by the transpiration method the dissociation pressures of a compound stated to be $UF_6 \cdot 3NaF$; the equation expressing their data

$$\log P_{\mathrm{mm}} = 10.88 - (5.09 \times 10^3)/T_{\mathrm{k}}$$

is plotted in Fig. 2 as a broken line. The large number of points from this work that fall close to the broken line indicate that the compound investigated by Cathers was also $UF_6 \cdot 2NaF$. The small but significant difference in slope between the two dissociation pressure lines for $UF_6 \cdot 2NaF$ may be due to intrinsic differences in the experimental methods used.

The enthalpy changes (kg. cal./mole of evolved gas) calculated from the lines obtained from the experimental data are -19.1 ± 0.2 for uranium hexafluoride (compared to -23.2 for Cathers' data), -18.2 ± 0.3 for tungsten hexafluoride, and -13.1 ± 0.8 for molybdenum hexafluoride.

Conclusion

The compounds $UF_6 \cdot 2NaF$, $WF_6 \cdot 2NaF$, and $MoF_6 \cdot 2NaF$ have been prepared by gas–solid reaction. These compounds are predictably stable according to coordination number calculations and the preparation of related compounds but their preparation by gas–solid reaction has thwarted previous investigators.

The successful preparation was due to the use of high-surface-area sodium fluoride made by treating ordinary sodium fluoride with hydrogen fluoride in excess of the amount required to produce $NaF \cdot 4HF$ at less than 50°, followed by rapid removal of the hydrogen fluoride by pumping, and finally by heating with pumping. Also, sorption, in some cases, was very sensitive to temperature.

For a number of preparations the data suggest that the $UF_6 \cdot 2NaF$, $WF_6 \cdot 2NaF$, and $MoF_6 \cdot 2NaF$ were mixed on the average with 0.01, 0.11, and 0.24 mole, respectively, of unreacted sodium fluoride. No intermediate compounds between NaF and $MF_6 \cdot 2NaF$ were found, although previous investigators have reported intermediate compounds such as $UF_6 \cdot 3NaF$.

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Hexachlorotungstate(V) Compounds

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The alkali metal hexachlorotungstate(V) salts, $MWCl_6$, have been synthesized, where M = Na, K, Rb, and Cs. The potassium salt has been synthesized by three independent routes: (i) reaction of WCl_6 with KI at 125°, (ii) reaction of WCl_6 with K_2WCl_6 at room temperature, and (iii) reaction of $K_2WO_4 \cdot WO_3$ with CCl_4 in a sealed tube at 400°. The salts are green and can be converted into the red M_2WCl_6 salts by heating under vacuum at 280–300°. Tetraphenylarsonium hexachlorotungstate(V) has been prepared by reaction of tetraphenylarsonium chloride with tungsten(V) chloride in chlorobenzene. Magnetic susceptibilities and visible and ultraviolet spectra are reported.

Introduction

As part of a long-range program involving weak field, octahedral d^1 complexes,[1,2] we became interested in the syntheses of salts of the WCl_6^- ion. Coincidentally with our first isolation of $KWCl_6$, an article appeared by Kennedy and Peacock[3] reporting the preparation of a series of WCl_6^{2-} compounds. Since the preparative method was similar to the one we had found successful for WCl_6^- salts, we decided to undertake an investigation of the relationship between the quadrivalent and quinquevalent hexachlorotungstate compounds.

Experimental

Starting Materials.—The metal iodides used were commercially obtained reagent grade materials. NaI and KI were dried under vacuum at 110° just before use. CsI and RbI were opened, handled, and stored in a drybox.

Tungsten(VI) chloride was prepared by the reaction of WO_3 with hexachloropropylene,[4] or, alternatively, by the reaction of WO_3 with CCl_4 in a bomb.[5,6] Some WCl_6 preparations were sublimed to check the purity of the preparation.

Tungsten(V) chloride was prepared by the reaction of red phosphorus with WCl_6.[7]

Preparation of Compounds.—*All manipulations were performed in a dry nitrogen atmosphere.*

Preparation of M^IWCl_6 Compounds.—$NaWCl_6$, $KWCl_6$, $RbWCl_6$, and $CsWCl_6$ were prepared by grinding the appropriate metal iodide with an equimolar quantity of WCl_6 until a finely divided, intimate mixture was obtained. Such a mixture was dark red in color, usually also stained with some free I_2 which

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[1] S. M. Horner and S. Y. Tyree, *Inorg. Chem.*, **2**, 568 (1963).

