under conditions of dynamic vacuum. The CsF-catalyzed fluorination of $(CF_3)_2C(NF_2)CFO$ and $(CF_3)_2C{=}C{=}O$ occurs readily below −20° to give nearly quantitative conversion to the respective fluoroxy compounds. With $(CF_3)_2C(NF_2)C(O)OSO_2F$, fluorination occurs more slowly and is encouraged by slightly higher temperatures (20°). In this case, $(CF_3)_2C(NF_2)CF_2OF$ and decomposition products are obtained. Under no conditions tried was it possible to retain the fluorosulfate moiety in the molecule.[24]

These fluoroxy compounds are not sensitive to glass or moisture but do attack mercury with vigor. Advantage of their action on acidic iodide solution was taken to determine the number of oxidizing equivalents. The experimental value of about 1.9 agrees fairly well with a theoretical two-electron change.

As is often typical of fluorosulfate-containing compounds of this type, small amounts of moisture tend to produce a cloudy solution and Kel-F stopcock grease is readily dissolved. It is advantageous to work in glass systems with Teflon stopcocks and without standard taper joints.

The mass spectral data are consistent with the proposed structures, although a molecule ion was obtained only in the case of $(CF_3)_2C(OSO_2F)C(O)OSO_2F$. For every molecule CF_3^+ was the predominant species.

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The Preparation and Some Properties of the Lanthanide Oxidecarbides, Ln_4O_3C

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Abstract: A series of lanthanide oxidecarbides (Ln = La, Nd, Gd, Ho, Er) of fcc symmetry has been prepared by reducing the sesquioxide with appropriate mixtures of graphite and the corresponding lanthanide metal. The neodymium analog, which was studied extensively, was found to have the approximate stoichiometry Nd_4O_3C. The X-ray powder diffraction pattern of this phase is indexable on cubic symmetry and has a lattice parameter, a_0 = 5.1407 ± 0.0001 Å. The X-ray intensities are consistent with a NaCl-type lattice. Vapor-phase chromatographic analysis of the hydrolysis products suggests the presence of C^{4-} ions in the structure. Data presented indicate that this is a carbon-stabilized monoxide phase which is common to the lanthanide series.

Attempts to prepare oxidecarbides of the heavier analogs of $Nd_2O_2C_2$[1] by reduction of the sesquioxide either by graphite or by a lanthanide metal–graphite mixture produced a cubic phase which is shown in this study to be an oxidecarbide. This phase contains significantly less carbon than the formerly reported $Ln_2O_2C_2$ phase and has been prepared in pure form by many different techniques. Five lanthanide elements (La, Nd, Gd, Ho, Er) have been shown to exhibit this phase, and it probably exists throughout the entire series.

Two other oxidecarbides exhibiting similar cubic-type structures have been reported: a zirconium oxidecarbide phase[2] produced by plasma furnace reduction of zirconium dioxide with graphite, and the previously reported uranium monoxide now said to be an oxidecarbide.[3] The uranium phase is reported to exhibit a wide range of oxygen/carbon ratios, and the zirconium ($ZrC_{1-\epsilon}O_\epsilon$) phase is a simple solid solution derived from the cubic ZrC. The value of the lattice parameter of the zirconium species lies between those of the ZrC and ZrO, and a thermodynamic treatment of uranium oxidecarbide was based on a binary mixture of UO and UC. In fact, both compounds have been interpreted by use of a model of a carbon atom-substituted fcc NaCl-type monoxide lattice.

