The very weak bands in the spectrum at 28.1 and 28.3 kK do not appear to change intensity much as the crystal ages. They may be due to some spin-forbidden process, but this cannot at present be further specified. Likewise the nature of the weak shoulders above 31 kK cannot at present be determined.

Registry No. K_2SnCl_6, 16923-42-5; K_2MnCl_6, 16923-41-4.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this project.

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Reactions of the $W(CO)_5Cl^-$ Anion with WCl_6

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Received December 28, 1972

The reaction of $W(CO)_5Cl^-$, WCl_6, and Cl^- was examined in CH_2Cl_2 solution with the hope that $W_2Cl_9{}^{3-}$ could be synthesized according to $W(CO)_5Cl^- + WCl_6 + 2Cl^- \rightarrow W_2Cl_9{}^{3-} + 5CO$. However, mixtures of other products were formed. Adjustment of the stoichiometry led to either $WCl_6{}^{2-}$ or $WCl_6{}^-$ depending on the $W(CO)_5Cl^-$:WCl_6 ratio. Polynuclear chlorotungstates, $W_2Cl_9{}^{2-}$ and $W_4Cl_{17}{}^{2-}$, along with $W(CO)_6$ and $WCl_4(CO)_2$ and/or $W(CO)_4Cl_3{}^-$, were formed only when Cl^- was not present initially. In tetrahydrofuran, however, $WCl_4(THF)_2$ and $W(CO)_4Cl_3{}^-$ were the products. The reaction of $W(CO)_6$ and WCl_6 was found to yield W_2Cl_9O.

Although polynuclear halometalates are generally formed by nature's wish rather than by man's design, we have recently attempted to develop a more rational synthesis of the $W_2Cl_9{}^{3-}$ anion. Originally prepared by the reduction of W(VI) in aqueous hydrochloric acid solution,[1] this anion has been synthesized according to several similar but modified procedures,[2,3] including one from this laboratory.[4] The reaction, which is by no means well understood, apparently proceeds by way of the one-electron reduction product $WOCl_5{}^{2-}$, followed by a two-electron reduction to $W_2Cl_9{}^{3-}$.[5] The involvement of $Cl_5WOWCl_5{}^{4-}$, recently proposed to be a W(III)-W(V) mixed-valence ion, has been discussed by Konig.[6,7]

An alternate route, which we hoped would lead rationally to the synthesis of this anion, uses the notion that WCl_6 can serve as an easily reduced tridentate ligand. The reducing agent, $W(CO)_5Cl^-$, was chosen because CO should be easily displaced under oxidative conditions. The planned reaction was then

$$W(CO)_5Cl^- + WCl_6 + 2Cl^- \rightarrow W_2Cl_9{}^{3-} + 5CO \qquad (1)$$

We envisioned that $W(CO)_5Cl^-$ would react with WCl_6 by stepwise facial displacement of CO, with concomitant electron transfer, to form a series of unstable intermediates that would terminate with $Cl_3WCl_3W(CO)_2Cl^-$. Displacement of CO from this anion should proceed smoothly due to the relatively high formal oxidation state of the tungsten atom to which this ligand is bound. Providing the solvent could not easily compete for these coordination sites, the reaction with Cl^- should lead to the desired product. However, the results of this experiment showed that man's design remained subservient to nature's wish.

Experimental Section

Reagents and Procedures. All solvents were of reagent grade quality and were dried prior to use by standard procedures. The alkylammonium halides were dried in a drying pistol over P_4O_{10} at 50°. Commercially available WCl_6 was purified by fractional sublimation (150°, 0.1 Torr) immediately before use. The method of Abel, *et al.*,[8] was used in the preparation of $[R_4N]W(CO)_5Cl$ (R = C_2H_5, n-C_3H_7, n-C_4H_9).

Reactions were performed in evacuated, greaseless glass vessels connected to a vacuum line. The general procedure in those reactions in which CO was evolved was to allow the reaction to proceed until gas evolution ceased. The reaction mixture was then frozen with liquid nitrogen and CO was removed for measurement through a series of traps by a Toepler pump.

