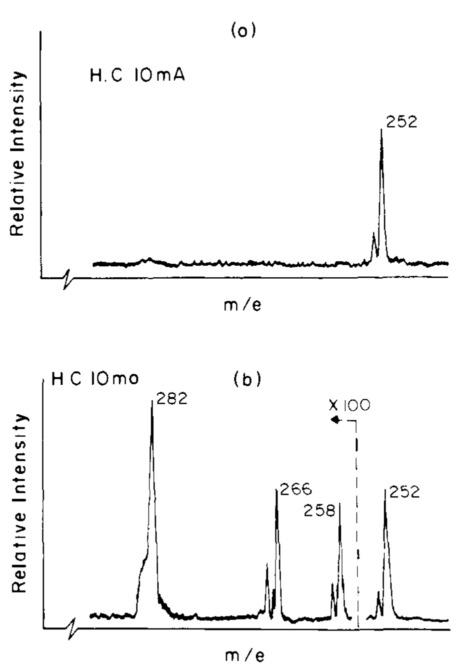
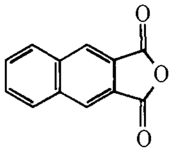
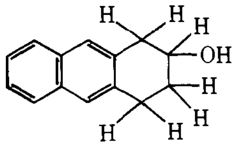


Figure 2. Field desorption mass spectra: (a) benzo[*a*]pyrene (*m/e* 252), nonirradiated; (b) benzo[*a*]pyrene, irradiated 40 min.

anthracene reference spectrum (Figure 1a) suggests that the *m/e* 198 peak is due to a photoproduct. Although end ring opening is not favorable for anthracene, the production of a dicarboxylic acid may occur under the possibly strong oxidative conditions at the emitter surface during ultraviolet irradiation. Loss of water from the diacid before or during field desorption would lead to the production of naphthalene 2,3-anhydride (**1**) (*m/e* 198). A more remote possibility might be the formation of a highly reduced compound (**2**) at the emitter surface.



1



2

Mass spectra of irradiated samples of benzo[*a*]anthracene and pyrene exhibit weak peaks corresponding to diones of the two compounds. No other peaks are evident.

In addition to the parent ion peak at *m/e* 252, the mass spectrum of irradiated benzo[*a*]pyrene (Figure 2b) exhibits mass peaks at *m/e* 258, 266, and 282. The mass peak at *m/e* 282 corresponds to a dione. The mass peaks at *m/e* 258 and 266 are not yet identified. As with anthracene, the absence of contaminant or artifact (e.g., cluster ion) peaks in the reference spectrum of benzo[*a*]pyrene (Figure 2a) suggests that the two peaks in question represent photoproducts.

The results of this investigation demonstrate that FDMS can be used to identify photoproducts of PAH adsorbed on carbon. The absence of observed photoproducts in the case of coronene suggests that PAH may not be as reactive on carbon as on silica gel or alumina.

Detection and identification of primary reaction products appear possible with a modified field desorption ion source. The use of conventional mass spectrometry for this task is difficult because of the opposing requirements of high light absorption to generate large numbers of free radicals and of relatively low pressures to enable rapid diffusion into the ionization chamber. By contrast a field desorption sample is introduced into the source in a relatively concentrated, solid phase adsorbed on an emitter. Although reactive gases, such as oxygen, cannot be introduced at pressures greater than 10^{-3} Torr, their partial pressures at the surface of the emitter are greatly increased by the high electric field necessary for ionization.[17] Therefore, adsorbed state photoreactions should proceed under normal field desorption operating conditions. Furthermore, if a free radical production rate of a few picograms per second occurs with about 1 μg of sample, it would be possible to detect and identify the radicals with the instrument used in this study. Plans are currently being developed to conduct in situ experiments.

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Douglas F. Barofsky,* Edward J. Baum*
Department of Chemistry, Oregon Graduate Center
Beaverton, Oregon 97005
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Crystal Structure of "Carboxyethylgermanium Sesquioxide"

Sir:

During the past 2 decades the development of the organic chemistry of germanium has been extensive.[1,2] This has been due in part to the semiconducting nature of the element and to the anticipated similarities in chemical and physical properties to silicon.

