium(III) reaction products (Table 1). Mössbauer spectra of thermal decomposition products of europium(III) iodide nonahydrate are presented in Figure 2. The chemical isomer shift data from these spectra along with the results of the chemical analyses are summarised in Table 1. A typical differential thermal analytical profile for the nonahydrate obtained at a heating rate of 5 K min^{-1} is presented in Figure 3. Differential thermograms obtained at the higher heating rate of 10 K min^{-1} were similar in profile but displaced by *ca.* 20 K to higher temperatures. This is probably due to rather poor thermal conductivity within the sample. However, despite the temperature displacement the differential thermal profiles shed some light on the thermal decomposition reactions when considered in conjunction with the Mössbauer spectral evidence and mean chemical compositions.

In considering the thermal decompositions as described under (*i*) in the Experimental section, the Mössbauer spectrum of the 368 K decomposition product exhibits only a single absorption peak (Figure 2) at -0.28 ± 0.02 mm s^{-1}. The consistency of the europium(III) chemical isomer shift (Table 1) up to decomposition temperatures of 398 K indicates that the chemical environment of the europium nucleus must be similar in these hydrated species. The hydrated compounds at 298 and 368 K yield iodine to europium atomic ratios of 3 : 1 and the relative percentages of iodide and europium indicate the presence of phases corresponding to $EuI_3{\cdot}9H_2O$ and $EuI_3{\cdot}7.5H_2O$ respectively assuming homogeneity of the latter. The nonahydrate has been reported by Kwestroo and van Hal.[10] At 398 K the presence of some europium(II) in the decomposition products is evident (Figure 2) from the Mössbauer spectrum; the isomer shift of -13.56 ± 0.09 mm^{-1} is indicative of anhydrous europium(II) iodide but evidence at higher temperatures (Table 1 and the text below) would suggest that europium(II) iodide monohydrate is the predominant europium(II) species. Assuming the recoil-free fractions of the europium(II) and europium(III) are the same, then the ratio of peak areas $Eu^{II} : Eu^{III}$ of 0.97 : 1 and the ratio of iodine to europium of 2.55 : 1 point to the presence of mixed phases of hydrated europium(II) and europium(III) iodides. The europium(III) component can be ascribed to

Table 1. Mössbauer spectral parameters and chemical analysis data for the thermal decomposition of $EuI_3{\cdot}9H_2O$ in a closed system

Temp. (K) (decomp.)	δ [a]/mm s^{-1}			Analysis (%) [c]			
	Eu^{III}	Eu^{II}	$Eu^{II} : Eu^{III}$ [b]	I	Eu	I : Eu [d]	Mean formula
298	-0.29 ± 0.02		0	54.9	21.7	3.03 : 1	$EuI_3{\cdot}9H_2O$
				(54.8)	(21.9)		
368	-0.28 ± 0.02		0	56.7	22.5	3.03 : 1	$EuI_3{\cdot}7.5H_2O$
				(56.9)	(22.7)		
398	-0.29 ± 0.03	-13.56 ± 0.09	0.97 : 1	56.3	26.5	2.55 : 1	
423	-0.15 ± 0.03	-13.52 ± 0.03	4.55 : 1	61.2	35.6	2.06 : 1	
445		-13.37 ± 0.04	∞	60.7	35.9	2.03 : 1	$EuI_2{\cdot}H_2O$
				(59.9)	(35.9)		
573	$+0.07 \pm 0.09$	-13.36 ± 0.03	6.17 : 1	59.6	36.8	1.95 : 1	

[a] δ For EuOI is $+0.18 \pm 0.04$ mm s^{-1}. [b] From Mössbauer spectral peak areas. [c] Calculated values in parentheses. [d] From chemical analysis.