Reactions of $[(C_4H_9)_4N]W(CO)_5Cl$, WCl_6, and $[(C_4H_9)_4N]Cl$. 1:2:5. The addition of 25 ml of a CH_2Cl_2 solution of $[(C_4H_9)_4N]W(CO)_5Cl$ (0.45 mmol) and $[(C_4H_9)_4N]Cl$ (2.24 mmol) to solid WCl_6 (0.90 mmol) caused a vigorous evolution of CO. At the end of 1 hr, gas evolution had ceased and 95% of the available CO had evolved. The electronic spectrum of this solution indicated that the only chromophoric species present in solution was $WCl_6{}^{2-}$ (1.3 mmol). An infrared spectrum of this solution indicated the absence of compounds containing CO. The product was isolated by adding ether until the yellow-green solution became cloudy and then cooling to −80°. The pastel green, microcrystalline solid was filtered off at −80° to prevent formation of an oil. After filtration, the solid was washed with the cold distillate from the mother liquor, allowed to warm to room temperature, and dried under vacuum. *Anal.* Calcd for $[(C_4H_9)_4N]_2WCl_6$: Cl, 24.2; W, 20.9. Found: Cl, 24.1; W, 21.4.

1:5:5. When $[(C_4H_9)_4N]W(CO)_5Cl$ (0.79 mmol) and $[(C_4H_9)_4N]Cl$ (3.92 mmol) in 25 ml of CH_2Cl_2 were added to solid WCl_6 (3.91 mmol), immediate evolution of CO occurred. Gas evolution appeared to cease after 15 min, but the solution was stirred for 1 additional hr to ensure complete reaction. At the end of that time, it was found that 96% of the available CO had evolved. One milliliter of solution was taken by syringe and diluted to 5 ml. The electronic spectrum indicated that the only chromophoric species present in solution was $WCl_6{}^-$. Large orange platelets of $[(C_4H_9)_4N]WCl_6$ were obtained by the addition of ether. The elemental analysis indicated a small quantity of some impurity. Recrystallization did not remove the

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(2) H. B. Jonassen, A. R. Tarsey, S. Cantor, and G. F. Helfrich, *Inorg. Syn.*, 5, 143 (1957).

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(5) J. J. Lingane and L. A. Small, *J. Amer. Chem. Soc.*, 71, 973 (1949).

(6) E. Konig, *Inorg. Chem.*, 2, 1238 (1963). Although Konig believed the ion to be $W(OH)Cl_5{}^{2-}$ at that time, he provides an excellent explanation of the observed color changes that occur during the reduction of W(VI) in strong hydrochloric acid solution. The ion was formulated correctly as $Cl_5WOWCl_5{}^{4-}$ by R. Colton and G. G. Rose, *Aust. J. Chem.*, 21, 883 (1968).

(7) E. Konig, *Inorg. Chem.*, 8, 1278 (1969).

(8) E. W. Abel, I. S. Butler, and J. E. Reid, *J. Chem. Soc.*, 2068 (1963).

contaminant, but a satisfactory analysis was obtained by exchanging the cation. A 0.2-g sample of the compound was added to a solution (20 ml) containing a considerable excess of $[(C_2H_5)_4N]Cl$. After reducing the volume of the solution and cooling, dark green crystals of $[(C_2H_5)_4N]WCl_6$ formed. *Anal.* Calcd for $[(C_2H_5)_4N]WCl_6$: Cl, 40.3; W, 35.0. Found: Cl, 40.3; W, 35.2.

