Preparation, Characterisation, and Europium-151 Mössbauer Spectra of Some Carbides, Nitrides, Nitride-carbides, Cyanides, and Thiocyanates of Europium

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The reaction of europium metal with HCN and $(CN)_2$ at elevated temperatures has been shown to yield Eu_2C_3, EuC_2, and compounds of the type EuN_xC_y. *X*-Ray parameters for these phases are reported and they are shown by ^{151}Eu Mössbauer spectroscopy to be band systems. EuN is shown to be ionic and to contain Eu^{3+} ions. The reactions in liquid NH_3 of europium with HCN, C_2H_2, and NH_4SCN have been shown to produce europium(II) and europium(III) cyanide, europium(III) acetylide, and europium(III) thiocyanate respectively. The width of the ^{151}Eu Mössbauer resonance is discussed in relation to possible bonding situations and the relationship between chemical isomer shift and bond ionicity is considered.

THIS work arises from earlier studies on lanthanon–carbon and lanthanon–nitride–carbide systems[1-3] and uses the ^{151}Eu Mössbauer resonance to provide a simple and unambiguous determination of the valency states of europium in such phases. The work also supplements other studies on the thermal decomposition of lanthanon hexacyanoferrates[4] and provides data on some new pseudohalides of europium which are compared to the existing data on the halides. Gallagher and Schrey[4] used a variety of methods including the Mössbauer technique to study the thermal decomposition of $EuFe(CN)_6,5H_2O$ but were unable to identify the europium-containing phases; on the basis of the work presented below it appears that europium(II) and europium(III) cyanides are formed as intermediates in the decomposition with EuN and EuN_xC_y phases appearing at a later stage.

Europium in common with all other lanthanons forms a nitride, EuN, with the rock-salt structure. Its lattice parameter is 5·014 Å[5] and this lies on a smooth plot of lattice parameter against atomic number of the lanthanon. Only two nitrides, CeN and PrN, do not lie on this plot and this is thought to reflect the existence of Ln^{4+} in these compounds. Similarly EuN, since it lies on the plot, has been assumed to be ionic and to contain Eu^{3+} but no direct confirmation of this has previously been reported.

Carbide phases of lanthanons known to exist are Ln_3C, Ln_2C_3, but EuC_2 has been reported by various workers.[6,7] Eick[6] prepared the compound from the elements in a tantalum pressure bomb at 1050 °C and reported the structure as the tetragonal CaC_2 type with $a = 4{\cdot}045$ Å, $c = 6{\cdot}645$ Å. Because the lattice parameters were so large in comparison to those of the Ln^{3+} dicarbides it was concluded that Eu^{2+} ions were present and that the carbide was wholly ionic. However attempts to repeat Eick's preparation failed[7] and a lower symmetry structure has been suggested.

There is no published information on nitride–carbide phases of europium and in fact little data on other Ln–C–N systems.[1,2] It was felt that a study of the changes in the oxidation state of europium with changing C/N ratio would give valuable insight into the nature of these phases.

The main reason for the lack of data and for some of the confusion is the preparative difficulty arising from the high volatility of the metal and its ease of oxidation. This has been the major problem in this work and it led to the investigation of methods based on HCN[3] and to the use of liquid ammonia as a solvent medium for the reactions of europium with HCN, C_2H_2, and NH_4SCN.[8]

EXPERIMENTAL

Europium metal (Rare Earths Products Ltd.) had a purity >99·9% with respect to other metals. Carbon (Morganite Ltd.) was from a special high-purity rod. Nitrogen (B.O.C. Ltd.) was specified research grade. High purity >99·9% argon (B.O.C. Ltd.) was used to purge the glove box and arc furnace. Ammonia gas (Cambrian Gases Ltd.) was dried over sodium metal. Research Grade C_2H_2 and $(CN)_2$ (Cambrian Gases Ltd.) were dried over P_4O_{10}. Liquid HCN (I.C.I. Ltd.) contained <1% impurity in the form of H_2O and oxalic acid and before use was evaporated from P_4O_{10} into storage bulbs on the high vacuum system used throughout the work.

