deduced which require only s, p, and d orbitals. Rare earth oxides have the well-known AM_2O_3 structure[25] in which seven oxygen atoms are coordinated to each metal atom. In this regard, neodymium shows a coordination number of nine in $Nd(H_2O)_9(BrO_3)_3$. Most recently, also, Thompson and Loraas[26] have reported evidence for a coordination number larger than six in the rare earths forming mixed complexes with N-hydroxyethylenediaminetriacetic acid and glycine, ethylenediaminediacetic acid, and N-hydroxyethyliminodiacetic acid.

It is not possible to state whether the heptabicarbonato complex represents the coordinatively saturated species, but evidently coordination numbers greater than six are known for the heavy elements. Future research in this area should be directed toward elucidating the role of f orbitals in these complexes and in determining the dentate character of the ligands.

Even though the comprehensive analysis of the data that has been presented may be somewhat in error, justification for its presentation is believed to derive from the facts that (1) it provides an estimate of the interesting complexing situation of the rare earths in carbonate and bicarbonate systems and (2) it points out real differences between the neodymium and europium sequence of compounds.

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[25] A. F. Wells, "Structural Inorganic Chemistry," 2nd Ed., Oxford at the Clarendon Press, New York, N. Y., 1950, p. 91.

[26] L. C. Thompson and J. A. Loraas, *Inorg. Chem.*, **2**, 89 (1963).

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The Preparation and Some Properties of a Europium Dicarbide Phase

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A previously unreported lanthanon dicarbide, EuC_2, has been prepared in a stainless steel bomb by the reaction of the metal with graphite. The lattice parameters, some chemical properties, and a comparison of this phase with other dicarbide phases are presented.

Introduction

The crystal structure and some chemical properties of several tetragonal rare earth dicarbides have been reported.[1-4] However, no carbide of europium has been mentioned, and, since europium is an element which differs in many ways from its neighbors, it seemed desirable to investigate the europium–carbon system and determine whether or not a dicarbide could be prepared.

Experimental

Two techniques were used in the preparation of the dicarbide phase. In the first of these, weighed quantities of a powdered mixture of calcined europium sesquioxide (99.8% pure), obtained from the Michigan Chemical Company, St. Louis, Michigan, and spectrographic grade graphite, in the ratio of one mole of the sesquioxide to 7.1 moles of graphite, were placed into a graphite crucible which previously had been outgassed by maintaining it at 1630° by induction heating in the vacuum system until the residual pressure in the system was 4×10^{-6} torr or less. No deposit was observed on the walls of the heating assembly when the weight of the crucible remained constant to ± 0.5 mg. Temperature was measured by sighting with a Leeds and Northrup disappearing-filament type optical pyrometer through a prism and optical window into a black body hole situated in the bottom of the crucible.

The crucible, charged with the oxide–carbon mixture, was covered with a snug-fitting, outgassed graphite lid through which a 0.040-in. diameter hole had been drilled, and was heated, as described above, to about 1450° until the deposit which effused from the orifice and condensed on the Vycor vacuum jacket began to flake. Care was exercised to ensure that none of the condensed phase was lost. The crucible was subsequently heated until no europium could be detected in the crucible, and from weight differences of the crucible, the weight of the unreacted graphite could be determined. The condensate was immediately hydrolyzed with either 6 *N* hydrochloric or nitric acid, filtered, and analyzed for europium by weighing the calcined oxalate precipitate. The quantity of carbon in the condensate was determined by direct weighing of the residue that remained after the hydrolysis.

In the other technique, europium metal (99% pure), obtained from the Michigan Chemical Company, St. Louis, Michigan, together with graphite in the ratio of 2 moles of carbon to 1 mole of europium was inserted into a small stainless steel bomb machined from 1-in. bar stock. The cavity of the bomb, which was $^3/_8$ in. in diameter and $^5/_8$ in. high, was charged under an atmosphere of dry helium. The bomb was sealed with a platinum gasket and then heated under a flow of helium in a resistance tube furnace for 12 hr. at about 1050° and then cooled slowly. The bomb was opened and the sample removed from the bomb and stored in a glove box filled with purified helium.

Weighed samples of the bomb contents were hydrolyzed in approximately 3 *N* HCl, digested for 2 hr., and then filtered to remove the free graphite, which subsequently was dried and weighed. The europium was precipitated as the oxalate and determined gravimetrically, as described above. Bound carbon was determined by difference. The absence of iron in the dissolved samples was demonstrated by a qualitative iron test.

The gases produced by hydrolysis in some runs were swept

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[1] F. H. Spedding, K. Gschneidner, Jr., and A. H. Daane, *J. Am. Chem. Soc.*, **80**, 4499 (1958).

[2] R. C. Vickery, R. Sedlacek, and A. Ruben, *J. Chem. Soc.*, 498 (1959).

[3] M. von Stackelberg, *Z. Elektrochem.*, **37**, 542 (1931).

[4] L. Brewer and O. Krikorian, *J. Electrochem. Soc.*, **103**, 38 (1956).