Reactions of $[R_4N]W(CO)_5Cl$ and WCl_6. 1:1; $R = C_2H_5$. Tungsten hexachloride (2.88 mmol) was added to a solution of $[(C_2H_5)_4N]W(CO)_5Cl$ (2.87 mmol) in 50 ml of CH_2Cl_2. The reaction was allowed to proceed until CO evolution ceased (5.64 mmol after 36 hr). The solution was filtered into a 50-ml volumetric flask; then the violet solid which remained was washed with the distillate of the mother liquor until the cold washings were virtually colorless. The electronic spectrum of this substance and the elemental analysis indicated that it was $[(C_2H_5)_4N]_2W_2Cl_9$ (0.59 mmol). *Anal.* Calcd for $[(C_2H_5)_4N]_2W_2Cl_9$: Cl, 33.7. Found: Cl, 33.6. The volume of the filtrate was then adjusted to 50 ml. The infrared spectrum of this solution contained bands at 2058 and 1978 cm^{-1}, with the latter being the most intense. One milliliter of this solution was removed by syringe and evaporated under a stream of nitrogen. Sublimation of the residue at 40° led to the recovery of $W(CO)_6$, which was then redissolved in CH_2Cl_2. Quantitative infrared spectroscopy indicated that the yield, corrected to 50 ml, was 0.99 mmol. Another 0.5 ml of the stock solution was diluted to 25 ml with CH_2Cl_2 and examined in the visible region of the spectrum. Bands indicative of $W_4Cl_{17}^{2-}$ (see below) were found and the corrected yield was estimated to be 0.79 mmol.

1:1; $R = n\text{-}C_4H_9$. Freshly sublimed WCl_6 (1.86 mmol) was added to 20 ml of CH_2Cl_2 containing $[(n\text{-}C_4H_9)_4N]W(CO)_5Cl$ (1.85 mmol). After 48 hr, it was apparent that Co evolution had ceased with a total of 5.69 mmol being evolved. The solution was transferred to a 25-ml volumetric flask and diluted to the mark with CH_2Cl_2 which was added by distillation. An aliquot (0.5 ml) was removed by syringe and diluted to 25 ml. The electronic spectrum contained bands (with corresponding absorbancies) at 6000 (0.855), 6300 (sh), 9400 (0.727), and 10,500 (sh) Å. The infrared spectrum contained bands at 1978 (vs), 2008 (sh), and 2053 (w) cm^{-1}. The band at 1978 cm^{-1} was undoubtedly due to $W(CO)_6$, but the identity of all other species in solution was not determined. Attempts to cause crystallization resulted only in intractable oils.

1:2; $R = n\text{-}C_4H_9$. The reaction of $[(n\text{-}C_4H_9)_4N]W(CO)_5Cl$ (0.80 mmol) with WCl_6 (1.60 mmol) in 20 ml of CH_2Cl_2 proceeded with evolution of CO. After about 15 min, a yellow precipitate appeared, but this solid dissolved on continued stirring. A measurement after 36 hr indicated that 93% of the available CO had evolved. The reaction mixture was then filtered to give a dark solid and an emerald green solution. The solid was shown to be WCl_4 (0.78 mmol) from an X-ray powder pattern[9] and by analysis. *Anal.* Calcd for WCl_4: Cl, 43.5; W, 56.5. Found: Cl, 42.8; W, 56.9. Ether was allowed to diffuse into the filtrate which resulted in a mass of black acicular crystals. After filtration, the product was recrystallized from CH_2Cl_2 and ether to yield 0.36 mmol of $[(n\text{-}C_4H_9)_4N]_2W_4Cl_{17}$. *Anal.* Calcd for $[(n\text{-}C_4H_9)_4N]_2W_4Cl_{17}$: C, 21.1; H, 3.95; N, 1.54; Cl, 33.1; W, 40.4. Found: C, 21.4; H, 4.45; N, 1.66; Cl, 33.4; W, 39.7. An infrared spectrum of the mother liquor indicated that the only carbonyl compound present was $W(CO)_6$ (0.03 mmol). In a separate experiment, the yellow precipitate was shown to be $W(CO)_4Cl_2$ by its infrared spectrum[10] (KBr: 1939 (s), 1988 (s), 2014 (s) and 2100 (s) cm^{-1}) and by analysis. *Anal.* Calcd for $W(CO)_4Cl_2$: Cl, 19.3. Found: Cl, 18.8.