Arc-furnace preparations used a specially designed furnace described in detail elsewhere.[1-3] The details of the apparatus and experimental conditions for the liquid ammonia work are also given elsewhere.[8]

Europium was analysed by igniting samples to Eu_2O_3. Nitrogen was determined by the Kjeldahl method, and carbon was determined in the manner described earlier.

All *X*-ray data were obtained with Fe-filtered Co-K_α radiation using a Debye–Scherrer camera of 11·46 cm in diameter.

Infrared spectra were obtained on a Perkin-Elmer 125 spectrometer from specimens mulled in Nujol.

The Mössbauer spectra were obtained using a source of

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[7] R. H. Flowers, R. L. Faircloth, and F. C. W. Pummery, *J. Inorg. Nuclear Chem.*, 1968, **30**, 499.

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SmF_3 incorporating ^{151}Sm. This source had a recoilless fraction of 0·15 at 300 K and gave a line width of 2·75 mm s^{-1} for an EuF_3 absorber. Measurements were made using two spectrometers. One was a constant acceleration spectrometer with a saw-tooth wave form described by Cooper.[9] With this instrument, velocity calibrations were carried out before and after each spectrum. An N.S.E.C. model AM1 constant-acceleration spectrometer with a triangular wave form was also used. Specimens were prepared by mulling in vacuum grease and then pressing the mull between two sheets of aluminium foil. These operations were performed in an inert atmosphere glove box. Spectra were usually obtained at 78 K in order to reduce the rate of decomposition or air attack and to increase the percentage absorption. Even with thick samples (25 mg cm^{-2} of Eu) counting times of 1 day were necessary and typical running times were 2—3 days. Such long periods of data acquisition precluded direct calibration with a europium compound and a procedure using iron foil and EuF_3 was developed. Changes in the velocity scale, and the position of the zero velocity on the scale, were monitored by calibration with an enriched ^{57}Fe foil and a $^{57}Co/Pd$ source. The results obtained in each experiment could thus be referred back to one standard spectrum of EuF_3 *via* the iron-foil calibration for that spectrum. The spectra were fitted by Lorentzian line-shapes.[10, 11]

RESULTS AND DISCUSSION

It has been found useful in this work to divide the compounds studied into three classes: ionic europium(II), ionic europium(III), and band systems. All previously reported compounds of europium with the exception of the intermetallic $EuRh_2$ and $EuPd_3$ [12] can be assigned to one of these classes, each of which covers a distinct region of chemical isomer shift (δ) with respect to EuF_3 as set out in Table 1. The two ionic series differ by an amount due to the change in shift which accompanies the total transfer of one 4*f* electron whereas within each series the shift varies as a result of 6*s* electron transfer, and possibly donation into the 5*d* and 6*p* orbitals. The extent of such a transfer of 6*s* electrons in terms of ionicity in isostructural compounds is described by Gerth, *et al.*[13] Within the band systems the situation is more subtle and the range of shifts involved, and therefore the changes in electron density at the nucleus, are somewhat greater.

TABLE 1

Range of published isomer shifts, δ, for europium compounds relative to EuF_3 as zero [12]

Class of Compound	δ/(mm s^{-1})
Ionic europium(III)	$-0·2$ to $+0·9$
Band systems	$-11·4$ to $-7·6$
Ionic europium(II)	$-13·9$ to $-10·9$

The nitride (EuN) was the easiest compound to prepare and was obtained by direct reaction between the metal and nitrogen gas at 850 °C. *X*-Ray diffraction data and chemical analyses confirmed that the product was single phase with the stoicheiometric composition EuN and a face-centred cubic unit cell, a_0 5·014 Å, in accord with the data of others. The chemical-isomer shift value in Table 2 suggests that the EuN is an ionic solid containing only europium(III). The value for δ implies that there is more *s* electron density on the Eu^{3+} ion than in any previously observed ionic europium(III) compound. A larger shift of $+4·2$ mm s^{-1} has been observed for trivalent europium in the intermetallic system $EuPd_3$.[14]