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had been released. The scale of the preparation varied from 1 to 10 g. The mixture was heated 3 days or longer in a sealed tube at temperatures ranging from 80 to 130°. The tube was placed in a furnace so that only the end containing the mixture was heated. Iodine sublimed to the cool portion of the tube. In some preparations, especially those involving Cs or Rb salts, it was necessary to remove the product, regrind it, and reheat it, sometimes more than once, to effect complete removal of free I_2 to the cool portion of the tube. When all I_2 had been removed, the tube was opened and the product ground to a fine green powder.

Alternatively, mixtures containing excess WCl_6 (up to a 2:1 mole ratio of WCl_6:MI) were prepared. After heating as usual in a tube, the excess WCl_6 was removed either by evacuation for several hours at approximately 100° or by Soxhlet extraction of the product with dry CCl_4.

Anal. for typical, different preparations. Calcd. for $NaWCl_6$: W, 43.82; Cl, 50.70. Found: W, 43.5, 43.1; Cl, 50.3, 50.8. Calcd. for $KWCl_6$: W, 42.19; Cl, 48.84. Found: W, 42.0, 41.8, 41.5; Cl, 48.2, 48.4, 48.2. Calcd. for $RbWCl_6$: W, 38.15; Cl, 44.12. Found: W, 37.1, 36.6, 38.1; Cl, 43.1, 42.0, 43.4. Calcd. for $CsWCl_6$: W, 34.72; Cl, 40.18; Cs, 25.10. Found: W, 33.9, 35.6, 35.2; Cl, 37.6, 38.5, 40.6; Cs, 24.1 (on the sample whose analyses are listed last).

The colors of the $MWCl_6$ salts ranged from green-black $NaWCl_6$ to medium green $CsWCl_6$. All are sensitive to moist air, turning red-purple and then blue, with $NaWCl_6$ decomposing instantly, while $CsWCl_6$ remains green for ~1 hr.

Preparation of $(C_6H_5)_4AsWCl_6$.—Approximately 1.4 g. of WCl_5 was combined with an equimolar quantity of $(C_6H_5)_4AsCl$ in a flask, to which 60 ml. of dry chlorobenzene was added. The mixture was stirred at room temperature for 6 hr. During the reaction a rust-brown precipitate formed under a red-brown solution. The precipitate was filtered, washed with chlorobenzene, and dried by evacuation for 17 hr. at room temperature. An 84% yield of the rust-brown, microcrystalline product was obtained; m.p. 253–256°.

Anal. for different preparations. Calcd. for $(C_6H_5)_4AsWCl_6$: C, 36.95; H, 2.58; W, 23.58; Cl, 27.28. Found: C, 35.68; 35.60; H, 2.56, 2.68; W, 23.24, 23.16; Cl, 26.71, 26.97.

Tetraphenylarsonium hexachlorotungstate(V) is stable in moist air, soluble in CH_2Cl_2, $CHCl_3$, and acetone, and insoluble in CCl_4, benzene, and absolute ethanol.

Preparation of $KWCl_6$ by Bomb Reaction.[5,6,8]—Tungsten(VI) oxide and K_2CO_3 in slightly greater than a 2:1 mole ratio were fused in a platinum dish to produce $K_2WO_4 + WO_3$. The fusion product was finely ground, and approximately 4 g. was placed in a 100-ml. glass ampoule containing approximately 30 ml. of CCl_4. The ampoule was sealed and heated in a bomb to 400° for 4–6 hr. The ampoule was cooled and opened. The black solid product was crushed, and the small excess of WCl_6 formed was extracted with CCl_4 in a Soxhlet extraction apparatus. The CCl_4-insoluble portion was black, with a thin purple coating. The product was observed to be dark green when ground in a mortar.

Anal. Calcd. for $KWCl_6$: W, 42.19; Cl, 48.83. Found: W, 41.82; Cl, 48.70.

Other properties (magnetic moment, ultraviolet spectrum, X-ray powder patterns, etc.) of $KWCl_6$ prepared in this manner were identical with the properties of the products of the KI–WCl_6 method described above.

A longer reaction time (24 hr. at 400°) produced a purple product with analyses and magnetic moment indicating about 40% contamination with K_2WCl_6.