TABLE I
INTERPLANAR *d*-SPACINGS OF EuC_2

Miller indices (*hkl*)	d_{calcd}, Å.	d_{obsd}, Å.	$I_{rel}{}^{a}$
101	3.450	3.450	m
002	3.322	3.322	m
110	2.853	2.853	s
112	2.165	2.169	w
200	2.006	2.020	w
103	1.936	1.941	w
211	1.747	1.748	m

[a] s, strong; m, medium; w, weak.

with helium into a U-tube which was packed with glass wool and cooled with liquid nitrogen. Those gases which condensed were then analyzed using a flame ionization gas chromatographic unit which had been standardized with welding-grade acetylene and natural gas.

A portion of the carbide sample was examined by X-ray powder diffraction with copper Kα ($\lambda\alpha_u$ = 1.5418 Å.) radiation using both a 114.59-mm. powder camera and a Siemens diffractometer.

Results

In the reduction experiments in which the sesquioxide was heated with graphite, approximately 90% of the material inserted into the crucible could be accounted for by assuming that carbon monoxide was produced in a stoichiometric manner as a result of the reduction of Eu_2O_3, according to the equations

$$Eu_2O_3(s) + 3C(s) \longrightarrow 2Eu(g) + 3CO(g)$$
$$Eu_2O_3(s) + 7C(s) \longrightarrow 2EuC_2(g) + 3CO(g)$$

The hydrolyzed condensate contained free carbon, and the europium to free carbon ratio varied from 0.3 to 1.2, depending upon the hydrolytic and heating procedure.

The reaction between europium metal and carbon in the stainless steel bomb produced an easily removable black powder which gave an X-ray powder photograph characteristic of a body-centered tetragonal structure similar to that reported for the other rare earth dicarbides, with the lattice parameters a_0 = 4.045 and c_0 = 6.645 Å. Interplanar *d*-values, together with their observed intensities, are listed in Table I.

The X-ray powder photographs indicated the presence of a minor phase which was assumed to be a rare earth carbide with a different type of crystal structure. This second phase could be obtained in somewhat higher concentrations in samples which contained a lower C/Eu ratio and which had not been heated to as high a temperature.

A chemical analysis of the bomb contents indicated that the composition was $EuC_{1.87\pm0.50}$. According to the gas chromatographic analysis, the hydrolysis products consisted principally of acetylene with traces of methane and other hydrocarbons.

Discussion

An extrapolation of the data of Thorn and Winslow[5] for the trimeric and monomeric carbon species, $C_3(g)$ and $C_1(g)$, which are the principal vapor species in equilibrium with graphite at higher temperatures, indicates that at 1600° the partial pressure of each is about 2×10^{-12} atm. This extremely low pressure, substantiated by the constant weight obtained when empty graphite crucibles were heated at 1450–1500° for a few hours, indicated that any carbon which was found in the condensate when europium sesquioxide was heated with graphite probably left the crucible as a volatile europium carbon species. (Reaction between carbon monoxide gas and the vaporizing species could produce additional free carbon since, in these experiments, the pressure of carbon monoxide during a heating exceeded 10^{-3} torr.) However, the presence of a volatile carbide would not be surprising since, in mass spectrometric Knudsen effusion studies of lanthanum dicarbide, Chupka, *et al.*,[6] have observed gaseous LaC_2 to be a major component in the vapor.

The disturbing variation in the europium-to-graphite ratio in the condensate may result from either a difference between the heats of decomposition and sublimation of gaseous europium and europium dicarbide (since the temperature of the different runs was not identical), or it may result from the use of different acids in the hydrolysis technique, or from both. Since precise data could not be obtained readily by this method, additional sesquioxide–graphite experiments were not performed. Excessive heating of the mixture at 1450° depleted it of europium so the vapor pressure of this dicarbide appears to be much higher than that of the other lanthanons.

The volume of this unit cell (107 Å.^{3}) is substantially greater than that of the neighboring samarium and gadolinium dicarbides, 90.0 and 86.9 Å.^{3}, respectively, and in this respect is analogous to ytterbium dicarbide which, according to the data of Spedding, *et al.*,[1] is also larger than its neighbors. This behavior, which is indicative of a divalent metallic ion, is to be expected for europium, and it indicates that the dicarbide should be similar to an alkaline earth dicarbide. The lattice parameters and volume reported for strontium dicarbide (a_0 = 4.11 Å., c_0 = 6.68 Å., V = 112.7 Å.^{3})[7] are reasonably close to those observed for this compound, and the chemical reactivity also seems similar.

In all preparations, a second phase was apparent. This phase could be reduced to minor proportions by extended heating at 1060°, but could not be removed. The few extra lines observed in the X-ray diffraction pattern did not appear to correspond to the M_2C_3 or the M_3C phase reported by Spedding, *et al.*[1] Since a second phase was always present, a lack of variance in the lattice parameter of the dicarbide would be expected and was observed.

The black dicarbide hydrolyzes very rapidly, and exposure to the atmosphere results in the production of acetylene. For this reason, all manipulation of the sample must be carried out in an inert atmosphere.

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[5] R. J. Thorn and G. H. Winslow, *J. Chem. Phys.*, **26**, 186 (1957).