Several monoxides of lanthanide elements prepared by a variety of methods have been reported. Most methods effect reduction of the sesquioxide by carbon or by the corresponding metal. Achard, *et al.*, reported the europium, samarium, and ytterbium monoxides prepared by reducing the sesquioxides with carbon.[4–7] Other reports have appeared describing lower oxides, LaO, CeO, NdO, SmO, Sm_2O, YbO, and YO.[8,9] In many instances, the particular phase is described by only one report. When two or more reports have appeared on any phase, the published lattice parameters are often found to vary considerably, and only

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$EuO^{8,10,11}$ and $Eu_3O_4{}^{12,13}$ can really be said to be well characterized. Most of the other reported phases have been found to contain other components, usually nitrogen or carbon, which have often been described as contaminants having little to do with the character of the major phase. For example, the sample of YbO prepared by carbon reduction was reported to contain approximately 1% of that species.[5]

Experimental Section

Preparation. Samples were prepared by arc melting pressed pellets of lanthanide metal, its sesquioxide, and graphite (Ln:O:C in various desired ratios) in an atmosphere of purified helium.

A series of samples of varying initial Ln:O:C ratios was examined micrographically subsequent to arc melting in an effort to determine the ratio which gave specimens of greatest phase purity. Fractured pieces of the best preparation (determined as described above) were annealed by heating to 1650° for not more than 30 min in a previously outgassed ZrB_2, TaC, or graphite crucible in a helium atmosphere of approximately 10^{-2} torr. Such annealing allowed any eutectic material which might be found as an impurity to melt out. Several of the samples treated in this manner were cooled very slowly to determine if the cubic phase was truly stable at room temperature, or if it was simply a quenched high-temperature modification.

Samples of excellent purity were prepared subsequently by zone-melting a mixture with the appropriate ratio in a sealed molybdenum tube, using an MRC electron-beam zone melter (Model EZB-94).

Analysis. All manipulations were conducted in a dry, helium-filled glove box. Samples for analysis were weighed from finely ground and thoroughly mixed specimens. The metal analysis was accomplished gravimetrically by precipitation as the oxalate and subsequent ignition to the oxide. Total carbon was determined by combustion of the sample at 1100° in a stream of dry, purified oxygen, oxidizing the carbon monoxide so formed catalytically to CO_2, and drying and absorbing it in a tared ascarite absorber. Unbound carbon, found when the dissolved samples were filtered for the oxalate analysis, was collected, dried, and weighed, and its mass was subtracted from the total carbon content, determined by combustion, to give the mass of the bound carbon.

Oxygen was determined by the vacuum fusion method[14] in which the samples were dropped into a molten platinum bath which was confined in a graphite crucible. Carbon dissolved in the molten platinum reacted with the sample to liberate any oxygen present as carbon monoxide which was measured volumetrically.

X-Ray Analysis. The initial investigation utilized the Debye–Scherrer technique, employing cameras of 114.6-mm diameter and copper ($\lambda\alpha_u$ 1.5418 Å) radiation. Capillaries were filled and sealed in the helium-filled glove box to prevent hydrolysis of the sample. Later, both Siemens and Norelco diffractometers were employed both for intensity measurements and for investigations into possible superstructure lines. The powdered diffractometric specimens were mounted on glass slides with Canada balsam. When the powder–balsam surface was dry, another very thin layer of the balsam, diluted with xylene, was flowed over the sample to prevent subsequent hydrolysis.

Areas subtended by the (111) and (002) planes were measured with a polar planimeter.

Hydrolysis. An open, wide-mouthed vial containing a neodymium oxidecarbide specimen was placed carefully into a 500-ml flask so that the vial would remain upright. The flask was then sealed and evacuated, and subsequently 10 ml of water was admitted slowly through a stopcock. Care was taken both to preclude admission of air and to ensure that water droplets did not contact the sample. After 2 days, helium was admitted to the sealed flask to bring it to atmospheric pressure; gas samples of the contents were withdrawn with a syringe and subjected to gas chromatographic analysis in an F & M Model 810 gas chromatograph. Six-foot columns filled with 100–120 mesh Porapak Q (Waters Associates, Inc., Framingham, Mass.) and flame ionization detectors were used in the chromatograph. Retention times for methane and acetylene were determined using CP methane and acetylene.

