uranium trioxide, nitric acid, and water. The schematic diagram of the phase relations at the various temperatures is shown in Fig. 1 as per cent by weight.

It is seen from this triangular diagram that the hexahydrate has the greatest solubility while the dihydrate shows the least solubility. It also is noted that an increase of temperature influences the solubility of the hexahydrate to a greater extent than the lower hydrates. The solubility curves were determined for 30, 40, 50, and 59°; the highest temperature of 59° is one degree below the melting point of the hexahydrate. At this temperature, near extinction of the hexahydrate is noted due to the infinite solubility at 60°.

In the nitric acid-rich region, the acid decomposes and it becomes impossible to study the system in three components. In this region the compound $UO_2(NO_3)_2 \cdot N_2O_4 \cdot H_2O$ was identified. It had been prepared previously by Gibson and Katz[5] by treating uranium trioxide monohydrate with liquid nitrogen tetroxide.

The solubility curve in the region where $UO_3 \cdot n$-H_2O is the saturating phase shows that uranyl nitrate will dissolve uranium trioxide. In dilute solution one equivalent of acid will dissolve as much as 1.75 equivalents of uranium trioxide.[6] Sutton observed that the uranyl ion was capable of dissolving uranium trioxide and postulated the mechanism

$$UO_3 + UO_2^{++} \rightleftarrows U_2O_5^{++}$$

Heidt[7] and later Harris and Kolthoff[8] suggested that the following reaction represents the hydrolysis of the uranyl ion

$$UO_2^{++} + H_2O \rightleftarrows UO_2OH^+ + H^+$$

The equation representing the solution of uranium trioxide would be

$$UO_3 + UO_2^{++} + H_2O \rightleftarrows 2UO_2OH^+$$

Since the UO_2OH^+ ion probably can polymerize, the two equations are essentially the same and both illustrate the acidic characteristics of the uranyl ion.

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Structure and Magnetism of K_2ReH_8 and K_2TcH_8

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The recently reported compounds K_2ReH_8[1] and K_2TcH_8[2] are unique in being ternary transition metal hydrides having only hydrogen as the complexing ligand. As such their structure and physical properties are of considerable interest. In the present note we present a preliminary report on an X-ray structure determination for K_2ReH_8 and K_2TcH_8 and on the magnetic susceptibility of K_2ReH_8.

X-Ray Diffraction

Several single crystals of K_2ReH_8, grown by slow evaporation of an aqueous KOH solution and shown to be water-free by their infrared spectra, were mounted in sealed glass capillaries. Precession and Weissenberg photographs (Mo$K\alpha$) showed the Laue symmetry to be $D_{6h}-6/mmm$ with no systematic absences. The lattice constants are $a = 9.61$ and $c = 5.51$ Å. The measured density of 3.07 ± 0.10 g./cc., obtained pycnometrically in isopropanol, indicates definitely three formula weights per unit cell, the calculated density being 3.09 g./cc. The gross features of the diffraction intensities can only be fitted by placing three Re atoms in positions 1(a), 000, and 2(d), $\pm\ ^1/_3\ ^2/_3\ ^1/_2$, of space group $D_{6h}{}^1-P6/mmm$, positions also most logical on stereochemical grounds. Unfortunately the crystals were so large, 0.1–1.0 mm., that the absorption corrections are quite appreciable. Without accurate intensities the potassium atoms could not be located unambiguously, either in P6/mmm or any of its hexagonal or trigonal subgroups. We are in the process of mounting a well shaped, small crystal on which accurate intensities can be collected and absorption corrections made. When the potassium atoms have been located by X-rays, the hydrogens will be placed by neutron diffraction.

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X-Ray powder photographs (CrKα and CuKα) of K_2ReH_8 and K_2TcH_8 are virtually identical, with the same lattice constants as the single crystals of K_2ReH_8; they are the same both in intensity distribution and in *d*-spacings. Thus, the Re and Tc compounds are isostructural with lattice constants differing by less than 0.01 Å.

These results show that the metal atoms are widely spaced (smallest Me–Me distance = 5.51 Å.) in solid K_2ReH_8 and K_2TcH_8, and so they must exist in discrete MeH_8^{2-} ions. The large volume of the unit cell (440 Å.^{3}) indicates that the hydrogen atoms are occupying an appreciable amount of the space in the cell, *i.e.*, that they are essentially hydridic in character. Assuming reasonable volumes for the metal ions,[6] the effective volume of the hydride ion is at least 10.5 Å.^{3}, corresponding to a minimum average radius of about 1.1 Å. These figures are similar to those obtained by using the same computational methods for the alkali metal borohydrides,[4,5] and are slightly smaller than those for the alkali metal hydrides.[6] This decrease is not unexpected in view of the greater covalency in the borohydrides and in the rhenium and technetium hydrides.