[6] W. A. Chupka, J. Berkowitz, C. F. Giese, and M. G. Inghram, *J. Phys. Chem.*, **62**, 611 (1958).

[7] C. Herman, O. Lohimann, and H. Philipp, "Strukturbericht," Vol. 2, Edwards Brothers, Inc., Ann Arbor, Mich., 1937, p. 275.

The traces of methane and other hydrocarbons observed in the gas chromatographic analysis may have resulted from the hydrolysis of the unknown phase since their presence would not be expected if the dicarbide phase was pure.

From the data of Atoji,[8] it is possible to calculate the radii of the lanthanon ions in the dicarbide phases. Some of these radii are given in Table II, along with the metallic radii calculated from the lattice parameters reported by Spedding, *et al.*[1] The radii calculated from the dicarbide lattice parameters compare favorably with the metallic radii of the lanthanons with the exception of ytterbium. This discrepancy may be explained on the basis of the crystal structure of the metal. As Hall, *et al.*,[9] have shown, the metallic radius of ytterbium in its body-centered cubic crystalline modification, which is stable at high pressures, is 1.75 Å. Since the dicarbide is a body-centered type structure, its metallic radius would be expected to agree more closely with this form of the metal rather than with the closest-packed form of ytterbium that exists normally.

TABLE II

RADII OF LANTHANONS IN THE LANTHANON DICARBIDE PHASE (Å.)

	r_{metallic}[a]	C–C	r_{calcd}[c]
Sm	1.802	1.285[b]	1.880
Eu	1.984[d]	1.285[b]	2.038
Gd	1.802	1.285[b]	1.852
Tb	1.782	1.293	1.820
Yb	1.940 (f.c.c.) 1.75 (b.c.c.)[9]	1.287	1.768

[a] Metallic radius calculated from the lattice constants for the metal. [b] Average C–C distance given by Atoji.[8] [c] Metal radius calculated from the lattice constants of the dicarbide. [d] Calculated from data of F. H. Spedding, J. H. Hanak, and A. H. Daane, *AIME Trans.*, **212**, 379 (1958).

Previous attempts at the preparation of europium carbides have probably failed because the europium dicarbide that formed in the reaction either vaporized from the crucible as a dicarbide or disproportionated and left the reaction vessel in the form of gaseous elemental europium. Similarly, europium tetraboride has never been prepared—europium hexaboride is always the product when the europium sesquioxide and boron are mixed in the proper ratio to give the tetraboride. It would seem from this work that EuB$_4$ might be prepared by using a procedure similar to the one described above since the excess europium would be prevented from escaping. Preliminary experiments indicate that a higher temperature than is obtainable with a stainless steel bomb is necessary for this reaction to proceed.

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[8] M. Atoji, *J. Chem. Phys.*, **35**, 1950 (1961).

[9] H. T. Hall, J. D. Barnett, and L. Merrill, *Science*, **139**, 111 (1963).

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Coordination Compounds of Organotin and Organolead Halides

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The 1 to 1 addition compounds which are formed between trialkyl tin chloride or trialkyl lead chloride and the Lewis bases tetramethylene sulfoxide, N,N-dimethylacetamide, or N,N-dimethylformamide are reported. Structural evidence supplied by infrared and n.m.r. spectroscopy has been employed to establish the structure of these adducts as trigonal bipyramidal. The lead–hydrogen and tin–hydrogen n.m.r. coupling constants and equilibrium constants for the formation of some of these adducts in carbon tetrachloride solution are reported and discussed.

Introduction

In contrast to a number of addition compounds reported[2,3] for alkyl and aryl tin halides, the only addition compounds which have been reported for organolead halides are the poorly characterized amine "addition compounds" of triphenyllead chloride.[4] Although the addition compounds of the tin halides have been known for a relatively long time, systematic structural studies of the solids have been initiated only recently (see below). There is also a lack of data concerning the nature of the addition compounds in solution.

Our interest in the relative Lewis acidities of organotin and organolead halides has led us to a detailed investigation of the interaction between the Lewis acids, $(CH_3)_3SnCl$, $(C_2H_5)_3SnCl$, $(CH_3)_3PbCl$, and $(C_2H_5)_3PbCl$, and the Lewis bases, tetramethylene sulfoxide, (TMSO), N,N-dimethylacetamide (DMA), and N,N-dimethylformamide (DMF), in inert solvents, such as carbon tetrachloride and benzene. We have found that the interaction between $(CH_3)_3SnCl$ and TMSO, $(C_2H_5)_3SnCl$ and TMSO, and $(C_2H_5)_3PbCl$ and TMSO results in the formation of 1:1 addition compounds,

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[1] Abstracted in part from the Ph.D. thesis of N. A. Matwiyoff, University of Illinois, 1963; National Science Foundation Graduate Fellow, 1960–1963.

[2] R. K. Ingham and H. Gilman, *Chem. Rev.*, **60**, 459 (1960).

[3] D. L. Alleston and A. G. Davies, *J. Chem. Soc.*, 2050 (1962).

[4] L. A. Foster, J. J. Gruntfest, and C. A. Fluck, *J. Am. Chem. Soc.*, **61**, 1687 (1939).