Preparation of $M^I{}_2WCl_6$ Compounds Reported by Peacock[3] from M^IWCl_6.—When green $CsWCl_6$ or $KWCl_6$ was heated under vacuum to 250–300° for many hours, WCl_6 was lost and the compound turned to a red-purple color. Longer heating times were required to effect this change for the Cs than for the K compound. Analyses and physical properties indicate that the red-purple products were identical with the compounds reported by Peacock.[3] When 1 mole of WCl_6 per mole of $MWCl_6$ had been lost, evolution of WCl_6 stopped, indicating that the substances are not simply series of solid solutions.

Anal. for different preparations. Calcd. for K_2WCl_6: W, 38.72; Cl, 44.81. Found: W, 39.0, 39.3; Cl, 45.8, 45.1. Calcd. for Cs_2WCl_6: W, 27.76; Cl, 32.12; Cs, 40.12. Found: W, 28.66, 27.97; Cl, 32.53; Cs, 38.59.

Heating $NaWCl_6$ under vacuum to 280° resulted in a dirty white product which was apparently chiefly NaCl.

Anal. Calcd. for NaCl: Cl, 60.6. Found: W, 10.4; Cl, 58.9. These results confirm Peacock's[3] findings that the attempted preparation of Na_2WCl_6 gave NaCl as a decomposition product.

Preparation of M^IWCl_6 from $M^I{}_2WCl_6$.—An interesting reversal of the reaction described above was found to occur. Prolonged grinding of WCl_6 with an equimolar quantity of K_2WCl_6 produced green $KWCl_6$ even at room temperature. X-Ray powder patterns and ultraviolet spectra confirmed the identity of the $KWCl_6$. Although some reaction took place between Cs_2WCl_6 and WCl_6 on grinding at room temperature, heating to 100° in a tube was necessary to produce the pure green product. The identity of $CsWCl_6$ produced in this manner was likewise confirmed by ultraviolet spectra and X-ray powder patterns. Grinding of an excess of WCl_6 with $CsWCl_6$, followed by Soxhlet extraction with CCl_4, likewise produced green $CsWCl_6$.

Analyses.—Tungsten was determined gravimetrically as WO_3 after hydrolysis of the compounds in dilute nitric acid solution. Chlorine was determined gravimetrically on the filtrate by precipitation as AgCl. Potassium and cesium were determined gravimetrically as perchlorates.

Carbon and hydrogen analyses were performed by Micro-Tech Laboratories, Skokie, Ill.

Spectra.—Ultraviolet, visible and infrared spectra were determined on the compounds in KCl pellets. The KCl used was fused and stored in a drybox until ground in a drybox with the sample. The resulting mixture was transferred to a pellet die and layered so that the resulting pellet was coated with a layer of pure KCl. The pellet was pressed, and the spectrum determined, using a Cary Model 14 recording spectrophotometer and a pellet holder described previously.[1] Similar but more dilute pellets were prepared for observation of the infrared spectra.

Magnetic Susceptibilities.—Magnetic susceptibilities were determined at 20° only, using a Gouy balance and a permanent magnet described previously.[9]

X-Ray Powder Patterns.—X-Ray powder patterns were determined for a large number of representative samples of the preparations using a 114.59-mm. Norelco powder camera and Cu Kα radiation.

Results and Discussion

The experimental results indicate that both MW^VCl_6 and $M_2W^{IV}Cl_6$ can be prepared, and that the following equilibrium exists.

$$\underset{\text{green}}{2MWCl_6} \overset{\Delta}{\rightleftharpoons} \underset{\text{red}}{M_2WCl_6} + WCl_6$$

Although mixtures of $MWCl_6$ and M_2WCl_6 can be obtained, $MWCl_6$ is not a fortuitous mixture of M_2WCl_6 and WCl_6. In reactions starting with excess WCl_6, exhaustive removal of the excess WCl_6 by evacuation at low temperatures (120°) or by CCl_4 extraction resulted in the pure product $MWCl_6$. (It should be noted that Soxhlet extraction gave a better product than did pumping off the WCl_6.) Only after heating to above 160° under vacuum did the green $MWCl_6$ begin

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(9) S. M. Horner and S. Y. Tyree, *Inorg. Chem.*, **1**, 122 (1962).