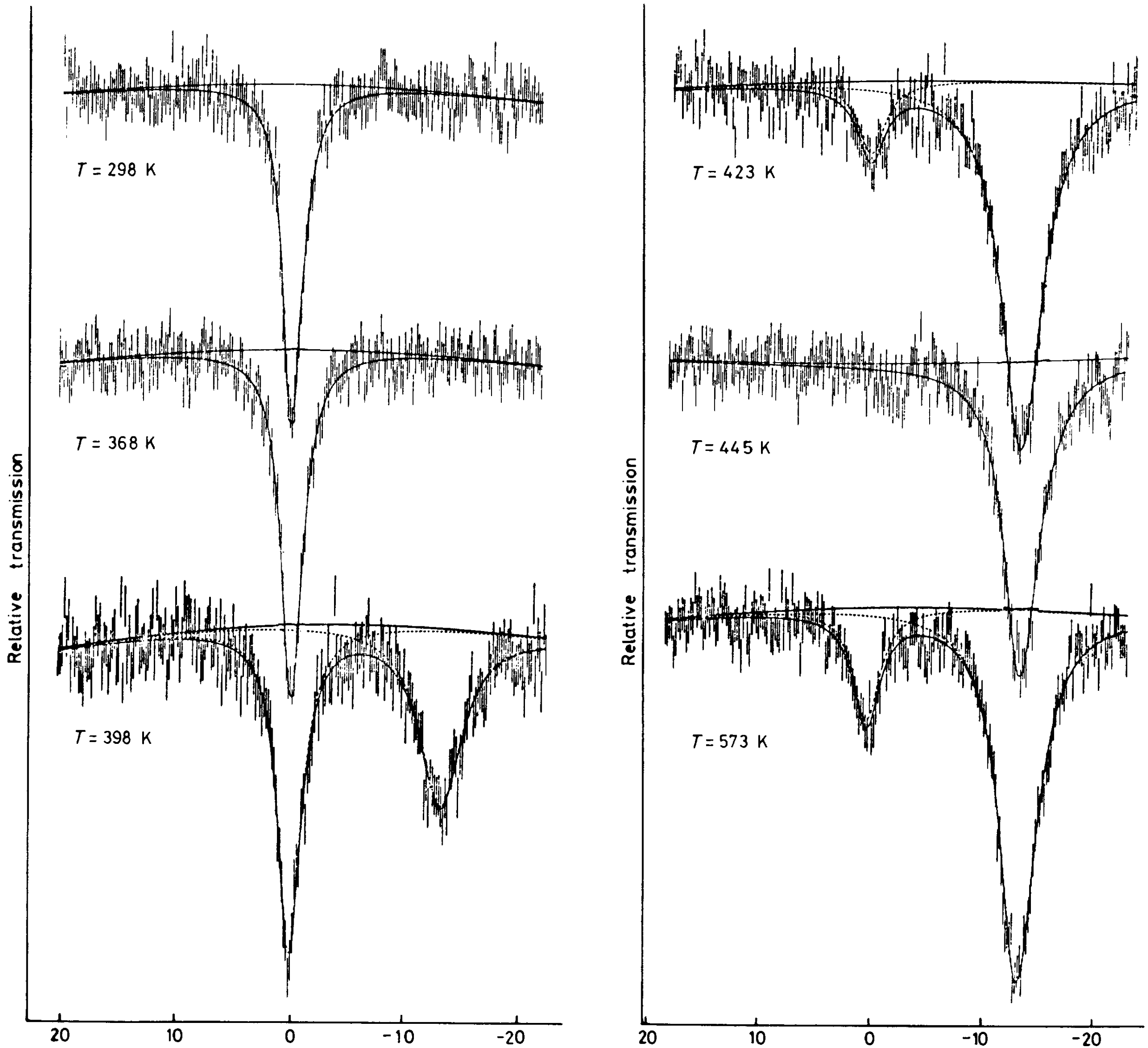

Figure 2. Mössbauer spectra for products prepared by method (*i*) (see Experimental section). The temperatures refer to the heating times in the furnace before measurement

