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The Reaction of $W_2Cl_9^{3-}$ with Alcohols

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When $[(n\text{-}C_4H_9)_4N]_3W_2Cl_9$ is heated with alcohols, yellow-green, diamagnetic $W_2Cl_4(OR)_2(ROH)_4$ ($R = CH_3$, C_2H_5, and $n\text{-}C_3H_7$) is obtained. The stoichiometry was confirmed from hydrogen evolution experiments using both $LiAlH_4$ and $LiAlD_4$. With the latter, mass spectroscopic analysis of the evolved gas indicated that half of the liberated hydrogen originated in the compound, proving that these reactions do not include reduction of the metal by $LiAlH_4$. All compounds were successfully related through alcohol-exchange reactions. The pmr and infrared spectra of the compounds are presented, but no definite conclusion concerning the nature of the bridging groups is obtained. The reactions of pyridine and DMSO with the ethoxoethanol compound have been shown to proceed with replacement of the bound alcohol only.

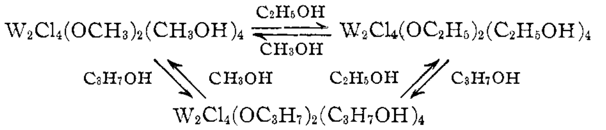
The reactions of $W_2Cl_9^{3-}$ have been of special interest,[1,2] particularly those which may exemplify effects fostered by the strong metal–metal bond.[3] Recently, in a study of the reactions of that anion with alkyl sulfides and phosphines using alcohol as the solvent, we discovered that considerable reaction between the solvent and the anion occurred. Subsequent studies in the absence of the sulfides and phosphines led to the isolation of $W_2Cl_4(OR)_2(ROH)_4$ ($R = CH_3$, C_2H_5, and $n\text{-}C_3H_7$). These products would be related by oxidative loss of hydrogen to $W_2Cl_4(OR)_6$, of which only the compound with $R = C_2H_5$ is known.[4] In addition, the electrolysis of solutions of WCl_6 in ethanol produces a substance which was originally formulated[5] as $W_2Cl_4(OC_2H_5)_6$, but subsequent studies[4] indicated that the oxidation state was less than +5. From the color, crystal form, and solubility, it would appear that this compound is $W_2Cl_4(OC_2H_5)_2(C_2H_5OH)_4$.

Experimental Section

Preparation of Compounds.—All compounds were prepared by refluxing in a nitrogen atmosphere 2.8 g of freshly recrystallized $[(n\text{-}C_4H_9)_4N]_3W_2Cl_9$ in 200 ml of the appropriate alcohol. In methanol and ethanol the reaction times were 10 and 20 min, respectively, while in 1-propanol about 1.5 hr was required. The green, diamagnetic crystals were then obtained by cooling the reaction solution. The relative insolubility of the methoxomethanol compound prevented recrystallization, but the remaining compounds were recrystallized from $CHCl_3$ by cooling a saturated solution in an ice bath. Yields were generally 50–75%. *Anal.* Calcd for $W_2Cl_4(OCH_3)_2(CH_3OH)_4$: C, 10.3; H, 3.2; W, 52.6; Cl, 20.3. Found: C, 10.2; H, 2.8; W, 52.3; Cl, 20.8. Calcd for $W_2Cl_4(OC_2H_5)_2(C_2H_5OH)_4$: C, 18.4; H, 4.4; W, 46.9; Cl, 18.1. Found: C, 18.4; H, 4.2; W, 46.9; Cl, 18.4. Calcd for $W_2Cl_4(OC_3H_7)_2(C_3H_7OH)_4$: W, 42.4; Cl, 16.4. Found: W, 42.6; Cl, 16.4. A molecular weight determination of $W_2Cl_4(OC_2H_5)_2(C_2H_5OH)_4$ in $CHCl_3$ (8.43×10^{-3} *M*) gave 735 which is to be compared to the theoretical value of 784. The mass spectrum gave a series of peaks which are presumed to belong to the parent ion in the region of 780–788 mass units.

$W_2Cl_4(OCH_3)_2(CH_3OH)_4$ is slightly soluble in $CHCl_3$ and insoluble in most other common solvents. $W_2Cl_4(OC_2H_5)_2(C_2H_5OH)_4$ is very soluble in $CHCl_3$ and CH_2Cl_2 and partially soluble in alcohols, benzene, tetrahydrofuran, CCl_4, and CS_2. This compound reacts with pyridine, DMSO, and CF_3COOH at room temperature to form brown, air-sensitive products. The solubility properties of $W_2Cl_4(OC_3H_7)_2(C_3H_7OH)_4$ were similar to those of the ethoxoethanol compound. All of the compounds were insoluble in water, relatively inert to acids and oxidizing agents, but readily attacked by bases leading to decomposition.

