the same stability and are in reasonable agreement with the results of previous investigators (Table IV). The present investigation, however, does not give supporting evidence for the existence of the CdF_2 species previously suggested with a formation constant $\beta_2 = 3.4$.[1] The irreversibility of the reduction waves of Ni(II), Co(II), Cr(III), and Ti(III) prevented application of the method to these ions.

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Contribution from the Brookhaven National
Laboratory, Upton, New York

Compound Formation by γ-Irradiation of Xenon–Fluorine Mixtures

By Donald R. MacKenzie and Richard H. Wiswall, Jr.

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Mixtures of Xe and F_2 in slightly greater than 2:1 mole ratio of F_2 to Xe were exposed, in prefluorinated nickel containers, to high-intensity γ-radiation from Co^{60} sources. The pressure was observed to fall, as it would if the two elements combined, and a solid product was later obtained from the container, by sublimation. This resembled the product of the thermal reaction carried out according to the procedure of Claassen, *et al.*,[1] both in appearance and chemical behavior. Analysis of the solid obtained from one of the irradiations was carried out by hydrolyzing a weighed sample in NaOH solution and determining fluoride in the solution. Results of the analysis indicated a composition $XeF_{3.0}$, suggesting a mixture of difluoride and tetrafluoride. For a given composition it is possible to calculate a radiation yield from the pressure drop and other parameters of the experiment. Conditions of the experiment were as follows: initial F_2/Xe ratio, 2.6; initial pressure, 18.6 p.s.i.g.; volume of container, 330 cc.; temperature, 64°; length of irradiation, 130 hr.; ΔP, -6.0 p.s.i.; dose rate (to Fricke dosimeter), 4.0×10^6 rads/hr. Calculation gives a G-value for consumption of Xe of 3.4 atoms per 100 e.v. absorbed in the gas mixture.

The fact that radiation brings about fluorination of xenon suggests its use in the synthesis of other rare gas compounds. Several such experiments have been tried. Mixtures of krypton and fluorine, xenon and chlorine, and xenon and oxygen were irradiated in the Gamma Facility, and a mixture of xenon and oxygen was irradiated in the Brookhaven graphite reactor. No compounds were observed in any case. Apparently any compounds which might be capable of formation with the help of radiation are unstable to either the radiation or the slightly elevated temperatures prevailing during the experiments.

The use of ionizing radiation provides a new approach to the study of the mechanics of the xenon–fluorine reaction. Due to the large number of primary processes involved in the radiation-induced reaction, one would not expect it to follow the same course as the photochemical reaction. Indeed the latter yields only XeF_2, regardless of the initial xenon–fluorine ratio.[2] Further work is being done to determine the effect on product composition of varying the xenon–fluorine ratio in the radiation-induced reaction.

Acknowledgment.—We wish to acknowledge the assistance of F. W. Bloch and W. D. Riel in carrying out the experiments with xenon and chlorine and xenon and oxygen.

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[1] H. H. Claassen, H. Selig, and J. G. Malm, *J. Am. Chem. Soc.*, **84**, 3593 (1962).

[2] J. L. Weeks, C. L. Chernick, and M. S. Matheson, *ibid.*, **84**, 4612 (1962).

Contribution from the Department of Chemistry,
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Octahedral Silicon–Oxygen, Germanium–Oxygen, and Tin–Oxygen Bond Lengths from Interplanar Spacings in the Phthalocyanino Polymers $(PcSiO)_x$, $(PcGeO)_x$, and $(PcSnO)_x$[1]

By William J. Kroenke, Laurel E. Sutton,
Ralph D. Joyner, and Malcolm E. Kenney

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In the search for inorganic oligomers and polymers in this Laboratory, attention has been given to phthalocyanino rings linked together by metal–oxygen chains, *i.e.*, PcAlOAlPc, PcAlOSi(Pc)OAlPc, PcAlOSi(Pc)-OSi(Pc)OAlPc, HOSi(Pc)OSi(Pc)OH, $(PcSiO)_x$, and $(PcGeO)_x$.[2] Both the phthalocyanino rings and the groups III and IV metal–oxygen chains used in these have the advantage of being inherently stable. In addition the use of the bonding positions of the metal rather than those of the benzene rings of the chelate for polymerization gives stable links between the monomer units. In the complexes formed in this way the symmetrical ring system is unsubstituted and thus unweakened by pendant groups on the benzene rings and the chain is stabilized because the metal in it is in a high coordination number and because the whole chain is encased by the ring.

Further work has now established that another member of this series, $(PcSnO)_x$, can be prepared by the

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[1] Support for this work came both from National Science Foundation Grant NSF-G15833 and from Air Force Office of Scientific Research Contract AF 49(638)-773. It is based on portions of the Ph.D. thesis of William J. Kroenke. Pc = the phthalocyanino ligand.