Results

Preparatory. Very little information about stoichiometry can be deduced from reactant molar ratios used in the arc melter since considerable carbon was expelled from the hearth and a thin layer of sesquioxide was frequently deposited on the walls of the melter. However, if a partial pressure of carbon monoxide was introduced into the helium atmosphere of the arc melter, significant amounts of sesquioxide were found by X-ray powder diffraction techniques in the product with the heavier lanthanides (Gd, Ho, and Er). When similar preparatory mixtures of the lighter lanthanides (La, Nd) were arc melted under a carbon monoxide atmosphere, the $Ln_2O_2C_2{}^{1,4}$ phase was the only product.

Micrographic examination of the arc-melted samples invariably indicated the presence of a small amount of gold-colored impurity distributed through the silver-gray major phase. The "herringbone" patterns of the minor phase suggested that it melted at a lower temperature than the major phase. That this was true was shown conclusively when most of this minor gold-colored phase melted from a sample in an annealing experiment leaving in the unfused major phase voids of size and shape similar to the areas originally occupied by the minor gold-colored phase. The gold-colored material recovered from the crucible (ZrB_2) exhibited the diffraction pattern characteristic of the dicarbide, thereby indicating that it was probably a graphite–dicarbide eutectic.

Zone-melting techniques also produced samples of excellent phase purity. These high-purity samples were used for the oxygen analysis, much of the carbon analysis, and all of the diffractometric investigations.

Analytical. Analytical results, including the standard deviation of the measurements, are as follows: Nd, 90.50 ± 0.23%; O, 7.90 ± 0.02%, and C, 1.82 ± 0.7%. The standard deviation of the oxygen determination, ±0.02%, probably does not represent the true accuracy of the measurement, particularly when the hydrolytic nature of the phase is considered. A more reasonable limit of error is ±0.25%. These data indicate a stoichiometry of $Nd_4O_{3.1_5\pm0.10}C_{1.0\pm0.3}$ or approximately Nd_4O_3C.

X-Ray Analysis. No peaks other than those assignable to face-centered cubic symmetry were found in the diffractometer tracings. This observation indicates (a) either a lack of or a statistical distribution of lattice vacancies, and (b) a probable lack of ordering of the carbon sites.

The measured intensities of the (111) and (002) peaks were compared to those values calculated for both an NaCl and ZnS lattice type by assuming that an Nd^{3+} ion and an oxygen atom located at the respective sites approximate the electron density of the Nd_4O_3C species. The scattering factors reported by Cromer and Waber[15] were used for these calculations. The temperature factor of oxygen was assumed to be 1.5 and that of neodymium 0.6, and the absorption error was considered to be negligible. The calculated and experimental data are presented in Table I.

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Table I. Calculated and Observed Intensities for the (111) and (002) Planes of Nd_4O_3C

Structure type	Plane (111)	(002)
ZnS (calcd)	100.0	33.2
$NdO_{0.79}C_{0.24}$ (obsd)	100.0	66.4 ± 1.2[a]
NaCl (calcd)	100.0	68.6

[a] Standard deviation of measurement.

The intensities of other planes were calculated, but the differences between them were not significant enough to demonstrate a preference of one structure over the other. However, these observed intensities were in general agreement with those calculated for both structures. On the basis of the data presented in Table I, we conclude that the oxidecarbide possesses a NaCl-type fcc structure having a lattice parameter, a_0 = 5.1407 ± 0.0001 Å, where the error reported is the standard deviation of a least-squares fit of the powder data.

Samples prepared with excess metal, carbon, and oxygen showed an invariant lattice parameter. However, since the X-ray powder diffraction technique would be insensitive to slight deviations in the O/C ratio, an invariant lattice parameter can be interpreted only as an indication of a narrow homogeneity range. The phases which coexisted with Nd_4O_3C seemed to vary as the carbon monoxide pressure was altered. At temperatures of about 1500° and a partial pressure of CO of about 25 torr, $Nd_2O_2C_2$ and graphite were present, while at the same temperature and at partial pressures of less than 10^{-4} torr, NdC_2 and graphite were observed.

