oxide which has been prepared for neptunium was Np_3O_8.[2] Evidence is presented in this paper to show the existence of $NpO_3 \cdot 2H_2O$. In a previous communication[3] it was reported that a brown precipitate was formed when bubbling ozone through a solution of Np(V) in a $LiNO_3$–KNO_3 eutectic at 150°. This brown precipitate was separated from the salt by washing the salt mixture with water and then drying the product. This product has been identified as $NpO_3 \cdot 2H_2O$.

The brown precipitate is separated from the molten nitrate by cooling the melt and washing the water-insoluble solid many times with distilled water to remove all traces of the soluble salt matrix. The compound then is dried in an air oven at 90 to 100° overnight. This compound is very soluble in dilute mineral acids to give a solution of essentially pure NpO_2^{+2} (at least 98%) as shown by spectrophotometry. Thus this compound contains neptunium in the (VI) state. Emission spectroscopy shows that no other metallic cation is present; neither lithium nor potassium exist in any significant amounts in this compound. Thus the brown compound is not a neptunate such as K_2NpO_4.

The X-ray powder pattern of the compound is similar to $UO_3 \cdot 2H_2O$. Table I is a comparison of the $\sin^2 \theta$ values for the strongest lines of $NpO_3 \cdot 2H_2O$ with those of $UO_3 \cdot 2H_2O$.[4]

TABLE I

COMPARISON OF $\sin^2 \theta$ FOR $NpO_3 \cdot 2H_2O$ AND FOR $UO_3 \cdot 2H_2O$

$NpO_3 \cdot 2H_2O$	$UO_3 \cdot 2H_2O^4$
0.0103	0.0110 s
.0415	.0440 mw
.0465	.0462 s
.0484	.0485 ms
.0569	.0571 s
.0587	.0591 ms
.1538	.1545 m+

Specific activity measurements show the compound to contain 72 ± 2% neptunium; $NpO_3 \cdot 2H_2O$ contains 73.8% neptunium. Thus it is concluded that $NpO_3 \cdot 2H_2O$ has been made.

Similar preparations were attempted using molten $LiClO_4$ at 260° as the solvent. Again, with ozone bubbling through a solution containing Np(V), a brown precipitate is formed. However, the identity of the recovered compound is unknown. This time the compound is soluble in dilute acids with difficulty. The resulting solution contains neptunium only in the (V) state. Again emission spectroscopy shows no other metallic ions to be present. The X-ray pattern of this compound is similar to Np_3O_8.[5] Table II compares the $\sin^2 \theta$ values for this compound with those of Np_3O_8[6]; only the strong lines are given. However, this compound cannot be Np_3O_8 because Np_3O_8 dissolves in dilute acid to yield both NpO_2^+ and NpO_2^{+2} ions. This must be a neptunium(V) oxide.

TABLE II

COMPARISON OF $\sin^2 \theta$ FOR NEPTUNIUM(V) OXIDE AND Np_3O_8

Neptunium(V) oxide	$Np_3O_8^6$
0.0489	0.0492
.0543	.0547
.0828	.0831
.0882	.0886
.1414	.1422
.1579	.1587
.2178	.2190
.3318	.3326

Unfortunately the mechanism of oxide formation is more complicated than so far indicated. The preparations from the molten nitrate eutectic did not always result in $NpO_3 \cdot 2H_2O$. Sometimes the unknown Np(V) compound, the same as from the molten perchlorate, was produced. The similarity was verified by the X-ray patterns. In only a single instance was $NpO_3 \cdot 2H_2O$ prepared from the lithium perchlorate melt. It is likely that the temperature is the important variable. The furnace used in these experiments had considerable temperature gradients. It already has been shown[3] that Np(VI) in molten salts is reduced to Np(V) with increasing temperature which in turn is unstable to still higher temperatures.

Further work is in progress with both these compounds. Oxygen analysis must be performed. Precipitation reactions from molten salts should prove to be a valuable technique in the preparation of many new and interesting compounds.