It is worth nothing that the X-ray diffraction results provide an independent confirmation of the stoichiometry of the rhenium compound, at least as far as the K/Re ratio goes. This is of interest in view of the recent report[7] that a solid having the stoichiometry $KReH_4 \cdot 2H_2O$ has been isolated by a procedure which is essentially identical with that found to yield K_2ReH_8. Moreover, the published infrared spectra of $KReH_4 \cdot 2H_2O$[7] show absorptions in the metal–hydrogen stretching and bending regions at precisely the same wave lengths as we find for K_2ReH_8. These facts suggest that the two compounds are not essentially different. Since the diffraction intensities require that there be three Re atoms per unit cell, we calculate for the stoichiometry $KReH_4$ (the crystals used were anhydrous) a density of 2.65 g./cc., in complete disagreement with the measured density.

Magnetic Susceptibility

The magnetic susceptibility of solid K_2ReH_8 was measured for us by H. J. Williams using a pendulum magnetometer.[8] The sample used was shown to be free of non-rhenium impurities by emission spectroscopic analysis. The infrared spectrum established the absence of $KReO_4$. The susceptibility was found to be independent of temperature from 295 to 80°K., with a mean value over this range of $\chi_M = -64 \pm 10 \times 10^{-6}$ c.g.s./mole. A measurement of the susceptibility of $NaBH_4$ at room temperature gave $\chi_M = -28 \times 10^{-6}$ c.g.s./mole. Taking $\chi_A(Na^+) = -6.8 \times 10^{-6}$ c.g.s./mole[9] and $\chi_A(B^{+3}) = -0.2 \times 10^{-6}$ c.g.s./mole,[10] we get $\chi_A(H^-) = -5.3 \times 10^{-6}$ c.g.s./mole in $NaBH_4$. This value will be used in making the diamagnetic correction for hydride in K_2ReH_8. With $\chi_A(K)^+ = -14.9 \times 10^{-6}$ c.g.s./mole[9] and diamagnetic $\chi_A(Re^{+6}) = -16 \times 10^{-6}$ c.g.s./mole,[10] the corrected susceptibility of K_2ReH_8 is $\chi_M' = +25 \times 10^{-6}$ c.g.s./mole. The n.m.r. spectra of solutions of K_2ReH_8 also indicate that in the dissolved state K_2ReH_8 is diamagnetic or at most only very slightly paramagnetic.[1] Since K_2ReH_8 has an odd electron, its very small paramagnetic susceptibility is surprising, especially in view of the X-ray diffraction results showing that Re–Re bonding does not occur in this compound. A possible explanation is that the unpaired electron is in an orbital derived from the t_{2g} set for which $<L + 2S> = 0$, the small temperature independent paramagnetism being due to the second-order Zeeman effect between the occupied level and the next higher one from which it is split by a large spin–orbit coupling. For a spin–orbit coupling constant $\zeta = 4000$ cm.$^{-1}$ the theory[11] predicts a temperature independent $\chi'_M \sim 85 \times 10^{-6}$ c.g.s./mole. On this basis a greater paramagnetism is expected for K_2TcH_8 since spin–orbit coupling is less in the second transition series. Thus, for $\zeta = 1450$ cm.$^{-1}$,[12] the predicted temperature independent susceptibility is $\chi'_M \sim 240 \times 10^{-6}$ c.g.s./mole. Another possible explanation of the very low paramagnetism of K_2ReH_8 is that it actually consists on the average of $1ReH_8^- + 1ReH_8^{3-}$ with the $5d^2$ ion spin-paired, as has been postulated in other systems.[13]

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Greater paramagnetism for K_2TcH_8 would require uncoupling of the spins in the technetium compound.

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The Preparation of $MoCl_4 \cdot 4(C_6H_5)_3AsO$

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In an extension of the study of reactions between molybdenum pentachloride and oxygen donors,[1] the reaction of molybdenum tetrachloride with the same donor molecules has been investigated. The triphenylarsine oxide adduct was the only Mo(IV) complex isolable.