Electrical Conductivity. Semiquantitative measurements on a pressed pellet of Nd_4O_3C indicated a conductivity of the same order of magnitude as that of a piece of neodymium metal of similar dimensions.

Hydrolysis. The graphic display of the chromatographic output presented a very intense peak attributable to methane and a weaker peak assignable to acetylene. The acetylene peak tailed off with two shoulders, presumably due to minor hydrolysis products similar to acetylene.

Planimeter measurements of the areas under the peaks, corrected for differences in detector response to methane and acetylene, indicated that the hydrolysis mixture consisted of 96 ± 3% methane and 4 ± 2% acetylene, along with some other minor mixed hydrocarbons.

The oxidecarbide surface hydrolyzed very rapidly in atmospheric moisture, but the resulting sesquioxide layer appeared to protect the interior core. When 1 *N* HCl was used in the analytical procedure to dissolve the sample, the hydrolysis was often pyrophoric. Apparently this vigorous oxidation produced free carbon since the free carbon content of such samples was greater than that found in samples hydrolyzed more slowly with first a small amount of distilled water, then acid.

Discussion

This ternary phase appears to be a carbon-stabilized lanthanide monoxide. The apparently fixed C/O ratio is markedly different from the variable C/O ratio evidenced by the $ZrO_{1-\epsilon}C_{\epsilon}$ and $UO_{1-\delta}C_{\delta}$ phases reported previously; however, fixed C/O ratios have been observed in other lanthanide oxidecarbides.[1,4] There are several possibilities for placement of carbon atoms in the crystal lattice. They may be situated either (a) as C^{4-} methanide ions occupying one-fourth of the octahedral anion sides, (b) as randomly oriented C_2^{2-} acetylide units occupying one-eighth of the octahedral anion sites (leaving anion vacancies), or (c) as a combination of the two.

Since the hydrolysis products consist principally of methane with but a trace of acetylene and its analogs, the carbon appears to be present as a methanide ion. Even though the hydrolysis was effected principally by water vapor, some minor reaction of two methanide ions to form acetylene and subsequent reduction to more hydrogenated analogs cannot be precluded. Additionally, the total absence of traces of a dicarbide cannot be proved, but most of the carbon present must be assumed to be in the form of methanide ions. Thus, the second case and, for the most part, the third case described in the preceding paragraph may be eliminated. The hypothesis of methanide ions is consistent with the X-ray powder diffraction results. That the cubic phase appears to be crystallographically stable at both room and elevated temperatures and not just a quenched high-temperature modification substantiates further this hypothesis since acetylide-containing carbides usually exhibit symmetry different from cubic at room temperature due to the presence of the anisotropic acetylide species.[16]

Furthermore, if the carbon were to exist in this phase in the form of acetylide ions, the formal oxidation state of the metal would be 1.75, compared to the value of 2.50 based on the methanide assumption. Since, even when a lanthanide ion is combined with a strongly reducing anion, its observed formal oxidation number is generally not less than two, the higher value seems the more likely. In addition, the lattice parameter observed for this phase (5.1407 Å) is almost identical with the value reported for NdN (5.151 Å)[17] in which the metal exhibits the trivalent state.[18] If the effective anionic radius of the oxidecarbide is computed as the average of the radii of the respective ions weighted according to their atomic percentages, a value identical with that of the nitride ion is obtained.[19]

On the basis of the work described in this paper, it appears that the incompletely characterized monoxide phases discussed in the introductory section are really ternaries, consisting of metal, oxygen, and carbon or nitrogen. The SmO phase, for example, has been reported to be an oxidenitride, and attempts to prepare it in the absence of nitrogen or carbon have, to date, been unsuccessful.[20] In all probability, any reported lanthanide or actinide monoxide, except possibly EuO, prepared by carbon reduction of the sesquioxide is, in reality, an oxidecarbide.