Alcohol-Exchange Reactions.—In these reactions 0.3 g of the compound was added to 40 ml of the alcohol and refluxed in a nitrogen atmosphere. The following reaction scheme was substantiated by a comparison of the infrared spectra of the products with spectra of authentic samples and in some cases by chloride analysis.



$$\begin{tikzcd}
\mathrm{W_2Cl_4(OCH_3)_2(CH_3OH)_4} \arrow[rr, shift left, "\mathrm{C_2H_5OH}"] \arrow[dr, shift right, "\mathrm{C_3H_7OH}"'] & & \mathrm{W_2Cl_4(OC_2H_5)_2(C_2H_5OH)_4} \arrow[ll, shift left, "\mathrm{CH_3OH}"] \arrow[dl, shift left, "\mathrm{C_3H_7OH}"] \\
& \mathrm{W_2Cl_4(OC_3H_7)_2(C_3H_7OH)_4} \arrow[ul, shift right, "\mathrm{CH_3OH}"'] \arrow[ur, shift left, "\mathrm{C_2H_5OH}"] &
\end{tikzcd}$$

It is noteworthy that, when 1-propanol and its corresponding anion were present either in the substrate or as the solvent, the reaction times were always 1–3 hr, while the remaining two interchanges were accomplished in less than 30 min.

Active Hydrogen Determination.—The apparatus and procedure were conventional, and only $W_2Cl_4(OC_2H_5)_2(C_2H_5OH)_4$ was examined. This compound has only limited solubility in more suitable solvents such as dibutyl ether, but it is fairly soluble in tetrahydrofuran. When the compound was added to solutions of either $LiAlH_4$ or $LiAlD_4$ in this solvent, an immediate evolution of gas occurred and was complete within 10–15 min. A brown, insoluble product and a clear solution resulted. In two determinations using $LiAlH_4$, 4.03 and 4.22 mol of H_2 were evolved per mole of compound. With $LiAlD_4$, similar results were obtained in three determinations. Samples were then withdrawn, passed through liquid nitrogen traps to remove the solvent, and then equilibrated over a white-hot tungsten filament for 20 min. The mass spectra of the resulting mixtures were then recorded, and the percentages of deuterium were calculated.[6] The results were 50, 49, and 49% in the three determinations.

Instrumentation.—The pmr spectra were recorded with a Varian HA-100 spectrometer, while the infrared spectra were obtained using a Perkin-Elmer Model 621 spectrometer. A Cary Model 14 spectrophotometer was used for all electronic spectra. Mass spectra were obtained with Consolidated Electrodynamics Corp. Model 21-620 and Associated Electrical Industries Model MS-9 mass spectrometers. Molecular weights were determined by osmometry with a Mechrolab Model 301-A instrument.

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(1) R. Saillant, J. L. Hayden, and R. A. D. Wentworth, *Inorg. Chem.*, **6**, 1497 (1967).

(2) J. L. Hayden and R. A. D. Wentworth, *J. Am. Chem. Soc.*, **90**, 5291 (1968).

(3) R. Saillant and R. A. D. Wentworth, *Inorg. Chem.*, **7**, 1606 (1968).

(4) O. J. Klejnot, *ibid.*, **4**, 1668 (1965).

(5) A. Fischer and L. Michiels, *Z. Anorg. Allgem. Chem.*, **81**, 102 (1913); A. Fischer, *ibid.*, **81**, 170 (1913).

(6) R. Maruca, J. D. Odom, and R. Schaeffer, *Inorg. Chem.*, **7**, 412 (1968).

Results and Discussion

Mass spectroscopic and osmometric data have indicated the dimeric nature of $W_2Cl_4(OC_2H_5)_2(C_2H_5OH)_4$, in accordance with the observed diamagnetism. However, the complexity of the mass spectrum due to the isotopic distributions of tungsten and chlorine precluded an accurate mass determination. Thus, it was possible that the preparative reaction did not yield a compound containing W(III) but rather proceeded according to

$$W_2Cl_9^{3-} + 6ROH \longrightarrow W_2Cl_4(OR)_4(ROH)_2 + 3Cl^- + 2HCl + H_2$$