Carbide Phases.—(*a*) *Acetylides.* Several attempts to prepare EuC_2, Eu_3C, and Eu_2C_3 from the elements failed. *X*-Ray diffraction data, chemical analysis, and Mössbauer spectroscopy gave no indication of the presence of these carbides but pointed to a mixture of residual europium metal, graphite, and europium oxides. Two alternative approaches were then tried. The first involved the reaction between acetylene and europium in liquid ammonia. A rapid reaction produced a red-brown solid which was consistently shown by its Mössbauer spectrum to be mainly an ionic europium(III) compound with only a trace of europium(II). There was never sufficient of the europium(II) material to determine its chemical isomer shift. The details of the europium(III) compound are given in Table 3. Analyses of these preparations confirm a mixed product containing Eu, C, and H but *X*-ray examinations revealed little crystallinity and the material was essentially amorphous. A reaction with H_2O vapour showed that the brown powder was easily hydrolysed under very mild conditions [1] to produce a gas which was pure acetylene. A sodium preparation also produced material readily evolving pure C_2H_2 under these conditions. The hydrolysis behaviour of lanthanide carbides has previously been studied in detail under the conditions used here and the hydrocarbon product distribution always showed the acetylene to be present only as 80% of the hydrocarbons with some 20% of C_2H_4 and C_2H_6. The reduced hydrocarbons arise from the reaction of C_2H_2 with H_2 on the surface of these metallic specimens. Thus it seems that the product from europium and C_2H_2 in liquid ammonia is, like the sodium case, an acetylide, probably $Eu(HC_2)_3$.

The repeatability of the preparation and the constant appearance of the europium(III) state is notable. It is therefore surprising that when the reaction was carried out in the presence of 50 atomic percent of calcium a mixed product was obtained which incorporated two europium-containing phases (see Table 3). Approximately two-thirds of the europium was present in an ionic europium(II) form and the remainder was a europium(III) compound that was probably not the acetylide. Hydrolysis again produced 100% of acetylene which

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strongly suggests that the europium(II) compound is most likely a mixed calcium europium(II) acetylide $Eu_xCa_{1-x}(C_2H)_2$. Since chemical analysis showed varying amounts of nitrogen to be present it is felt that the europium(III) compound could be the amide but this was not definitely established. *X*-Ray data would have been valuable at this stage but all the products were amorphous and attempts to anneal them resulted in rapid blackening, decomposition, and production of europium metal.

(b) *Nitride-carbides and carbides.* A reaction known to be useful from earlier studies of lanthanide carbides and nitride-carbides [2,3] was tried. Lanthanide metals arc-melted under argon-HCN atmosphere always produced mixtures of nitride-carbide and sesquicarbide phases after very short reaction times and on prolonged heating these gave way to the dicarbides. Once again, due to volatility of europium metal, the method was not successful. Medium temperature reactions (850—1000 °C) between HCN or $(CN)_2$ and europium in sealed tubes did prove partly successful. Table 2 contains the results from some of these preparations.

TABLE 2

Preparations from solid europium metal and compounds (standard deviations to the last significant figures are given in parentheses)

System	Gross composition	Eu phases	*X*-Ray data (Å)	Chemical isomer shift $\delta/(\mathrm{mm\ s^{-1}})$	Line width $\Gamma/(\mathrm{mm\ s^{-1}})$
Eu + N_2 850 °C	$EuN_{0\cdot97}$	EuN	f.c.c., $a = 5\cdot014$	1·327(16)	2·90(8)
Eu + HCN 1000 °C	$EuN_{7\cdot96}C_{11\cdot5}$	EuN/C ss	f.c.c., $a = 5\cdot002$	1·65(30)	3·26(13)
		EuN_aC_b		−12·20(10)	4·26(42)
			carbon $(CN)_x$		
Eu + HCN 850 °C	$EuN_{1\cdot01}C_{6\cdot01}$	EuC_2	tetr., $a = 3\cdot73$, $c = 6\cdot18$	−10·57(21)	5·93(73)
		Eu_2C_3	b.c.c., $a = 8\cdot37$		
			graphite + extra lines		
Eu + $(CN)_2$ 1000 °C	$EuN_{4\cdot9}C_{3\cdot89}$	EuC_2	tetr., $a = 3\cdot73$, $c = 6\cdot18$	−10·70(20)	5·80(70)
		Eu_2C_3	b.c.c., $a = 8\cdot37$ + extra lines		
EuN + C argon arc	$EuN_{0\cdot3}C_{4\cdot2}$	EuN/C ss	f.c.c., $a = 5\cdot005$	1·13(7)	2·76(21)
		EuN_xC_y	f.c.c., $a = 5\cdot141$ + graphite	−10·96(5)	3·24(18)

ss = Solid solution.