We wish to report the first crystal structure of a novel "organogermanium sesquioxide" resulting from the hydrolysis of an organogermanium trichloride. It can reasonably be expected that the analogues of organogermanium sesquioxides and organosilicones might have a similar unique crystal structure. As with the alkyl and aryl chlorosilanes, the complexity of the hydrolysis products of organogermanium halides increases with the number of halogen atoms present.[3] The triols derived from the trihalides all dehydrate to form polymeric solids which dissolve like dioxides in hydrohalic acids. The polymeric solids are also soluble in alkalis, from which they may be reprecipitated by carbon dioxide.[4] The general composition of the polymers corresponds to the anhydride formula $(RGe)_2O_3$. The alkyl and aryl germanium oxides are polymeric solids and exhibit no definite melting points. To date, no structures of organogermanium oxides prepared by hydrolysis of a trihalide parent compound have been reported.

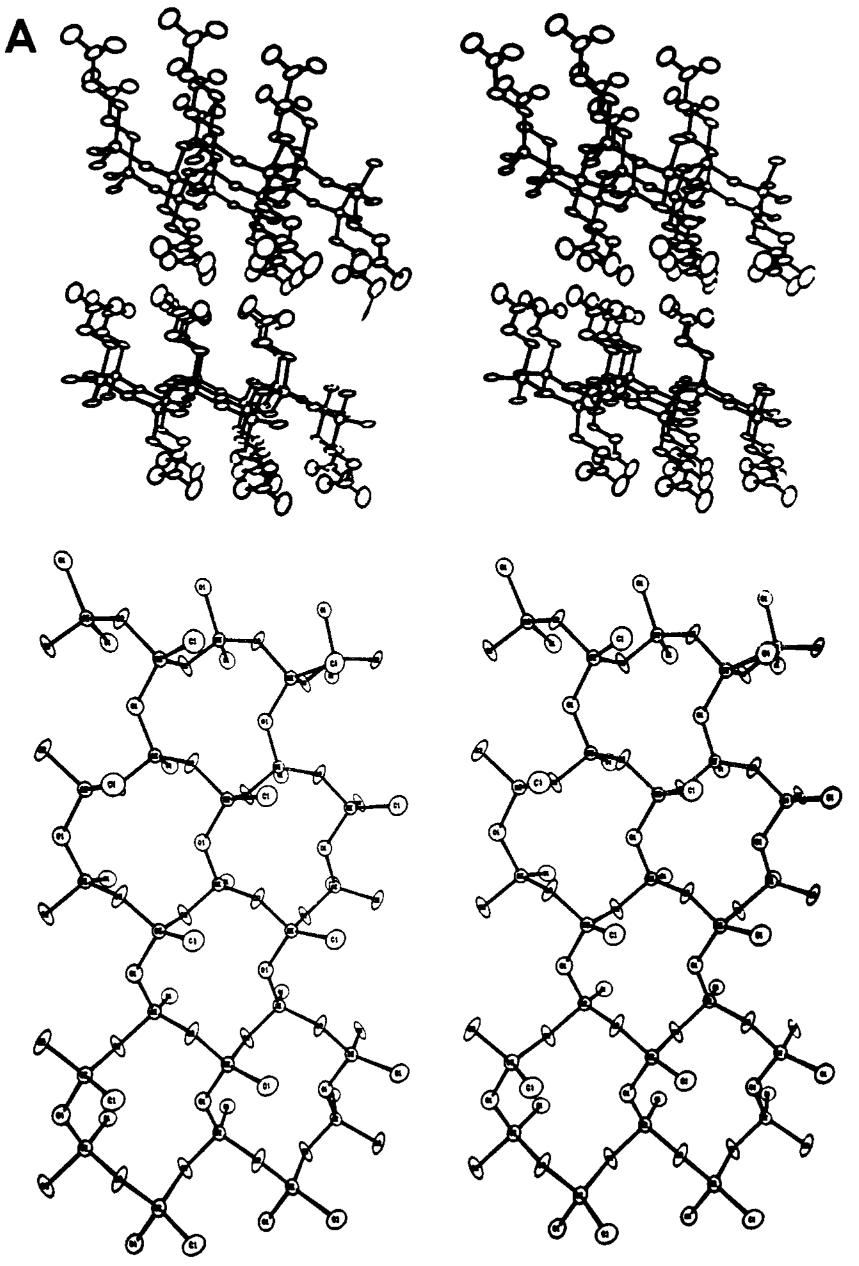


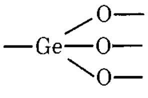
Figure 1. (A) A stereoview of a portion of the $O_3(GeCH_2CH_2CO_2H)_2$ array. Atomic ellipsoids represent equiprobability surfaces of thermal displacement and contain 50% of the probability distribution. The sizes and shapes of the atoms are determined by their final anisotropic thermal parameters and by their perspective view. (B) A stereoview showing the layer network of $O_3(GeCH_2CH_2CO_2H)_2$ and the atomic numbering scheme. The carboxylate chains have been omitted for clarity.