Experimental

Reagents.—Reagent grade carbon tetrachloride was used as solvent. The oxygen donors were prepared as described by us previously.[1]

Molybdenum tetrachloride was prepared by two methods. The first method, described in an earlier report from this Laboratory,[2] was found to be not as reliable as we had supposed. About as often as not the product is a mixture of $MoCl_4$ and $MoCl_5$. Nonetheless, on occasion, excellent samples of the tetrachloride were obtained by this method. *Anal.* Calcd. for $MoCl_4$: Cl, 59.65; Mo, 40.35. Found for a good preparation: Cl, 59.78; Mo, 39.24. Perhaps a better test of the purity of the preparation was its ability (or failure) to give a pure white precipitate upon reaction with $(C_6H_5)_3AsO$ as described below.

The alternate method was reported by Epperson[3] and depends upon the reaction of MoO_2 with CCl_4 in a sealed tube. The principal impurity in the products of this method proved to be unreacted MoO_2. In cases of incomplete conversion the product is easily separated from unreacted starting material by virtue of the solubility of the former in CCl_4. *Anal.* Found for a good preparation: Cl, 58.31, 58.73; Mo, 39.67, 40.17.

Analyses.—Molybdenum and chlorine analyses were performed as described previously.[1] Carbon and hydrogen analyses were done by Micro-Tech Laboratories, Skokie, Illinois.

Preparation of the Complex.—All operations were performed in a nitrogen atmosphere. A small amount (0.2–0.3 g.) of $MoCl_4$ was dissolved in 100 ml. of CCl_4. Sufficient $(C_6H_5)_3AsO$ to give a six- or eightfold excess (2–3 g.) was dissolved in 300 ml. of CCl_4, cooled to room temperature, and filtered. The red $MoCl_4$ solution was decanted slowly into the $(C_6H_5)_3AsO$ solution. It is decolorized instantaneously and a flocculent white precipitate forms. Care must be taken not to add too much $MoCl_4$, or the precipitate takes on a green color. The precipitate was filtered, washed with CCl_4, and dried. The resulting white powder is soluble in CH_2Cl_2, $CHCl_3$, and acetone. It is very slightly soluble in CCl_4. It is insoluble in water and apparently unaffected by contact with the same substance for several hours; m.p. 161–163°. *Anal.* Calcd. for $MoCl_4 \cdot 4(C_6H_5)_3AsO$: Cl, 9.30; Mo, 6.29; C, 56.67; H, 3.96. Found (on several preparations): Cl, 9.42, 9.93, 9.45, 9.18; Mo, 6.24, 6.81, 6.68; C, 53.50; H, 3.81.

Attempted Preparations of Other $MoCl_4$ Complexes.—A CCl_4 solution of $(CH_3)_2SO$ instantly decolorized CCl_4 solutions of $MoCl_4$, but evaporation produced no identifiable product. When the procedure for preparing the complex was used with $(C_6H_5)_3PO$ substituted for $(C_6H_5)_3AsO$, the red color of $MoCl_4$ did not disappear instantly. After 5–10 sec. the color did fade, and a white flocculent precipitate appeared. We feel that the precipitate was the phosphine oxide analog of the arsine oxide complex; but it changed rapidly to a yellow color, and all that could be isolated from the solution was yellow-orange $MoO_2Cl_2 \cdot 2(C_6H_5)_3PO$.[1]

Physical Measurements.—Magnetic susceptibility determinations and infrared spectra were obtained as described previously.[1] Conductance measurements were made in purified nitrobenzene.

Results

Magnetic susceptibility determinations on three different preparations showed the complex to be diamagnetic. For one determination $\chi_m' = -276 \times 10^{-6}$ c.g.s. units, after all diamagnetic corrections were made.

Infrared spectra showed three peaks in the region of the uncomplexed As–O stretching frequency, taken as 878 $cm.^{-1}$.[4] The observed peaks were 900, 878, and 848 $cm.^{-1}$. The maximum shift in the As–O frequency is -30 $cm.^{-1}$. The splitting of the As–O peak has been noted before.[1,4]

Conductance measurements were made on one preparation only. The molar conductance of a 10^{-3} M solution was 5.2×10^{-3} $cm.^2$ ohm^{-1} $mole^{-1}$, indicating that it is essentially a non-electrolyte in nitrobenzene.

Discussion

Three anionic, octacoördinate Mo(IV) complexes have been reported previously,[5-7] Mo-

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