ml. of a solution of 30.3 g. (0.30 mole) of d-*n*-propylamine in diethyl ether was added over a period of 11 hr. to 400 ml. of a vigorously stirred ether solution of 50 g. (0.14 mole) of hexachlorotriphosphonitrile. The oil obtained after drying the solution over calcium chloride, evaporating, and removing the unreacted hexachloro compound was purified by fractional distillation at 0.01 mm. pressure.

The di-*n*-butylamino derivative was prepared similarly.

Acknowledgment.—This investigation was supported by the Materials Laboratory of Wright Air Development Command, Wright-Patterson Air Force Base, Ohio, under Contract AF-33-(616)-7918. Reproduction of this communication in whole or in part is permitted for any purpose of the United States Government.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY
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The Formation Constants of Copper, Cadmium, and Zinc Fluoride Complexes

BY ŠTEFICA S. MESARIĆ AND DAVID N. HUME

Received March 23, 1963

A number of previous workers[1–3] using a variety of methods have found evidence for weak complex formation between fluoride and copper(II), cadmium, and zinc ions in aqueous solution. Indications of weak complex formation with these metal ions were also observed in the course of a survey of the polarographic behavior of a number of cations in fluoride-containing supporting electrolytes, and because of the particular applicability of the polarographic method[4] to weakly complexing systems, we have undertaken to examine several of them in some detail.

Experimental

The general technique utilized was that used in previous investigations.[5] The particular modifications necessary for the application to fluoride media (plastic apparatus, Tygon coated capillary, etc.) have been described.[6] The capillary employed had an $m^{2/3}t^{1/6}$ value of 1.67 mg.$^{2/3}$ sec.$^{1/6}$. Measurements were carried out at constant ionic strength (1.0 *M* for copper and 2.0 *M* for cadmium and zinc) in mixtures of sodium perchlorate and sodium fluoride. The pH was maintained at 5.0 ± 0.2 and the temperature at 25 ± 0.1°. The reduction waves of millimolar copper, zinc, and cadmium in both the sodium perchlorate and sodium perchlorate–sodium fluoride mixtures were well defined and showed good linearity with slopes close to the theoretical value when log $[(i_a - i)/i]$ was plotted against E. Addition of a maximum suppressor was found to be unnecessary.

Results

The results are summarized in Tables I–III. The conventional plot of $F_0(X)$ in each instance was linear, indicating the presence only of the free metal ion and the monofluoro complex. The value of β_1 for the formation (stability) constant of the MF^+ species in each system was estimated from the limiting slope of the $F_0(X)$ plot. The limiting slopes hold well in the range 0–0.3 *M* fluoride and it is not necessary to rely on data taken at higher concentrations where the ionic environment is appreciably changed from that of pure sodium perchlorate solutions. The precision of the measurements leads to an uncertainty of about ±0.5 in each constant. All three metals show complexes of about

TABLE I

ANALYSIS OF $E_{1/2}$ DATA FOR COPPER IN FLUORIDE MEDIUM

(F^-), *M*	$E_{1/2}$ *vs.* s.c.e.	$F_0(X)$
0.00	+0.021	1.00
.01	.020	1.08
.05	.017	1.37
.10	.012	2.01
.20	.012	2.18
.30	.007	2.99
.40	.004	3.76
.80	.001	5.98

TABLE II

ANALYSIS OF $E_{1/2}$ DATA FOR CADMIUM IN FLUORIDE MEDIUM

(F^-), *M*	$E_{1/2}$ *vs.* s.c.e.	$F_0(X)$
0.00	−0.559	(1.000)
.05	− .563	1.37
.10	− .566	1.72
.15	− .568	2.01
.20	− .569	2.19
.30	− .573	2.97
.50	− .575	3.48
.60	− .577	4.06

TABLE III

ANALYSIS OF $E_{1/2}$ OF ZINC IN FLUORIDE MEDIUM

(F^-), *M*	$E_{1/2}$ *vs.* s.c.e.	$F_0(X)$
0.00	−0.999	(1.00)
.05	−1.003	1.37
.10	−1.006	1.72
.15	−1.008	2.01
.20	−1.011	2.54
.25	−1.012	2.75
.30	−1.014	3.21
.50	−1.018	4.40
.60	−1.020	5.11

TABLE IV

COMPARISON OF REPORTED β_1 VALUES

Author	Copper	Zinc	Cadmium
Ahrland–Rosengren[a]	9 ± 1	5.9 ± 0.6	. . .
Connick–Paul[b]	5.0 ± 1	5.4 ± 1	. . .
Leden[c]	. . .	. . .	2.9
This paper	6.8 ± 0.5	7.0 ± 0.5	6.4 ± 0.5

[a] Potentiometric: quinhydrone, 1 *M* $NaClO_4$. [b] Potentiometric: Fe(III)/Fe(II), 0.5 *M* $NaClO_4$. [c] Potentiometric: Cd–Hg, 1 *M* $NaClO_4$

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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.

Acknowledgments.—We are indebted to the International Atomic Energy Agency for a fellowship for Štefica Mesarić, 1960–1961, and to the United States Atomic Energy Commission for partial support under Contract AT(30-1)-905.

CONTRIBUTION FROM THE BROOKHAVEN NATIONAL
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Compound Formation by γ-Irradiation of Xenon–Fluorine Mixtures

BY DONALD R. MACKENZIE AND RICHARD H. WISWALL, JR.

Received March 26, 1963

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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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,
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Received April 13, 1963

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.

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