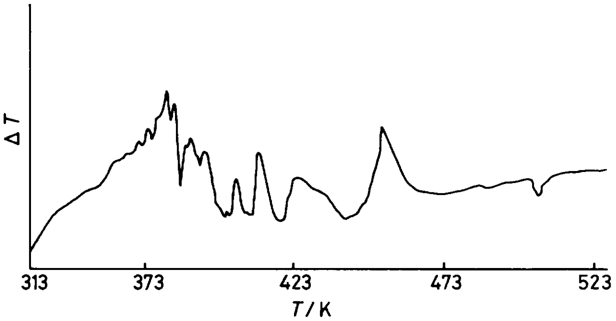

Figure 3. Typical differential thermogram for $EuI_3{\cdot}9H_2O$ at a heating rate of 5 K min^{-1}

hydrated europium(III) iodide rather than europium iodide oxides as the chemical isomer shifts are different. Furthermore, the sample was soluble in water whereas the iodide oxide is insoluble. Anhydrous europium(III) iodide can be excluded as a product since the overall percentage by weight of iodine was found to be only 56.3 whereas even that for anhydrous europium(II) iodide is 62.5.

At 423 K the Mössbauer spectrum (Figure 2) of the thermal decomposition products is dominated by a europium(II) absorption at -13.52 mm s^{-1} accompanied by a smaller europium(III) maximum again indicating mixed-phase products. These, however, were readily soluble in water, thus eliminating the presence of iodide oxide. That any significant fraction of the total is present as anhydrous europium(III) iodide is ruled out by the overall percentage of iodide (61.2%).

The decomposition product resulting from heating the nonahydrate at 445 K gave a Mössbauer spectrum having a single europium(II) peak at -13.37 mm s^{-1} (Figure 2). In conjunction with the results of the chemical analysis (Table 1) the spectrum is consistent with the predominance of a single substance, europium(II) iodide monohydrate, which could be produced according to the overall reaction shown in equation (3). Further evidence for this general transformation comes

$$EuI_3{\cdot}nH_2O \xrightarrow{445\ K} EuI_2{\cdot}H_2O + (n - 1)H_2O + 0.5\ I_2 \quad (3)$$

from the presence of iodine sublimate at the cold end of the sealed glass reaction tube and from the i.r. spectra. (A monohydrate of europium(II) bromide is known.[16]) This scheme would imply that the change of valency state of the europium occurs before complete dehydration. The differential thermograms of which Figure 3 is typical point to major endothermic transformations up to around 445 K followed by a relatively featureless range. Below 445 K, on the Mössbauer spectral evidence and from chemical analysis, the europium valency change and dehydration is occurring roughly in the range 368—445 K while only dehydration occurs below 368 K.

At 573 K, there is a re-emergence of a europium(III) peak at 0.07 ± 0.09 mm s^{-1} in the Mössbauer spectrum. This is in the iodide oxide isomer shift region and the presence of this substance is collaborated by the insolubility of part of the product in water unless acidified with a mineral acid. The iodide to europium ratio (Table 1) provides further supportive evidence for the presence of this substance. It is clear that anhydrous europium(III) iodide does not result from thermal reactions of the type described. Furthermore, they are unsatisfactory for the preparation of anhydrous europium(II) iodide in a pure state. In addition, it has been found that even if released water vapour is continuously removed from the reaction zone under vacuum, a pure anhydrous di-iodide is not produced.

Table 2. Products from the dehydration of $EuI_3{\cdot}9H_2O$ in the presence of ammonium iodide

Sample	Final heating temp. (K)	Analysis (%) * Eu	I	I : Eu	δ/mm s^{-1}
(1)	573	36.8	61.1	1.99 : 1	-13.47 ± 0.07
(2)	673	36.6	61.1	2.00 : 1	-13.26 ± 0.07
(3)	723	35.3	58.4	1.98 : 1	-13.56 ± 0.06
(4)	773	36.4	58.5	1.93 : 1	-13.52 ± 0.05

* EuI_2 requires Eu, 37.4; I, 62.5%.

Table 2 provides a summary of results from the chemical analysis and Mössbauer spectra of the products obtained by dehydration of europium(III) iodide nonahydrate in the presence of ammonium iodide at various temperatures. For final heating temperatures of 573—723 K the Mössbauer spectra indicated that europium(III) was absent. However, sample (3) was hydrated while (4) showed evidence for the presence of iodide oxide. The expected error in the chemical analysis is around 0.5% and hence some 1—2% of impurity remains in the best preparations [samples (1) and (2)]. This is in accordance with the observations of Ishü *et al.*[17] At decomposition temperatures below 573 K the products always contained some residual ammonium iodide. Thus there is an optimum temperature range of *ca.* 150 K above 570 K for the preparation carried out on the time-scale used in this work.