in which the product formally contains W(IV) and differs only from the W(III) compound by two hydrogen atoms. The hydrogen analyses are not sufficient evidence to rule out this possibility. Attempts to determine the oxidation state of the metal atoms by quantitative methods involving standard oxidants were erratic. However, the reaction of the compound with $LiAlH_4$ proceeded with the liberation of 4 mol of H_2 per mole of compound. This observation alone will not suffice to determine experimentally the stoichiometry of the compound since two alternatives are possible

$$W_2Cl_4(OR)_2(ROH)_4 \xrightarrow{LiAlH_4} W_2Cl_4(OR)_6^{4-} + 4H_2 \qquad (1)$$

or

$$W_2Cl_4(OR)_4(ROH)_2 \xrightarrow{LiAlH_4} W_2Cl_4(OR)_6^{2-} + 2H_2$$
$$W_2Cl_4(OR)_6^{2-} \xrightarrow{LiAlH_4} W_2Cl_4(OR)_6^{6-} + 2H_2 \qquad (2)$$

In reaction 1, half of the liberated hydrogen would have originated in the compound, but in reactions 2, only one-fourth would have a similar origin. To distinguish between these alternatives, the reaction was repeated using $LiAlD_4$. The resulting gas mixture contained 50% of the heavier isotope and indicated that only reaction 1 was correct. Thus, the compound must formally contain W(III).

The electronic spectra (Table I) of the three compounds in $CHCl_3$ were almost identical; each showed a band in the region of 13,600 cm^{-1} ($\epsilon \sim 150$) and another around 23,500 cm^{-1} ($\epsilon \sim 3000$). This close similarity can only mean that all compounds formally contain W(III), a result which is substantiated by the interconversion of all compounds through alcohol-exchange reactions.

Table I

Electronic Spectra[a]

$W_2Cl_4(OR)_2(ROH)_4$	Band max × 10^{-3}, cm^{-1}
R = CH_3	13.62 (127), 23.6 (3580)
R = C_2H_5	13.60 (167), 23.5 (2980)
R = n-C_3H_7	13.55 (142), 23.5 (3360)

[a] All spectra were measured in $CHCl_3$. Molar extinction coefficients are given in parentheses.

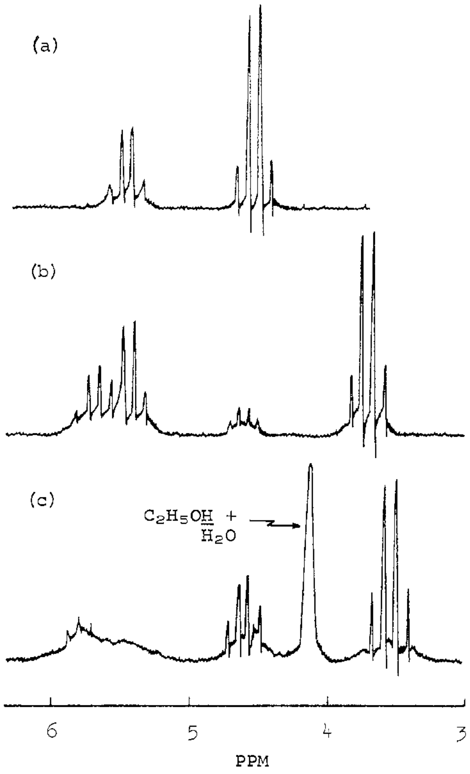

Figure 1.—Low-field portion of the pmr spectra (a) of $W_2Cl_4(OC_2H_5)_2(C_2H_5OH)_4$ and its reaction products (b) with pyridine-d_5 after 15 min and (c) with DMSO-d_6 after 15 min. All chemical shifts are relative to internal TMS.

The low-field portion of the pmr spectrum of $W_2Cl_4(OC_2H_5)_2(C_2H_5OH)_4$ is shown in Figure 1. The two quartets centered at δ 4.54 and 5.46 ppm (J = 7 cps for each) are in the ratio of 2:1. The set at higher field must then belong to the methylene protons of the bound alcohol. A complex set of lines due to the methyl protons is also found at δ 1.3 ppm. No resonance due to the hydroxyl protons could be found between δ 20 and -10 ppm. The infrared spectrum in polar and nonpolar solvents contains a broad band at 3350 cm^{-1} which arises from hydrogen bonding of the hydroxyl groups. Presumably, then, the lack of an observable signal in the pmr spectrum is the result of proton exchange occurring at a rate such that the resonance is broad and buried in the base line. The nature of the hydrogen bonding is not presently known. While the methoxomethanol compound was too insoluble to obtain a spectrum, the propoxopropanol compound exhibited a complex pattern centered at about δ 0.9 ppm due to the methyl protons, two overlapping sextets at δ 1.66 and 1.86 ppm (J = 7 cps for each), and two triplets at δ 4.48 and 5.22 ppm (J = 7 cps for each). Again, no resonance due to the hydroxyl protons was found.