TABLE 3

Preparations in liquid ammonia

System	Gross composition	Probable Eu phases	*X*-Ray	$\delta/(\mathrm{mm\ s^{-1}})$	$\Gamma/(\mathrm{mm\ s^{-1}})$
Eu + C_2H_2	$EuC_{5\cdot7}H_{2\cdot8}$	$Eu(C_2H)_3$, trace $Eu(C_2H)_2$	Amorphous	0·81(3)	3·30(16)
Eu + Ca + C_2H_2	$Eu_{0\cdot57}Ca_{0\cdot41}$	$Eu_xCa_{1-x}(C_2H)_2$	Amorphous	−11·92(13)	4·97(45)
		Unknown Eu^{III}		1·26(18)	2·47(59)
Eu + HCN	$Eu(CN)_{2\cdot4}$	$Eu(CN)_2$	Possibly tetragonal	−13·00(25)	5·50(73)
		$Eu(CN)_3$	Cubic $a = 11\cdot3$	0·75(18)	2·74(5)
Eu + NH_4SCN	$Eu(SCN)_3$	$Eu(SCN)_3$	Amorphous	0·645(15)	2·98(80)
$EuCl_3$ + NH_3	$Eu(OH)_3$	$Eu(OH)_3$		0·58(4)	3·22(16)

The gross compositions reflect the presence of free carbon, cyanogen, and HCN polymers which could not be removed from the intimate mixtures. Hydrolyses of these products, in contrast with the materials prepared in liquid ammonia, gave the typical hydrocarbon distribution expected for metallic LnC_2 or Ln_2C_3 phases and thus lend weight to the belief that EuC_2 and Eu_2C_3 had been prepared. The lattice symmetries and lattice parameters of the europium-containing phases in these preparations are further strong evidence for the successful preparation of the di- and sesqui-carbides. The lattice parameter for the b.c.c. phase was $8\cdot36_8$ Å, in good agreement with the value expected for Eu_2C_3 from the parameters of other lanthanide sesquicarbides.

Lattice parameters for the tetragonal phase were $a = 3\cdot73$, $c = 6\cdot18$ Å; these are smaller than those reported by Eick [6] who found $a = 4\cdot045$, $c = 6\cdot645$ Å, and concluded that the europium was present as Eu^{2+} ions. As the value of $-10\cdot57$ mm s^{-1} found for the chemical isomer shift of EuC_2 in the present work lies on the borderline between ionic europium(II) and a band system, those lower values for the lattice constants incline us to think that in this compound there may be some delocalization of electrons. The b.c.c. phase was always very much the minor constituent and never present in sufficient amounts for its Mössbauer parameters to be determined reliably. An interesting feature of this work was that reactions attempted above 950 °C produced complex *X*-ray patterns in which neither the tetragonal nor the b.c.c. phase could be identified. A sharp change in the Mössbauer spectrum was also evident with the appearance of an ionic europium(III) resonance and the chemical isomer shift of the band compound δ moving to $-12\cdot2$ mm s^{-1}, which clearly indicates a change to an ionic europium(II) system. It could not be established whether this was a dicarbide of lower symmetry or a nitride-carbide of general formula EuN_aC_b, due once again to the intimate mixture of the phase with graphite and carbon-nitrogen polymer. It was felt that the europium peak arose from EuN saturated with carbon. Whether these changes represent an alteration in the initial reaction path or arise from the fact that Eu_2C_3 and tetragonal EuC_2 are not stable at this temperature cannot be decided.

Another feature of these HCN reactions was the complete absence of an f.c.c. nitride-carbide which commonly occurs in major amounts when lanthanides are arc-melted under HCN.[2,3] Any difference here between europium and other lanthanides might lie in the lower temperature of the europium reaction.