[2] R. D. Joyner and M. E. Kenney, *J. Am. Chem. Soc.*, **82**, 5790 (1960); J. E. Owen and M. E. Kenney, *Inorg. Chem.*, **1**, 334 (1962); R. D. Joyner and M. E. Kenney, *ibid.*, **1**, 717 (1962).

thermal vacuum dehydration of the new compound, $\mathrm{PcSn(OH)_2}$.[3] It also has been found that $(\mathrm{PcGeO})_x$ can be prepared by the usual vacuum dehydration technique. The nature of the Si, Ge, and Sn long-chain polymers has been determined by means of studies based on elemental analysis, infrared spectra, thermogravimetric analysis, and resistance to chemical attack. In general $(\mathrm{PcSiO})_x$ is quite stable chemically, $(\mathrm{PcGeO})_x$ less stable, and $(\mathrm{PcSnO})_x$ relatively unstable; for example, $(\mathrm{PcSiO})_x$ is unaffected by aqueous HF at 100°, aqueous 2 *M* NaOH at reflux, and $\mathrm{H_2SO_4}$ at room temperature, while $(\mathrm{PcGeO})_x$ withstands only the NaOH and $(\mathrm{PcSnO})_x$ does not withstand even the NaOH.

A feature of all these systems is that the great planar phthalocyanino ring predetermines the over-all stereochemistry, forcing the tetravalent metals into octahedral coordination, the aluminum into square pyramidal coordination, and the chains into a truly linear arrangement. In the case of the polymers a further feature of these stereochemically locked systems is that the size of the planar phthalocyanino ring simplifies the interpretation of the X-ray powder patterns sufficiently so that definite structural information can be obtained.

X-Ray powder photographs of $(\mathrm{PcSiO})_x$ reveal that the strongest reflection corresponds to an interplanar spacing of 3.32 ± 0.02 Å. The value of the spacing calculated from the second-order reflection is twice 1.659 ± 0.003 Å. The interplanar spacing of 3.32 Å. is attributed to the repeat distance of the polymer chain and if this is correct it follows directly that the adjacent phthalocyanino rings are stacked parallel in a "deck of cards" fashion. Because the oxygens are wedged between eight nitrogens it seems highly improbable that the SiOSi bond angle deviates from 180°. Therefore the value of 1.66 Å. must correspond to the octahedral Si–O bond length. For comparison it may be noted that ordinary tetrahedral Si–O bonds are in a range near 1.64 Å.[4]

X-Ray powder photographs of $(\mathrm{PcGeO})_x$ are very similar to those obtained for $(\mathrm{PcSiO})_x$. Here the strongest reflection corresponds to a spacing of 3.50 ± 0.02 Å. The value calculated from the second-order reflection is twice 1.746 ± 0.003 Å. The 3.50 Å. spacing is assigned to the repeat distance of the polymer chain and it is concluded that the rings are again stacked parallel. This interpretation gives an octahedral Ge–O bond length of 1.75 Å. The reported average tetrahedral Ge–O bond lengths in $(\mathrm{GeO_3})^{2-}$ are 1.84–1.86 Å.[4]

The X-ray data for $(\mathrm{PcSnO})_x$ are similar to those for $(\mathrm{PcSiO})_x$ and $(\mathrm{PcGeO})_x$ although the pattern is more diffuse. An intense line occurs corresponding to a spacing of 3.83 ± 0.03 Å. This is attributable to the repeat distance in the polymer chain. The value of this spacing based on the second-order reflection is twice 1.91 ± 0.02 Å. Again concluding that the rings are parallel and the chain is linear the octahedral Sn–O bond length is 1.91 ± 0.02 Å. The Sn–O bond length is reported to be 1.93–1.98 Å. in $\mathrm{Sn(OH)_6}^{2-}$.[4] It is interesting to note that even at the separation of 3.83 Å. the rings are still parallel.

An experiment has verified the assignment of these intense *d*-spacings. A sample of $(\mathrm{PcGeO})_x$ was heat-treated for 2.5 hr. at 500° under high vacuum. The infrared spectrum of the residue was identical with the spectrum of the starting material except that the absorption band resulting from the unsymmetrical stretching vibration of the Ge–O–Ge group shifted from 864 to 899 cm.$^{-1}$. X-Ray powder photographs revealed that the sample became more crystalline. The strongest X-ray line corresponded to a spacing of 3.48 ±0.02 Å. and the second-order reflection of this spacing to a value of twice 1.738 ± 0.003 Å. A simple picture that accounts for these phenomena is that an ordering of the polymer took place accompanied by a contraction of the Ge–O–Ge distance and an increase in the Ge–O bond strength. These data imply that the polymer units have special preferred orientation.

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[4] L. E. Sutton, "Interatomic Distances," The Chemical Society, London, 1958, pp. M35-41.

JOINT CONTRIBUTION FROM THE INSTITUT FÜR ANORGANISCHE
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The Structure of (Methylphenylamino)-methylphenylborane

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The existence of double bond character for the boron–nitrogen linkage of aminoboranes has long been advocated by Wiberg.[2] Recently, unsymmetrically substituted aminoboranes have become available and, based primarily on physicochemical constants, a suggestion has been made that such compounds may exhibit *cis–trans* isomerism.[3] Two recent short communications on the proton magnetic resonance spectra of two selected aminoboranes, substituted unsymmetrically at either the boron[4] or the nitrogen[5] atom,

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[1] (a) Technische Hochschule, Stuttgart; (b) Duke University; (c) University of Florida; (d) U. S. Army Research Office.

[2] E. Wiberg, *Naturwissenschaften*, **35**, 182 (1948).

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