The high conductivity of the Nd_4O_3C species is similar to that observed in lanthanide carbide phases

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and suggests bonding of an analogous nature.[21,22] Assuming this to be true, the metal ion should be in a tripositive oxidation state and should supply electrons into conduction bands. In this phase, each neodymium ion could presumably donate one-half electron to the conduction band, assuming all carbon units exist as C^{4-} ions and the stoichiometry is Nd_4O_3C. The silver-gray color of the phase is also indicative of conduction band occupation, but further conductivity and magnetic studies are needed before definite statements can be made about the bonding.

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Crystal and Molecular Structures of Methoxytetraphenylantimony and Dimethoxytriphenylantimony

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Abstract: The structures of methoxytetraphenylantimony, $(C_6H_5)_4SbOCH_3$, and dimethoxytriphenylantimony, $(C_6H_5)_3Sb(OCH_3)_2$, have been determined from three-dimensional single crystal X-ray diffraction counter data. Both compounds are monomeric and contain pentacoordinated antimony atoms. Methoxytetraphenylantimony crystallizes with eight molecules in space group Pbca of the orthorhombic system with cell dimensions of a = 14.81 (2), b = 16.95 (3), c = 16.74 (2) Å; V = 4202 Å^3. The conformation of the organic ligands around the antimony atom is that of a trigonal bipyramid with the methoxyl group occupying one of the apical positions. The Sb–O bond distance is 2.061 (7) Å. The apical Sb–C bond distance of 2.199 (14) Å is significantly longer than the equatorial Sb–C distances of 2.131 (11), 2.128 (13), and 2.097 (15) Å. The Sb atom is displaced 0.10 Å out of the equatorial plane toward the apical phenyl group. Dimethoxytriphenylantimony crystallizes with four molecules in space group $P2_1/c$ of the monoclinic system with cell dimensions of a = 11.51 (2), b = 9.40 (2), c = 17.30 (3) Å; β = 101.75 (1)°; V = 1832 Å^3. The trigonal bipyramidal conformation around the antimony atom has a carbon atom from each of the three benzene rings in the equatorial plane with Sb–C distances of 2.119 (10), 2.121 (11), and 2.119 (12) Å. The methoxyl groups occupy both apical positions with Sb–O bond distances of 2.039 (8) and 2.027 (8) Å. The conventional crystallographic R factors are respectively 2.8 and 3.4%. The nmr spectrum of methoxytetra-*p*-tolylantimony has been taken and a single sharp peak was observed for the *p*-methyl protons. This result suggests that this compound exists in solution either as a rapidly established equilibrium mixture of trigonal-bipyramidal and square-pyramidal configurations or as the latter configuration only.

Methoxytetraphenylantimony and dimethoxytriphenylantimony have been obtained by Briles and McEwen[2] by reaction of tetraphenylstibonium bromide with sodium methoxide in methanol solution. The preparation of the latter compound by this method is of particular interest in that it represents a clear case of a nucleophilic substitution reaction at antimony

$$(C_6H_5)_4Sb^+,Br^- + NaOCH_3 \longrightarrow NaBr +$$
$$(C_6H_5)_4SbOCH_3 \xrightarrow{CH_3OH} (C_6H_5)_3Sb(OCH_3)_2 + C_6H_6$$

Although the subject of pentacoordinate species has, in recent years, received considerable attention,[3] relatively few structures[4–10] of organic antimony(V) compounds containing alkyl or aryl groups have been clearly established. All but one of the known pentacoordinated group V elements adopt a trigonal bipyramidal geometry. The exception is pentaphenylantimony, $Sb(C_6H_5)_5$, which, unlike the phosphorus and arsenic homologs,[11] was found by Wheatley[12] to have an approximately square-pyramidal structure. The difference in energy between the trigonal bipyramid and the square pyramid for most compounds is probably small, and as such there may be specific ligand stabil-

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