Reaction of $W(CO)_6$ and WCl_6. A flask was charged with $W(CO)_6$ (1.0 mmol) and WCl_6 (1.0 mmol), evacuated, and maintained at −80° while approximately 20 ml of CH_2Cl_2 was added by distillation. The reaction mixture was allowed to warm to ambient temperature. After a 24-hr period at that temperature only 1.75 mmol of CO had evolved. Filtration yielded a green, insoluble solid which was visibly contaminated with $W(CO)_6$. The latter was removed by several washings with the solvent distillate. The solid was shown to be W_2Cl_9O (0.42 mmol). *Anal.* Calcd for W_2Cl_9O: Cl, 45.4; W, 52.4. Found: Cl, 45.5; W, 52.3. The infrared spectrum (Nujol mull) contained a band centered at 892 cm^{-1} with a shoulder at 882 cm^{-1}. The contents of the filtrate were not examined.

Reaction of $[(n\text{-}C_4H_9)_4N]W(CO)_5Cl$ and WCl_6 in Tetrahydrofuran. Freshly sublimed WCl_6 (1.0 mmol) was added to a solution of $[(n\text{-}C_4H_9)_4N]W(CO)_5Cl$ (1.0 mmol) in 20 ml of dry THF. The reaction, which was complete within 4 hr, yielded 1.27 mmol of CO. The tan powder was filtered, washed with THF, and dried under vacuum. This product is apparently a solvate of $WCl_4(THF)_2$. *Anal.* Calcd for $WCl_4(C_4H_8O)_2 \cdot 0.14C_4H_8O$: Cl, 29.6; W, 38.4. Found: Cl, 29.6; W, 38.5. The mother liquor was evaporated and the residue was dissolved in $CHCl_3$. The infrared spectrum of this solution exhibited bands characteristic of $W(CO)_4Cl_2$ and/or $W(CO)_4Cl_3^-$.

Reaction of $[(n\text{-}C_4H_9)_4N]_4W_4Cl_{17}$ with Excess $[(n\text{-}C_4H_9)_4N]Cl$. A solution of $[(n\text{-}C_4H_9)_4N]W_4Cl_{17}$ (9.07×10^{-3} mmol) and $[(n\text{-}C_4H_9)_4N]Cl$ (8.10×10^{-2} mmol) in CH_2Cl_2 was prepared in a 25-ml volumetric flask which was connected by a side arm to a 1-cm cell. The spectrum of the resulting solution indicated the presence of only $W_2Cl_9^{2-}$ in 50.1% yield based on the total quantity of tungsten added. In an identical experiment, the yield was 50.8%.

X-Ray Data for $[(n\text{-}C_4H_9)_4N]W_4Cl_{17}$. A single crystal of this substance was sealed in a thin walled glass capillary. A series of precession photographs using Ni-filtered Cu Kα radiation indicated Laue symmetry $2/m$ showing that the crystal belongs to the monoclinic system. The systematic extinctions, $0k0$ for $k \neq 2n$, are consistent with either $C_2^{\,2}\text{-}P2_1$ or $C_{2h}^{\,2}\text{-}P2_1/m$ space groups. The cell dimensions were determined by least-squares refinement of 12 independent reflections obtained on a Picker FACS-I diffractometer. The dimensions were $a = 27.782$ (4) Å, $b = 11.387$ (6) Å, $c = 10.618$ (6) Å, and $\beta = 114.1$ (1)°. The volume of the unit cell is then 3066 Å^3. The observed density, measured by flotation in $CHBr_3$ and $n\text{-}C_7H_{16}$, was found to be 1.99 g/cm^3. The molecular weight, based on the experimentally determined values of the density and the unit cell volume as well as two formula units per unit cell, was found to be 1838. This value compares favorably to the theoretical value of 1824.

Discussion of Results

Mononuclear Products. The reaction between $[(n\text{-}C_4H_9)_4N]W(CO)_5Cl$ and WCl_6 in the presence of Cl^- (1:1:2 mole ratio) did not proceed according to eq 1; rather, only 2.74 mol of CO is formed per mole of $W(CO)_5Cl^-$ originally present and quantities of $W(CO)_6$, $W(CO)_4Cl_2$ and/or $W(CO)_4Cl_3^-$,[10] and WCl_6^{2-} were detected. There was no evidence for the formation of $W_2Cl_9^{3-}$ even when the reaction solution was refluxed for several days. The nature of the actual products was rationalized according to the set of equations

