230 el^2 under the first peak. Even though this estimate may be in error by 10 to 15%, its magnitude and the position of the peak indicate that dilution to 5.0 *m* does not bring about extensive replacement of chlorines by water, but it must be admitted that the results for this solution are ambiguous and do not provide a unique determination of the coördination number for zinc. An assignment of area based on four-coördination leads to a reasonable picture, however.

On this assumption, we find that the area of the first peak lies between the values expected for two water–two chlorine neighbors and for one water–three chlorine neighbors per zinc, namely 216 and 250 el^2. The average coördination of zinc therefore would consist of about 2.4 chlorine and 1.6 water neighbors in 5.0 *m* solution. For this concentration, extraction measurements[3] indicate 2.2 waters per zinc.

Discussion

The results show that in very concentrated solution zinc has a coördination number of four and that its coördination is very much like that in crystalline zinc chloride, with water substituted, however, for part of the chlorine. There is a suggestion that the coördination is tetrahedral, as it is in the crystal, since there is a maximum in the RDF at about $\sqrt{8/3} \times 2.8 = 3.72$ Å. On the other hand, it must be admitted that, at least for the 27.5 *m* solution, chlorine–chlorine contacts would occur in this range regardless of the coördination of the zinc.

For the 27.5 and 8.5 *m* solutions, consideration of stoichiometry (two chlorines per zinc) and diffraction data (one water and three chlorine neighbors per zinc) makes inescapable the conclusion that half the chlorines, on the average, are shared between zincs. Assuming that all zincs are equivalent we therefore may describe the average coördination of zinc in solution in terms of $Zn(H_2O)Cl_2$ units which are coupled through one of the two chlorines per zinc. Any other description requires non-equivalence of zincs or the sharing of more than one chlorine per zinc. Although the RDF does not furnish enough detail about second nearest neighbors to permit a discussion of extended or long range structure, we believe that the results show convincingly the existence of shared ligands and that they provide a basis for understanding some of the unusual properties of the solutions.

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Boron–Nitrogen Compounds. VII.[1,2] B-Trifluororobazine

BY KURT NIEDENZU

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B-Trichloro- and B-tribromoborazine $(\text{-BX-NH—})_3$ are well known compounds and can be prepared by several methods.[3] B-Trifluoroborazine, however, has not been described in the literature. As a matter of fact, the knowledge of B-fluorinated borazines is extremely limited: B-trifluoro-N-trimethylborazine first was obtained on thermal decomposition of the methylamine adduct of dimethylfluoroborane[4]; B-trifluoro-N-trisilylborazine has been mentioned in the literature,[5] but no supporting data or analysis were presented; a vapor pressure of 5.9 mm at 24.1° was recorded for a material believed to be B-difluoro-N-trimethylborazine.[6] A more recent attempt to prepare fluorinated borazines resides in the interaction of diborane and tetrafluorohydrazine,[7] but has yet to be demonstrated as a preparative method. All this available information makes it appear that B-fluorinated borazines are either difficult to prepare or relatively unstable materials.

It now has been found that B-trifluoroborazine can be prepared easily through transhalogenation of B-trichloroborazine. The latter is commercially available[8] and a number of its reactions have been studied.[3] Halogen exchange at the boron atom, however, has not been reported.

Several fluorinating agents have been found suitable for the reaction

$$(\text{-BCl-NH-})_3 + 3\text{MF} \rightarrow (\text{-BF-NH-})_3 + 3\text{MCl} \quad (1)$$

where M is a metal ion. Potassium fluoride yielded small amounts of the desired product after extensive refluxing in high boiling solvents; isolation of the B-trifluoroborazine from the reaction mixture proved to be a difficult and tedious procedure.

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[1] Part VI: K. Niedenzu, H. Beyer, and J. W. Dawson, *Inorg. Chem.*, 1, 738 (1962).

[2] Supported by the U. S. Army Research Office (Durham).

[3] J. C. Sheldon and B. C. Smith, *Quart. Rev.* (London), 200 (1960).

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[5] S. Sujishi and S. Wirtz, *J. Am. Chem. Soc.*, **79**, 2447 (1957).

[6] H. I. Schlesinger, A. Finch, J. Kerrigan, and J. Murib, ONR Technical Report Project N356-255, July, 1956, p. 29.

[7] R. K. Pearson and J. W. Frazer, *J. Inorg. Nucl. Chem.*, **21**, 188 (1961).

[8] U. S. Borax Research Corp., Anaheim, California.