The stoichiometries of the compounds as well as their relatively simple pmr spectra indicate the probability that at least one bridge bond of $W_2Cl_9^{3-}$ was broken during the substitution reaction to yield symmetric structures consisting of two octahedra sharing a common edge. However, either chlorine or oxygen (alkoxo) bridging is possible. The infrared spectrum of the ethoxoethanol compound in $CHCl_3$ contains bands at 867 (m, sh), 897 (vs), 1052 (m, sh), and 1086 (s) cm^{-1}. Using the assignments for $W_2Cl_4(OC_2H_5)_6$,[4] the bands in the neighborhood of 900 cm^{-1} would be due to W–O stretching modes, while those between 1000 and 1100 cm^{-1} would be due to C–O stretching vibrations. The latter are undoubtedly correctly assigned, but the bands at about 900 cm^{-1} must have some other origin since they are absent in the methoxomethanol compound. All three compounds possess a weak band at about 750 cm^{-1} which may be a W–O stretching frequency. Each of the compounds also has a band with shoulders at about 300 cm^{-1} which may be assigned as a W–Cl stretching frequency. However, $W_2Cl_9^{3-}$ also has a band with shoulders at ~290 cm^{-1}, while the compound which has been formulated as either $K_2W(OH)Cl_5$[7] or $K_4[W_2OCl_{10}]$[8] has a band with shoulders at 305 cm^{-1}. The shoulders are not clearly defined in any of these cases. Therefore, changes in the symmetry (and charge) do not seem to produce characteristic and well-defined changes in this band system in these compounds. Accordingly, in view of the number of possible structures involving bridging chlorine and terminal ethoxide and alcohol, as well as those involving terminal chlorine and alcohol and bridging ethoxide, we do not regard the infrared spectrum as sufficiently diagnostic to decide on the nature of the bridging groups. If bridging alkoxides are present, three bridge bonds of $W_2Cl_9^{3-}$ would be required to break, but the mechanism need not be any more complex than that recently postulated[2] to explain the conversion of $W_2Cl_9^{3-}$ to $W_2Br_9^{3-}$.

These compounds appear to be particularly reactive to nitrogen and oxygen donors. For example, they react readily with pyridine and DMSO at room temperature to form brown, air-sensitive compounds. The reactions of the ethoxoethanol compound in saturated solutions of deuteriochloroform with these reagents have been followed using pmr, and the results after 15 min are shown in Figure 1. With excess pyridine-d_5 the bound alcohol is replaced, resulting in appropriate shifts in the spectrum. Most obvious of these is the disappearance of the resonance at δ 4.54 ppm and the appearance of another quartet at δ 3.71 ppm, which corresponds to the unbound alcohol. Simultaneously, the resonance centered at δ 5.46 ppm splits into two quartets with intensities of approximately 2:1. This last observation can only mean that the replacement reaction results in a mixture of products. No further reaction was noted after an additional 15 min. The reaction with DMSO-d_6 proceeds similarly,[9] but with less resolution of the downfield signals. However, as unbound alcohol appears, the signal due to its hydroxyl proton becomes apparent, which was not the case in the reaction with pyridine. After correcting the intensity of the resonance at 4.09 ppm for a known quantity of water, which was unavoidably present in the DMSO and whose protons are exchanging rapidly with those of the hydroxyl group of the unbound alcohol, the intensity ratio of the methylene protons of the unbound alcohol to the hydroxyl protons was 2:1, as expected. The ratio of the total intensity of the methylene protons of the alcohol, both bound and free, to the intensity of the similar protons of the bound alkoxide remained 2:1. These observations ensure that the reasonance at δ 4.54 ppm in the ethoxoethanol compound is in fact due to bound alcohol. The stoichiometry of the compound, previously deduced from hydrogen evolution experiments, is then substantiated. The products of these and similar reactions are now receiving investigation.

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[7] E. König, *Inorg. Chem.*, **2**, 1238 (1963).

[8] R. Colton and G. G. Rose, *Australian J. Chem.*, **21**, 883 (1968).

[9] It is readily seen in Figure 1 that the chemical shifts of the methylene protons of the unbound alcohol are dependent upon the solvent. The downfield shift of 0.2 ppm in solution containing pyridine is not unexpected: P. V. Demarco, E. Farkas, D. Doddrell, B. L. Mylari, and E. Wenkert, *J. Am. Chem. Soc.*, **90**, 5480 (1968).