$$W(CO)_5Cl^- + WCl_6 + Cl^- \rightarrow W(CO)_4Cl_2 + WCl_6^{2-} + CO \qquad (2)$$

$$W(CO)_4Cl_2 + WCl_6 + 4Cl^- \rightarrow 2WCl_6^{2-} + 4CO \qquad (3)$$

$$W(CO)_4Cl_2 + Cl^- \rightarrow W(CO)_4Cl_3^- \qquad (4)$$

$$W(CO)_5Cl^- + CO \rightarrow W(CO)_6 + Cl^- \qquad (5)$$

where reactions 4 and 5 have been known for some time.[10,11] Reactions 2 and 3 suggest that total conversion to WCl_6^{2-} could be accomplished according to

$$W(CO)_5Cl^- + 2WCl_6 + 5Cl^- \rightarrow 3WCl_6^{2-} + 5CO$$

Indeed, virtually quantitative yields of the products were obtained when the reactants were present in this stoichiometry. By increasing the relative quantity of WCl_6, it was also possible to allow a third oxidation–reduction to occur

$$WCl_6^{2-} + WCl_6 \rightarrow 2WCl_6^-$$

so that the complete reaction becomes

$$W(CO)_5Cl^- + 5WCl_6 + 5Cl^- \rightarrow 6WCl_6^- + 5CO$$

Near-quantitative yields of the products were obtained when the reactants were present in this stoichiometry.

The properties of alkylammonium salts of WCl_6^- and WCl_6^{2-} are given in Table I. The electronic spectra of solutions of $[R_4N]WCl_6$ ($R = C_2H_5$ and $n\text{-}C_4H_9$) have a common absorption band at 15,400 cm^{-1}; however, the colors of the crystalline compounds are very different. The compound is

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[9] R. E. McCarley and T. M. Brown, *Inorg. Chem.*, 3, 1232 (1964).

[10] J. A. Bowden and R. Colton, *Aust. J. Chem.*, 21, 2657 (1968). The infrared spectra of $W(CO)_4Cl_2$ and $W(CO)_4Cl_3^-$ are virtually identical, but these species are, of course, distinguishable through elemental analyses.

[11] J. A. Bowden and R. Colton, *Aust. J. Chem.*, 24, 881 (1971).

Table I. Properties of Compounds

Compd	Color	μ_{eff} (298°K)	ν,[a] cm^{-1}
$[(C_2H_5)_4N]WCl_6$	Dark green	0.64[b]	15,400 (4)
$[(n\text{-}C_4H_9]_4N]_2WCl_6$	Pastel green	1.39	29,400 (600), 25,000 (22), 15,400 (7), 12,730 (7)
$[(C_2H_5)_4N]_2W_2Cl_9$	Violet	1.87[c]	17,200, 13,500[d]
$[(n\text{-}C_4H_9)_4N]_2W_4Cl_{17}$	Black	1.95	18,670 sh (860), 15,390 (1560), 11,100 (1080), 9570 sh (810)

[a] All spectra were recorded using CH_2Cl_2 solutions. Extinction coefficients are given in parentheses. [b] Taken from ref 12. [c] Taken from ref 17 for $[(n\text{-}C_4H_9)_4N]_2W_2Cl_9$. [d] Saturated solution.

dark green with $R = C_2H_5$ as previously reported,[12] but the corresponding compound with $R = n\text{-}C_4H_9$ is orange. When WCl_6 was refluxed in $SOCl_2$ in the presence of $[(n\text{-}C_4H_9)_4N]$-Cl, a general method for the preparation of $[R_4N]WCl_6$,[12,13] a compound completely identical with the orange compound reported herein was obtained. Furthermore it was possible to prepare dark green $[(C_2H_5)_4N]WCl_6$ by simple metathesis from the orange $[(n\text{-}C_4H_9)_4N]WCl_6$. Thus, the color difference must be ascribed to a lattice effect, probably involving a charge-transfer process between adjacent WCl_6^- ions when the cation is small, rather than a chemical difference. Abundant charge-transfer spectra have also been found with the alkali metal salts of WCl_6^-.[14]

Although complex spectra, probably involving charge transfer, have been previously reported for red Rb_2WCl_6,[15] the spectrum of $[(n\text{-}C_4H_9)_4N]_2WCl_6$ is fairly simple (Table I). The magnetic moment of 1.39 BM at room temperature is only slightly less than the range of 1.43-1.47 BM found[15] for the alkali metal salts of WCl_6^{2-}.