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JOINT CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY
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Some Observations Relative to Digallane

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The literature contains references to digallane, Ga_2H_6,[1,2] to a polymeric $[GaH_3]_n$,[3b] to a gaseous GaH,[4] to a gallium–hydrogen solid of unknown formula,[5] and to a diethyl etherate, $(C_2H_5)_2OGaH_3$.[3] The compounds Ga_2H_6 and GaH have been questioned on the basis of periodic relationships.[6] The doubts on Ga_2H_6 and $[GaH_3]_n$ are now reinforced by experiment. Recent studies on gallium hydrides, initiated independently in

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two separate laboratories, have failed to provide any positive evidence for the existence of Ga_2H_6 or polymeric $[GaH_3]_n$ as separate stable molecular species, despite conscientious efforts to repeat earlier preparative procedures. Since the results from two separate laboratories lead to a common conclusion, this joint communication has been prepared.

Experimental

The Reduction of $GaCl_3$ by $LiAlH_4$ in Solvents.—The reaction between $LiAlH_4$ and $GaCl_3$ has been described in terms of three distinct processes

$$\begin{tikzcd} & & \mathrm{Ga_2H_6}\ \text{[reported stable to 130°][2]} \\ \mathrm{GaCl_3 + LiAlH_4} \arrow[r, dash, "\text{solvent}"] & {} \arrow[ur] \arrow[r] \arrow[dr] & \mathrm{[GaH_3]}_n\ \text{[reported stable to 140°][3b]} \\ & & \mathrm{(C_2H_5)_2OGaH_3}\ \text{[reported stable to 35°][3a]} \end{tikzcd}$$

In our hands all hydridic products which could be obtained from $LiAlH_4$–$GaCl_3$–solvent systems contained relatively large amounts of chloride which could not be removed by repeated vacuum line fractionation. The chloride-containing oils decomposed even at 0°.

In a typical run a 25-mmole sample of $LiAlH_4$ was mixed with 8 mmoles of $GaCl_3$ using about 100 cc. of solvent. Diethyl ether, dimethyl ether, benzene, and isopentane were all tried as solvents; $GaBr_3$ in benzene was also tried. Reaction times ranged from 1 to 19 hr. and reaction temperatures of −45, 0, 25, and 50° were used. In diethyl ether an oily product was obtained which decomposed when an attempt was made to fractionate it on the vacuum line. H_2, Ga, ether, and a solid residue were the products. In isopentane (0 to 25°) the oily product gave 1–2 atoms of hydridic H for each Cl. At 25° the oil gave H_2, Ga, and a white solid containing Ga and Cl.

The Reduction of $GaCl_3$ by Other Reagents.—$GaCl_3$ and LiH react to give unstable $LiGaH_4$ as described by Finholt, Bond, and Schlesinger.[7] $LiGaH_4$ (6 mmoles) and $GaCl_3$ (3 mmoles) in ether (30 cc.) at 20° for 48 hr. gave no volatile products and no ether-insoluble $(GaH_3)_n$.

Attempts to reduce $GaCl_3$ with $LiBH_4$ in diethyl ether at 20° gave diborane and a trace of H_2. No Ga_2H_6 was isolated.

Reaction of Gallium Trimethyl and H_2 in an Electric Discharge.—The original report[1,2] on Ga_2H_6 described its preparation by the reactions

$$2(CH_3)_3Ga + H_2 \xrightarrow[\text{discharge}]{\text{electric}} [(CH_3)_2GaH]_2 + CH_4 + \ldots\ldots$$

$$3[(CH_3)_2GaH]_2 + 4(C_2H_5)_3N \longrightarrow 4(CH_3)_3GaN(C_2H_5)_3 + Ga_2H_6$$