If anhydrous europium(III) iodide is capable of existence under ambient conditions, it is likely to decompose thermally at temperatures lower than either the corresponding chloride or bromide which are both known. The thermal decomposition [equation (4)] starts at *ca.* 590 K,[18] so that with final temperatures in excess of 570 K for dehydration and removal of ammonium iodide from the iodide reaction mixture it is hardly surprising that europium(III) iodide is not obtained by

$$EuCl_3 \longrightarrow EuCl_2 + 0.5\ Cl_2 \quad (4)$$

this method. A different approach is possible in which excess iodine is mixed with anhydrous europium(II) iodide. In this way the furnace temperature and duration of the heating period can be varied and the mass action effect of excess iodine may also be advantageous in stabilising the reaction ' product '. Except for sample (C) (Table 3) the reaction mixture was used directly to obtain the Mössbauer spectra but for chemical analysis, excess iodine first had to be removed. Two independent methods, sublimation and solvent extraction, were used for the latter purpose. Removal of iodine by sublimation would give the initial europium(II) iodide according to equation (2), whereas removal by moist benzene would convert europium(II) to hydrated europium(III) iodide by the overall reaction in equation (5). Any anhydrous europium(III)

$$2EuI_2 + I_2 + 2xH_2O \longrightarrow 2\ EuI_3{\cdot}xH_2O \quad (5)$$

iodide would simply undergo hydration. Thus, in the absence of europium(III) iodide oxide, the first method would give an iodide to europium ratio of 2.00 : 1 and the second a ratio of 3.00 : 1. Results of experiments are collected in Table 3. Samples (A) and (B) were treated by the sublimation procedure; the iodine to europium ratios are considerably less than 2.00 : 1. Samples (D), (E), and (G) were analysed by the benzene method. As a control experiment, anhydrous europium(II) iodide was mixed with iodine at room temperature and subjected to the benzene extraction; the ratio of iodine to

Table 3. Data relating to the study of the $EuI_2 + I_2$ system

Sample	Reaction time (h)	$\delta(Eu^{III})$/mm s^{-1}	$Eu^{III} : Eu^{II}$ [a]	I : Eu	Analysis (%) [b]	
					Eu	I
(A)	30	0.21 ± 0.12	0.76 ± 0.15	1.72	38.5	55.3
(B)	77	0.15 ± 0.03	0.81 ± 0.05	1.70	39.9	55.6
(C)	168	0.17 ± 0.06	0.22 ± 0.02	1.92	37.2	59.6
(D)	25	−0.49 ± 0.52	0.18 ± 0.08	2.83		
(E)	91	−0.02 ± 0.13	0.28 ± 0.08	2.83		
(F)	168	−0.02 ± 0.07	0.23 ± 0.03	2.79		
(G)	24	0.24 ± 0.21	0.20 ± 0.06	2.77		

[a] From Mössbauer spectral peak areas. [b] From chemical analysis (see text).

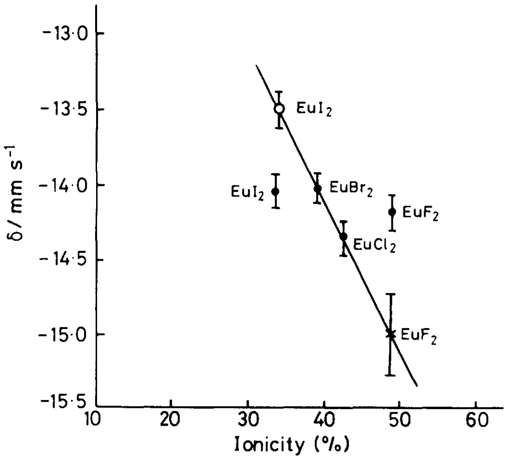

Figure 4. Isomer shift (δ) plotted as a function of percentage ionicity: data from ref. 6 (●), ref. 21 (X), and this work (○)