Polynuclear Products. When alkylammonium chloride was not added as a reactant,[16] polynuclear species were formed. If was found, however, that the nature of the products was a marked function of the nature of the alkylammonium cation as well as the solvent. When $[(C_2H_5)_4N]$-$W(CO)_5Cl$ and WCl_6 were present in equimolar concentrations in CH_2Cl_2, only 46% of the available CO was liberated. The other products consisted of $W(CO)_6$, an unidentified substance (ν_{CO} 2058 cm^{-1}), $W_2Cl_9^{2-}$ (which was previously obtained by the oxidation of $W_2Cl_9^{3-}$ with molecular halogens[17]), and $W_4Cl_{17}^{2-}$, a hitherto unknown ion. Changing the cation to $[(n\text{-}C_4H_9)_4N]^+$ but maintaining the same ratio of reactants and the same solvent resulted in 62% of the available CO being evolved and some $W(CO)_6$ being detected. One or two unidentified CO-containing compounds (ν_{CO} 2008 and 2053 cm^{-1}) were also present. The electronic spectrum appeared to point to $W_4Cl_{17}^{2-}$ along with an unidentified chromophore. It was very clear from this spectrum, however, that $W_2Cl_9^{2-}$ was absent. Since $[(C_2H_5)_4N]_2W_2Cl_9$ is virtually insoluble in CH_2Cl_2 while the corresponding $[(n\text{-}C_4H_9)_4N]^+$ salt is very soluble, it seems that the course of the reaction is altered by the precipitation of a key intermediate. The last reaction was also conducted in tetrahydrofuran, wherein vastly different products resulted. The *principal* reaction in that solvent appeared[18] to be

$$W(CO)_5Cl^- + WCl_6 \xrightarrow{THF} WCl_4(THF)_2 + W(CO)_4Cl_3^- + CO$$

but since the quantity of CO which was actually liberated slightly exceeds the amount predicted by this equation, still another unknown reaction must occur. Tan $WCl_4(THF)_2$ has been previously isolated in the reaction of WCl_6 with $Zn(CH_3)_2$ in tetrahydrofuran.[19]

When WCl_6 was initially present in twice the molar concentration of $[(n\text{-}C_4H_9)_4N]W(CO)_5Cl$ in CH_2Cl_2, 93% of the available CO was evolved and a trace of $W(CO)_6$ was isolated. In addition, WCl_4 and $W_4Cl_{17}^{2-}$ were formed in approximately a 2:1 mole ratio. No other products were found or even suggested by spectroscopy. Assuming that the ratio of products is exactly 2:1, electron and chlorine balance cannot be attained without also assuming that the solvent has also undergone some reaction which yields products which have not yet been isolated and identified. However, $[(n\text{-}C_4H_9)_4N]W_4Cl_{17}$ was easily isolated from this reaction, unlike the previous reaction in which the anion was observed by spectroscopy only. The analytical data were not sufficiently accurate to rule out alternate formulations: $[(n\text{-}C_4H_9)_4N]W_2Cl_9$ or $[(n\text{-}C_4H_9)_4N]_3W_6Cl_{26}$. The compound reacts with polar solvents, such as CH_3CN (to yield isolable $WCl_4(CH_3CN)_2$), CH_3NO_2, and $(CH_3)_2CO$, which precluded conductivity measurements. The molecular weight of the compound was determined by X-ray precession techniques. The observed molecular weight, based on the experimentally determined unit cell dimensions and density as well as two formula units per unit cell, was found to be 1838 which compares very well to the theoretical value of 1824 for $[(n\text{-}C_4H_9)_4N]W_4Cl_{17}$. This stoichiometry requires one unpaired electron in agreement with the observed magnetic moment of 1.95 BM per tetranuclear unit. The compound also reacts with excess Cl^- in CH_2Cl_2 to yield $W_2Cl_9^{2-}$, which was shown by spectroscopic techniques to contain 50% of the available tungsten. These observations suggest the reaction