Silver fluoride was found to be more useful for the reaction; the application of titanium tetrafluoride resulted in a considerable drop in the reaction time and eliminated the necessity for using solvents. After standing for a few minutes, a mixture of titanium tetrafluoride and B-trichloroborazine spontaneously warmed to about 40°. The mixture then was gradually heated to 130° under reduced pressure (*ca.* 50–80 mm.) and titanium chloride and B-trifluoroborazine were distilled off. The solid borazine was filtered from the distillate in an inert atmosphere and was washed with *n*-hexane. Final purification of the product was achieved through sublimation under vacuum.

B-Trifluoroborazine is a white crystalline material melting at 122° (subl.). It is soluble in such anhydrous solvents as ether and benzene, and was found to be sufficiently stable in the presence of moisture to be handled in the atmosphere.

Anal.[9] Calcd. for $B_3N_3F_3H_3$: B, 24.2; N, 31.2; F, 42.4; H, 2.2; mol. wt., 134.5. Found: B, 23.9; N, 31.1; F, 42.9; H, 2.2; mol. wt., 132.

Antimony fluorides and their mixtures with antimony chlorides also reacted spontaneously with B-trichloroborazine to yield B-fluorinated derivatives. On the basis of existing evidence it appears that, through variation of the experimental conditions, this procedure can be made to yield partially fluorinated borazines.

Furthermore, the metathetical reaction described in eq. 1 is not restricted to the fluorination of B-trichloroborazine itself, but certain substituted borazines can be reacted in an analogous manner. Thus B-trifluoro-N-trimethylborazine, m.p. 90.5° (lit.[4,5]: 85 and 88–89°, respectively), was obtained by a procedure analogous to that described above.

Since no special high vacuum equipment is necessary for the transhalogenation procedure, this method seems to be of general interest for preparing B-fluorinated borazines.

Experiments now are being done to improve the yields, which at present range between 25 and 40%, and to investigate the partially fluorinated products in more detail. Preliminary results indicate that, in the latter, chlorine is more reactive than fluorine and therefore is more easily replaced by other groups. This behavior could lead to the preparation of unsymmetrically substituted borazines of great variety.

CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT,
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Phase Relation in the System Uranium Trioxide–Nitric Acid–Water at Various Temperatures[1]

BY J. R. LACHER, KEITH ENSLEY, AND J. D. PARK

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In 1926 Coloni[2] studied the UO_3–H_2O–HNO_3 system at 25.0°. He reported the existence of the following hydrates of uranyl nitrate: $UO_2(NO_3)_2 \cdot 6H_2O$, $UO_2(NO_3)_2 \cdot 3H_2O$, and $UO_2(NO_3)_2 \cdot 2H_2O$. In 1941 Kraus and co-workers at Brown University made a further study of the system extending the curve into the UO_3 region.[3] They postulated a hydrate $UO_3 \cdot nH_2O$ as the solid phase as shown in Fig. 1.

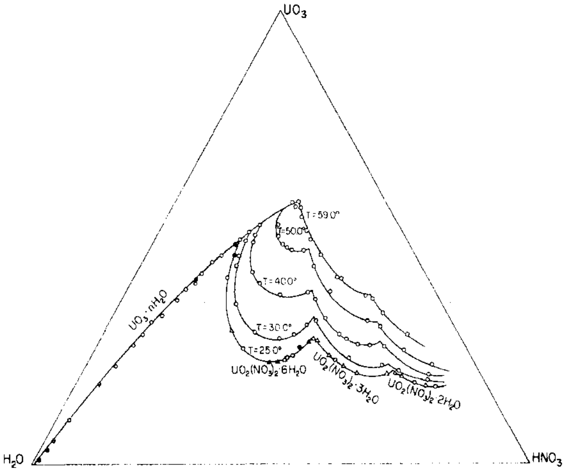

Fig. 1.—Phase diagram for the system UO_3–H_2O–HNO_3: Δ, Coloni; ●, Brown University; ○, this research.

This paper concerns the extension of the curve into the HNO_3-rich region and an investigation at higher temperatures. Standard procedures[4] were used to produce and equilibrate mixtures of

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[9] Analysis by the Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y. The molecular weight was determined cryoscopically in benzene; melting points were taken on a Mel-Temp Block in sealed tubes.

[1] This research is supported in part by the Atomic Energy Commission through the Uranium Division of the Mallinckrodt Chemical Works, St. Charles, Missouri.

[2] A. Coloni, *Bull. soc. chim.*, (4) **39**, 1243 (1926).

[3] Private communication.

[4] E. K. Ensley, "A Study of Some Chemical Properties of Uranium Compounds," Ph.D. Thesis, University of Colorado 1960.