Carboxyethylgermanium sesquioxide, I, was prepared[5] from trichlorogermane and acrylonitrile by the following method:

$$GeHCl_3 + CH_2{:}CHCN \rightarrow Cl_3GeCH_2CHCN \qquad (1)$$

$$Cl_3GeCH_2CHCN \xrightarrow[H+]{\text{hydrolysis}} \underset{\text{I}}{O_3(GeCH_2CH_2COOH)_2} \qquad (2)$$

I was then recrystallized from water to give a white powder which was sparingly soluble in water and insoluble in common organic solvents. A second recrystallization from water yielded small, transparent crystals. The material gave no indication of decomposition or melting below 320 °C. The IR spectrum (KBr) of I had a strong absorption 800-900 cm^{-1}, characteristic[6] of a germanium-oxygen network of the type



No absorptions attributable to Ge-OH species were noted.

A transparent crystal of dimensions 0.22 × 0.33 × 0.07 mm, mounted on a glass fiber, was used for preliminary x-ray examination and for data collection on a Syntex $P\bar{1}$ computer-controlled diffractometer equipped with a graphite-crystal incident-beam monochromator. The width at half-height for ω scans of several strong reflections was 0.3°.

The crystal was found to be monoclinic with extinctions: $h + k = 2n + 1$ for hkl and $l = 2n + 1$ for $h0l$, as expected for space group $C2/C$ or Cc. Space group $C2/c$ was confirmed by refinement in both space groups. Cell constants obtained by computer-centering of 15 strong reflections, followed by least-squares refinement of the setting angles are: $a = 9.180$ (7) Å, $b = 4.838$ (3) Å, $c = 22.694$ (14) Å, $\beta = 90.87$ (3)°. The calculated density is 2.238 g cm^{-3} for FW = 339.32 and $Z = 4$.

Intensity data were collected at 23 ± 1° with Mo $K\alpha$ radiation using the θ-2θ scan technique and a variable scan rate of 4 to 24°/min depending on the intensity of the reflection. Reflections (840, 663 unique) were measured in the range 0°

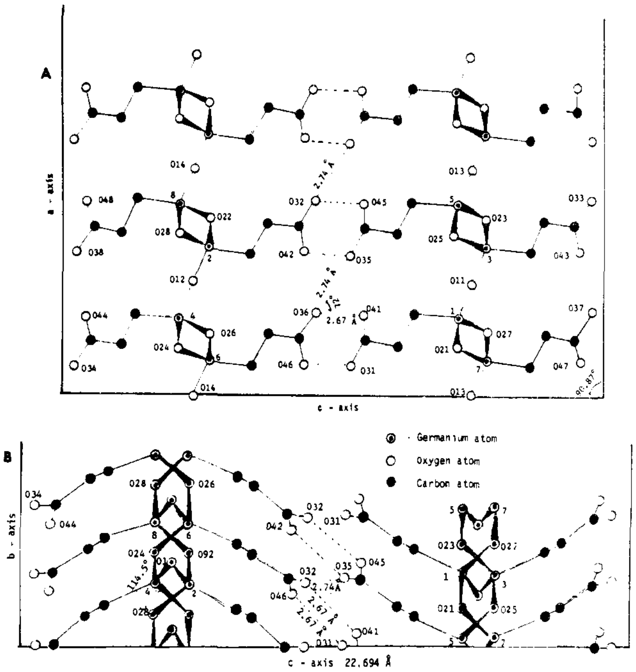


Figure 2. (A) Projection of unit-cell onto *a*–*c* plane of $O_3(GeCH_2CH_2CO_2H)_2$ array. (B) Projection of unit-cell onto b–c plane of $O_3(GeCH_2CH_2CO_2H)_2$ array.

$< 2(\text{Mo K}\alpha) \leq 45°$.