$$W_4Cl_{17}^{2-} + 4Cl^- \rightarrow W_2Cl_9^{2-} + 2WCl_6^{2-}$$

Since the molar absorptivity of WCl_6^{2-} never exceeds 1/260 of that of $W_2Cl_9^{2-}$ across the entire range of the spectrum which was examined (below 20,000 cm^{-1}), the detection of WCl_6^{2-} was virtually impossible under the conditions of the experiment.

The ease with which $W_2Cl_9^{2-}$ is obtained from $W_4Cl_{17}^{2-}$ in this experiment suggests that the former is present as a bound entity in the latter. A comparison of the infrared spectrum of $W_2Cl_9^{2-}$ with that of $W_4Cl_{17}^{2-}$ (Table II) does not contradict this suggestion since all of the features in the former are also present in the latter although shifted to higher wave numbers by 20-30 cm^{-1}. A recent detailed analysis[20] of the spectrum of $W_2Cl_9^{3-}$ has assigned all the bands near 300 cm^{-1} as primarily terminal Cl-W stretching frequencies while the band near 210 cm^{-1} is due to a bridging Cl-W stretching frequency (see Table II). Extension of these assignments to $W_2Cl_9^{2-}$ would seem straightforward. Similarly, the bands near 350 cm^{-1} in the spec-

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[12] K. W. Bagnall, D. Brown, and J. G. H. du Preez, *J. Chem. Soc.*, 2603 (1964).

[13] D. M. Adams, J. Chatt, J. M. Davidson, and J. Gerratt, *J. Chem. Soc.*, 2189 (1963).

[14] R. N. Dickinson, S. E. Feil, E. N. Collier, W. W. Horner, S. M. Horner, and S. Y. Tyree, *Inorg. Chem.*, 3, 1600 (1964).

[15] C. D. Kennedy and R. D. Peacock, *J. Chem. Soc.*, 3392 (1963).

[16] However, reaction 5 remains as a source of Cl^-.

[17] R. Saillant and R. A. D. Wentworth, *J. Amer. Chem. Soc.*, 91, 2174 (1969).

[18] Although we have made no claims about distinguishing the infrared spectra of $W(CO)_4Cl_2$ and $W(CO)_4Cl_3^-$, the facile formation of $W(CO)_4Cl_3^-$ from $W(CO)_4Cl_2$ with stoichiometric quantities of Cl^- leads us to believe $W(CO)_4Cl_3^-$ is formed in this reaction.

[19] W. Grahlert and K. H. Thiele, *Z. Anorg. Allg. Chem.*, 383, 144 (1971).

[20] R. J. Ziegler and W. M. Risen, Jr., *Inorg. Chem.*, 11, 2796 (1972).

Table II. Tungsten-Chlorine Vibrational Spectra

Compd	ν,[a] cm^{-1}
$[(n\text{-}C_4H_9)_4N]_3W_2Cl_9$	311 s, 284 s, 268 s, 211 m
$[(n\text{-}C_4H_9)_4N]_2W_2Cl_9$	322 s, 310 s, 222 m
$[(n\text{-}C_4H_9)_4N]_2W_4Cl_{17}$	355 s, 338 s, 242 m
W_2Cl_9O	375 s, 356 s, 314 m, 250 m

[a] Nujol mulls.

trum of $W_4Cl_{17}^{2-}$ are assigned to terminal Cl-W stretching frequencies while the band at 242 cm^{-1} is a bridging Cl-W stretching frequency. Although a more complex spectrum was expected, it was not observed. The general increase in the values of the stretching frequencies is probably due to the general increase in the average oxidation state of the W atoms.