Although arc preparations using europium and HCN were unsuccessful, reactions of short duration between EuN and graphite in an argon arc were possible before evaporation of europium was excessive. *X*-Rays showed that this process resulted in mixed products consisting of graphite and two f.c.c. phases. Examination by Mössbauer spectroscopy revealed the presence of two europium-containing compounds which were taken to be the f.c.c. phases. Once again the intimate mixture of phases and the unchanged graphite made chemical analysis impossible. The *X*-ray analysis, the ready evolution of ammonia on addition of water, and the value for the chemical isomer shift δ (Table 2) showed that one of the f.c.c. phases was an unchanged EuN-carbon solid solution. The hydrocarbons evolved on hydrolysis of the mixed product were shown to be 100% CH_4 showing that no C_2 units were present in the f.c.c. phases and no traces of Eu_2C_3 or EuC_2 were present.

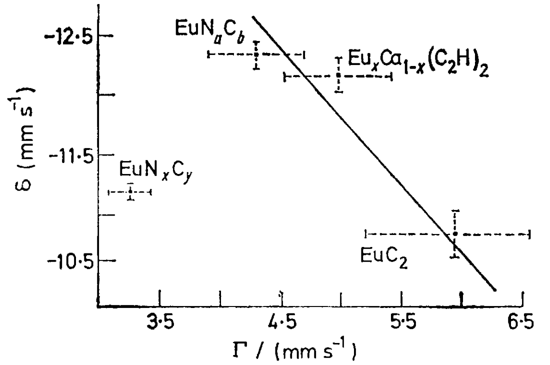

FIGURE 1 Relation between chemical isomer shift and line width for Eu-carbon phases

The value of the *X*-ray lattice parameter of the second f.c.c. phase is quite interesting in that it lies close to the extrapolated value of 5·15 Å for the so far unreported carbide Eu_3C.

With the exception of the 5·15 Å phase EuN_xC_y or Eu_3C, a relationship between chemical isomer shift and line width at half-height can be discerned for these phases so far described. Figure 1 shows that line width increases as δ increases. Qualitatively the same effect may be seen in the silicide and germanide.[15] Europium silicide has an unresolved broad line and the germanide with a large chemical isomer shift shows the beginning of resolution. The exception to this trend is also the most symmetrical phase, which might be the reason for the deviation. In the f.c.c. structure the *d*-orbitals most involved in bonding are the d_{z^2} and $d_{x^2-y^2}$ which can bond to the neighbouring atoms. The total electric field gradient is therefore expected to be zero and the fact that the line width is as great as 3·24 mm s^{-1} is probably due to the compound containing randomly distributed carbon atoms and the bonds are unlikely to be purely symmetrical about europium. In contrast, in the tetragonal EuC_2 phase where the bond model involves a π bond between Eu and the antibonding levels of the C_2^{2-} ion[16] the orbitals most likely to accomplish this are the d_{xz} and d_{yz}. This would produce a total positive contribution to V_{zz} resulting in the large line width observed.

Since there is a linear increase in quadrupole splitting, as suggested by the line widths, the population of the 5*d* orbitals must be proportional to the population of the 6*s* orbital. Hence one can say that the europium orbitals contributing to the conduction systems in these compounds are best described as hybrids of 6*s*, $5d_{xz}$, and $5d_{yz}$. Hence

$$\psi_{\mathrm{Eu}} = \frac{1}{\sqrt{(1+\beta^2)}}[\psi_{6s} + \beta\psi_{5d}]$$

where ψ_{5d} is any normalised linear combination of 5*d* orbitals and β is a constant for any system where the model holds.

This model is identical to that proposed by Wickman *et al.*[17] on the basis of the relationship between hyperfine fields and chemical isomer shift. One can take the results from Wickman's paper and obtain an approximate chemical shift of 5·5 mm s^{-1} per electron in ψ_{Eu} and using a value of −14 mm s^{-1} for the chemical isomer shift of Eu^{2+} one can assign the following values for the percentage of ψ_{Eu} in the band wave functions: for EuC_2 31%, for EuN_xC_y 28%, and for EuN_aC_b 16%.