One heavy atom was determined by direct methods and the structure was then solved by the heavy atom method. Using the 180 reflections with E greater than 1.25 and 1000 phase relationship 16 phase sets were produced. Using an E-map prepared from the phase set showing the best probability statistics (absolute figure of merit = 0.985, residual = 31.65) one atom was located. This atom was assigned a Ge scattering factor and refined in least-squares, resulting in agreement factors of $R_1 = 0.27$ and $R_2 = 0.34$. The remaining non-hydrogen atoms were located in succeeding difference Fourier syntheses.

In full-matrix least-squares refinement the function minimized was $\Sigma w(|F_0| - |F_c|)^2$ where the weight w is defined as $4F_0^2/\sigma^2(F_0^2)$. Only the 533 reflections having $F_0^2 > 3\sigma(F_0^2)$ were used in the refinement.

I has an infinite sheet structure which can be seen in Figures 1 and 2. Pertinent bond distances and angles for Ge, O, and C atoms are shown in Table I. (See paragraph at end of paper regarding supplementary material.) The basic unit of the infinite sheet network is a 12-membered ring made up of six Ge tetrahedra bridged by oxygen atoms. The carboxylate chains are arranged alternately above and below the Ge–O network around the ring. The sheets are bound together vertically by hydrogen bonds between the carboxyl groups attached to each sheet. The hydrogen-bonded O–O distance between nearest carbonyl groups is 2.67 Å. There also appears to be another hydrogen bond between the next nearest carbonyl groups (e.g., between O_{36}–O_{35}, Figure 2) in which the O–O distance is 2.74 Å. Although definite conclusions concerning such bifurcated hydrogen bonds must be postponed until neutron diffraction data are available. IR data do provide some evidence. The powder IR spectrum of I shows weak bands at 3400 and 2300–2500 cm^{-1} which may be attributed to such hydrogen bonding. Another feature of this crystal is the fact that the dihedral angle between the O_1–Ge–C_1 and Ge–C_1–C_2 planes is 164° rather than the normal value of 180°, and that between the Ge–C_1–C_2 plane and C_1–C_2–C_3 plane is 165°. The main reason for this conformation seems to be an accommodation to permit the observed hydrogen bond formation.

An infinite sheet structure similar to that of I is observed in the silicate anion $(Si_2O_5^{2-})$[7] and in organosilicon polymers derived from the silicate anion by grafting trimethylsilyl groups on both sides of the silicate sheet.[8] While the silicate sheets are bound by ionic attractions, I is the first reported organogermanium oxide having an infinite sheet structure bound together by hydrogen bonds.

An intriguing aspect of the crystal structure of I is that the cyclic structure of the infinite sheet's basic unit is similar to the crown ethers[9] which demonstrate novel metal ion and amino acid complexation. This unique feature of the structure may well be related to its reported biological activity.[5] It is noteworthy that I is sensitive to the phenylfluorene[10] coloring test for germanium oxide. It seems likely that in aqueous solution I dissociates into carboxyethylgermanetriol, $HOOCCH_2CH_2Ge(OH)_3$, II, resulting in an equilibrium between I and II. This could facilitate metal ion and amino acid complexation by I. Research on this subject is in progress.

Acknowledgment. This research was supported by a grant from the Asai Germanium Institute.[11]

Supplementary Material Available: A listing of bond distances, bond angles, and structure factor amplitudes (6 pages). Ordering information is available on any current masthead page.

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(11) This research was supported by the Asai Germanium Research Institute. The x-ray diffraction analysis was performed by the Molecular Structure Corporation, College Station, Texas 77840.
(12) On leave from the Asai Germanium Research Institute, Tokyo, Japan.

Minoru Tsutsui,* Norihiro Kakimoto,[12] Darrell D. Axtell
Department of Chemistry, Texas A&M University
College Station, Texas 77843

Hiroshi Oikawa
Department of Engineering, Toyo University
Kawagoe-shi, Saitama, Japan

Kazuhiko Asai
Asai Germanium Research Institute
Chofu-City, Tokyo, Japan

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Metal Clusters in Catalysis. 7.[1] Molecular Structure and Chemical Properties of a Novel Metal–Metal Bonded Nickel Complex

Sir:

In this communication we describe the synthesis, structure, and chemistry of a novel dinuclear complex which is formally "electron deficient" and possesses unusual chemical properties. The reaction of diphenylacetylene with bis(1,5-cyclooctadiene)nickel(0) at 20 °C yielded the dinuclear complex, (diphenylacetylene)bis(cyclooctadienenickel) (**1**). If one assumes