Efforts to prepare the $[(C_2H_5)_4N]^+$ and $[(n\text{-}C_3H_7)_4N]^+$ salts resulted in crystalline substances in which Cl:W = 4.25 ± 0.01 but with absolute analytical results which were slightly low. These results were initially ascribed to ether of crystallization since that solvent had been used to cause crystallization of these compounds from CH_2Cl_2 solutions. However, the infrared spectra did not indicate the presence of ether nor was it found by mass spectroscopy after heating the compounds under vacuum.

When $W(CO)_6$ and WCl_6 were present initially in equimolar concentrations in CH_2Cl_2, green, insoluble W_2Cl_9O was recovered. Oxygen abstraction from metal carbonyls is relatively well known,[21] although in many cases only the fragment containing carbon has been isolated.[22] The fate of that fragment in this reaction is, however, unknown. The insolubility of W_2Cl_9O readily distinguishes it from a fortuitous equimolar mixture of WCl_5 and $WOCl_4$ since the latter are soluble in CH_2Cl_2. This insolubility as well as the low magnetic moment of W_2Cl_9O (1.26 BM per dinuclear unit at room temperature) points to the likelihood that this compound exists as an extended chain throughout the lattice. The infrared spectrum contains a strong band at 892 cm^{-1} with a shoulder at 882 cm^{-1}, which is remarkably similar to the spectrum of $WOCl_4$.[23] The latter has bands at 894 and 878 cm^{-1} and a structure which consists of $WOCl_4$ units linked by oxygen atoms.[24] A weak but sharp band also appears at 1000 cm^{-1} in the spectrum of W_2Cl_9O, which is probably a terminal W-O stretching frequency. Bridging Cl is also indicated from the absorption at 250 cm^{-1} (Table II). Hence, W_2Cl_9O would appear to have a disordered structure in which the oxygen atoms are found in either bridging or terminal positions.

Conclusions

The presence of either free Cl^- or a donor solvent (tetrahydrofuran) has been found to interfere with the formation of reduced polynuclear chlorotungstates in the reactions of $W(CO)_5Cl^-$ and WCl_6. The nature of the products obtained from these reactions offers some area for speculation. The presence of $W(CO)_4Cl_2$ and/or $W(CO)_4Cl_3^-$ points to the possibility of the initial formation of a dinuclear intermediate, such as $Cl(CO)_4WCl_2WCl_4$. Symmetric cleavage of the bridging Cl bonds would lead to $W(CO)_4Cl_2$ while unsymmetric cleavage would lead to $W(CO)_4Cl_3^-$. Either product is also related to the other through reaction 4. The nature of the reactant causing the cleavage, as well as the fate of the other product, is unknown.. Further speculation would not seem to be warranted.

Registry No. $[(C_4H_9)_4N]W(CO)_5Cl$, 32424-54-7; WCl_6, 13283-01-7; $[(C_4H_9)_4N]Cl$, 1112-67-0; $[(C_4H_9)_4N]_2WCl_6$, 39981-28-7; $[(C_4H_9)_4N]WCl_6$, 39981-29-8; $[(C_2H_5)_4N]WCl_6$, 4009-42-1; $[(C_2H_5)_4N]W(CO)_5Cl$, 14780-97-3; $[(C_2H_5)_4N]_2W_2Cl_9$, 37359-90-3; $[(C_4H_9)_4N]_2W_4Cl_{17}$, 37359-92-5; $W(CO)_6$, 14040-11-0; W_2Cl_9O, 37359-94-7; $WCl_4(C_4H_8O)_2$, 34445-14-2; $[(C_4H_9)_4N]_2W_2Cl_9$, 12568-03-5; $[(C_4H_9)_4N]_3W_2Cl_9$, 39981-33-4.

Acknowledgment. This research was supported by the National Science Foundation under Grant GP-30544X.

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(21) See, for example, D. Curtis, *Inorg. Nucl. Chem. Lett.*, 6, 859 (1970).

(22) See, for example, M. R. Churchill and P. H. Bird, *J. Amer. Chem. Soc.*, 90, 800 (1968).

(23) D. M. Adams and R. G. Churchill, *J. Chem. Soc. A*, 2310 (1968).

(24) H. Hess and H. Hartung, *Z. Anorg. Allg. Chem.*, 344, 157 (1966).