Table 4. Structural data for crystalline europium(II) halides

Compound	Crystal system	Lattice parameters (Å)	Refs.
EuF_2	Cubic (fluorite)	a = 5.836(5)	*a*
$EuCl_2$	(*a*) Orthorhombic	a = 4.49(3) b = 7.49(9) c = 8.91(4)	*b*
	(*b*) Orthorhombic	a = 4.443(13) b = 7.462(15) c = 8.861(17)	*c*
$EuBr_2$	(*a*) Orthorhombic	*a*, *b*, and *c* not reported	*b*
	(*b*) Tetragonal	a = 11.574(6) c = 7.098(5)	16
$EuBr_2{\cdot}H_2O$	Orthorhombic	a = 11.46(20) b = 4.291(5) c = 9.20(10)	16
EuI_2	(*a*) Monoclinic	a = 7.62(2) b = 8.23(3) c = 7.88(2) β = 98.0°	*d*
	(*b*) Orthorhombic	a = 15.12(3) b = 8.18(2) c = 7.83(2)	*d*

[a] K. Lee, H. Muir, and E. Catalano, *J. Phys. Chem. Solids*, 1965, **26**, 523. [b] W. Döll and W. Klemm, *Z. Anorg. Allg. Chem.*, 1939, **241**, 239. [c] D. M. Laptev, I. S. Astakhova, N. M. Kulagin, and N. F. Bomko, *Zh. Neorg. Khim.*, 1976, **21**, 1181. [d] H. Barnighausen and N. Schultz, *Acta Crystallogr., Sect. B*, 1969, **25**, 1104.

europium obtained was 3.00 : 1 as predicted by equation (5) above. Again the results suggest the formation of oxy or hydroxy products in spite of stringent precautions to exclude air and/or moisture. Samples (C) and (F) originate from the same reaction mixture divided into two portions. A Mössbauer spectrum was obtained for (F) and then the excess iodine was removed by the benzene method before chemical analysis. Sample (C) had excess iodine removed by sublimation before Mössbauer spectroscopy and chemical analysis on the residue. If any anhydrous europium(III) iodide was present in the sample and subsequently decomposed to europium(II) iodide after sublimation this would be reflected in a change of europium(III) isomer shift when (F) and (C) are compared. Alternatively, if europium(III) iodide oxide was the europium(III) species present in the reaction mixture the isomer shift would remain the same in both (F) and (C). A change in isomer shift is evident (Table 3) but the poor statistics associated with the observed values detract from the usefulness of the results and leave this matter unresolved. Thus firm evidence for the formation of anhydrous europium(III) iodide by the reactions discussed in this paper has not been obtained. Although several references have been made to this substance in the literature, they either deal with it in abstract thermodynamic terms, describe reactions which have failed to produce it, or omit information on the origin of their specimen.[1–7,19]

Gerth *et al.*[6] have reported chemical isomer shifts for the europium(II) halides. These are plotted in Figure 4 against ionicity as defined by Saunderson.[20] If the isomer shift for europium(II) fluoride obtained by Wickman *et al.*[21] and the value resulting from the present work for europium(II) iodide (Table 2) are substituted for those of Gerth *et al.*,[6] the data lie on a straight line. This suggests that the dihalides are isostructural. However, published data suggest otherwise as is evident from Table 4. The dibromide and di-iodide each would seem to be dimorphic. In view of problems associated with purity of these substances, in particular complete exclusion or removal of water, further independent crystallographic studies on this series would appear to be desirable.

As $\delta\langle r^2\rangle$ is positive for the europium-151 nucleus, it follows that the *s* electron density at the nucleus decreases as the ionicity increases. The trend observed in the relation between isomer shift and ionicity has been used to monitor 6*s* electron participation in bonding. The results in Figure 4 imply that as the bonding becomes more covalent in the series $EuF_2 < EuCl_2 < EuBr_2 < EuI_2$ there is increased participation of the 6*s* orbitals in the bonding.

Acknowledgements

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