(c) *Pseudohalides and halides*. The inability to index the complex *X*-ray patterns in the cyanogen work reported above raised the question of the presence of unknown europium cyanides. The reaction of europium with HCN in liquid ammonia was always found to produce a mixed product consisting of $Eu(CN)_2$ and $Eu(CN)_3$. This yellow-orange mixture could be separated by leaching with absolute alcohol. The dicyanide exhibited a sharp infrared band at 2080 cm^{-1}, and a broad band at 460 cm^{-1}. On standing, on warming, or by reaction with water vapour, this compound disproportionated into $Eu(CN)_3$ and europium metal. The Mössbauer spectrum indicated that the compound only contained europium(II) ions with $\delta = -13{\cdot}00$ mm s^{-1}. The line width was very broad and this can be attributed to participation of 5*d* orbitals in the bonding as outlined above. A rather poor *X*-ray pattern suggested a possible tetragonal symmetry for the unit cell and if so the europium orbitals most suitable for bonding with the CN^- are the $5d_{xz}$, $5d_{yz}$, and some $5d_{z^2}$ to allow for the

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tetragonal distortion. All these orbitals would give positive contributions to V_{zz}.

The more stable tricyanide had a broader i.r. spectrum than $Eu(CN)_2$ in the CN stretching region with two lines at 2180 and 2115 cm^{-1}. On the other hand the Mössbauer spectrum showed a single very sharp line characteristic of only europium(III) ions. On heating this compound to 600 °C, decomposition occurred to europium metal and paracyanogen, thereby explaining the absence of these cyanides in the earlier work.

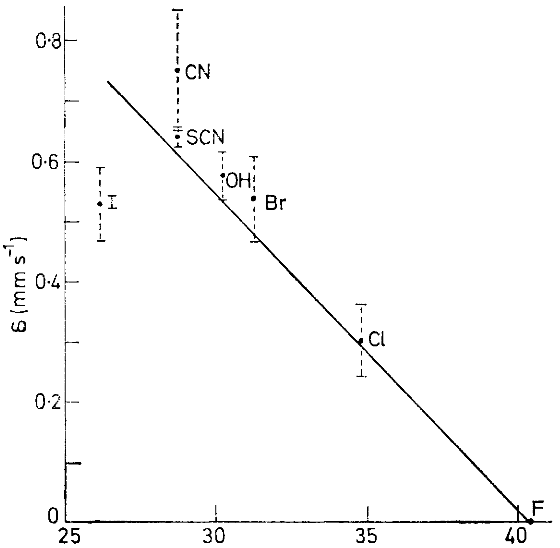

FIGURE 2 Relation between chemical isomer shift and bond ionicity for europium(III) halides and pseudohalides

A similar preparation using NH_4SCN produced only the trithiocyanate, a fact confirmed by the Mössbauer examination. This material was extremely sensitive to moisture, evolving H_2S and forming $Eu(OH)_3$ as two of the decomposition products. It was also light-sensitive, slowly decomposing to europium and some sulphur-containing product. These pseudohalides have not previously been available for Mössbauer examination and in view of their extreme moisture-sensitivity it was necessary also to determine the Mössbauer parameters of $Eu(OH)_3$. All the data are given in Table 3.

All three europium(III) compounds lie on the ionicity plot for europium(III) halides (Figure 2). This plot relates δ to the percentage ionicity of the Eu–X bond, as calculated by Sanderson's method.[18] Sanderson has evolved his own scale of electronegativities for use in these calculations but does not include values for Eu; this was therefore determined by interpolation from a graph of Sanderson's electronegativities against Allred and Rochow's. This gave a value of 1·1. There is no suitable ionicity plot for europium(II) halides; the plot presented by Gerth [13] is a rather random collection of four points and this makes it difficult to compare δ for $Eu(CN)_2$ with data for europium(II) halides.

The data established for these ionic compounds show that no cyanide was produced in the reaction between europium and HCN or $(CN)_2$. Further it does seem that there is some correlation between these results and the data on the vacuum thermal decomposition of europium hexacyanoferrate.[4] It seems likely that $Eu(CN)_2$ and $Eu(CN)_3$ are unstable intermediates in such a decomposition and that neither EuN nor EuC_2 nor a nitride-carbide arise in the course of such a reaction.

[1/2453 *Received, 22nd December,* 1971]

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