In our hands fractionation of the products from the discharge tube gave a viscous liquid which could be condensed at −15° along with hydrocarbons separated at −196° and unreacted $Ga(CH_3)_3$ separated at −95°. The viscous liquid in the −15° trap did not correspond in properties to the compound $[(CH_3)_2GaH]_2$ reported as a product in the original paper of Wiberg.[1] Although pyrolysis of $[(CH_3)_2GaH]_2$ should give 0.75 mole of H_2 per mole of $Ga(CH_3)_3$ formed, our product, separating at −15°, gave only 0.32 mole of $H_2/Ga(CH_3)_3$. Since the reported conversion of $(CH_3)_4Ga_2H_2$ to Ga_2H_6 demanded that $(CH_3)_4Ga_2H_2$ and $N(C_2H_5)_3$ be mixed in stoichiometric quantities, it did not seem appropriate to attempt the conversion with the poorly characterized products obtained from the discharge reaction. Difficulties in the preparation of Ga_2H_6 using $N(C_2H_5)_3$ as a reagent were also indicated by the relatively high stability of $H_3GaN(CH_3)_3$ isolated in a subsequent study.[8]

Displacement of GaH_3 from its Complex.—An attempt was made to liberate Ga_2H_6 by thermal decomposition of one of its weaker adducts. The first system studied can be represented by the equation

$$(CH_3)_3NGaH_3 + BF_3 + (CH_3)_2S \xrightarrow[-15°]{\substack{\text{solvent} \\ (CH_3)_2S}} (CH_3)_2SGaH_3 + (CH_3)_3NBF_3$$

The resulting $H_3GaS(CH_3)_2$ was purified by fractionation through a trap at −78°. When the excess of $(CH_3)_2S$ was removed at −70°, pure dimethyl sulfide–gallane was obtained. It decomposed quantitatively at room temperature to $(CH_3)_2S$, Ga, and 1.5 H_2.

In an analogous reaction, in the absence of solvent, $(CH_3)_3NGaH_3$ and B_2H_6 gave no reaction below room temperature, but at 20° gave a product which decomposed immediately to gallium and hydrogen. In no case was any real evidence for Ga_2H_6 obtained.

Discussion

Recently $(CH_3)_3NGaH_3$ has been synthesized,[8] and the properties of this material can be used as an index to the stability of Ga_2H_6. For example $(CH_3)_3NBH_3$ is stable at 125°,[9] whereas B_2H_6 decomposes at these temperatures to give hydrogen and higher boron hydrides.[10] Similarly, $(CH_3)_3NB_3H_7$ is fairly stable at 25° but the parent boron hydride, B_4H_{10}, decomposes on storage at room temperature. It is then logical to postulate that Ga_2H_6 would be significantly less stable than the known $(CH_3)_3NGaH_3$ and $(CH_3)_2SGaH_3$. The relatively low stability of the latter compounds[8] and our inability to prepare Ga_2H_6 cast serious doubt on previous literature reports relative to this compound.

A similar comparison of $(CH_3)_3NBH_3$ with $(CH_3)_2OBH_3$ and $(CH_3)_3NB_3H_7$ with $(C_2H_5)_2OB_3H_7$ suggests that $(C_2H_5)_2OGaH_3$ should, if formed, be much less stable than $(CH_3)_3NGaH_3$. Such a comparison also casts serious doubt upon the reported stability of the compound $(C_2H_5)_2OGaH_3$.

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Ammines of Osmium(I) and Osmium(0)

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Earlier work[1–3] has provided evidence for the existence of species interpreted as ammines of platinum(0) and iridium(0), *i.e.*, $Pt(NH_3)_4$ and $Ir(NH_3)_5$. We report here similar evidence for ammines of osmium(I) and osmium(0), $[Os(NH_3)_6]Br$ and $[Os(NH_3)_6]$; these were formed by the reactions

$$[Os(NH_3)_6]Br_3 + 2K^+ + 2e^- \longrightarrow [Os(NH_3)_6]Br + 2K^+ + 2Br^- \quad (1)$$

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