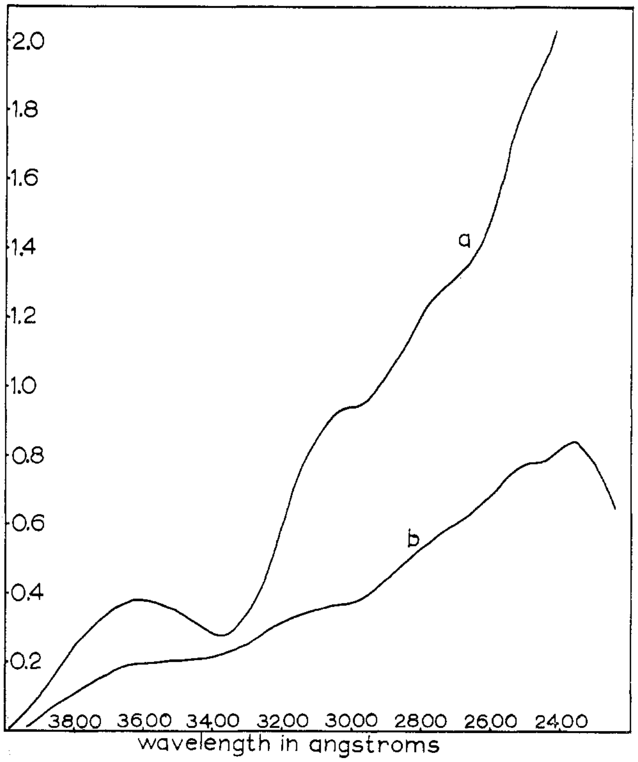

Fig. 1.—Absorbance *vs.* wave length for $MWCl_6$: a, concentrated pellet; b, dilute pellet.

to lose WCl_6 and turn red, and temperatures above 200° were required for complete conversion to M_2WCl_6.

The evidence of X-ray powder patterns confirms the above conclusions. All $MWCl_6$ compounds (M = alkali metal) have similar patterns, but different from those of the M_2WCl_6 compounds. Nor do the $MWCl_6$ patterns contain the M_2WCl_6 pattern superimposed upon other lines. Powder patterns indicate that the $MWCl_6$ compounds all have the same structure, but obviously a more complex one than that of the cubic M_2WCl_6 structures. The patterns of all M_2WCl_6 compounds prepared by us are similar to one another, and apparently a rather simple structure. Also, the pattern of our Cs_2WCl_6 can be indexed perfectly using Peacock's[3] value of a_0 = 10.27 Å., rendering certain the identity of our M_2WCl_6 compounds with his.

The ease of formation of $MWCl_6$ from $M_2WCl_6 + WCl_6$ appears to decrease from potassium to cesium. Complete reaction apparently occurred when K_2WCl_6 was ground for 15–20 min. with an equimolar amount of WCl_6 at room temperature. The cesium salt did not appear to react so readily. It has been pointed out in the Experimental section that the same trend was observed in the formation of $MWCl_6$ from $MI + WCl_6$, the sodium and potassium compounds releasing I_2 upon grinding at room temperature, while the rubidium and cesium compounds required prolonged heating and regrinding. Following the same trend, $KWCl_6$ evolved WCl_6 to form K_2WCl_6 at a lower temperature and in a shorter reaction time than for the corresponding reaction of the cesium salt.

It was observed that upon exposure to moisture, the $MWCl_6$ compounds turned to a red-purple color. Only in the case of the cesium salt was the red product stable enough to investigate, the others progressing on to yield tungsten blue. A sample of green $CsWCl_6$ was stirred with air-free H_2O, immediately producing an insoluble red-purple compound. The red solid was isolated, and its X-ray powder pattern was found to be identical with that of Cs_2WCl_6. No OH stretching frequency was observed in the infrared spectrum of the product. The evidence suggests that a disproportionation reaction is the first step in the decomposition of $MWCl_6$ compounds.

The infrared spectrum (down to 650 cm.$^{-1}$) of all compounds prepared except $(C_6H_5)_4AsWCl_6$ was essentially blank. No O–H or W═O stretching frequencies were observed except in cases where partial decomposition took place while the spectrum was being run.

The magnetic moments of the WCl_6^- compounds were severely depressed, as Peacock[3] observed for the WCl_6^{2-} compounds. Values are tabulated in Table I. Since the variation of μ_{eff} for different preparations is significant, all values are given.

TABLE I

Compound	μ_{eff} (20°)
$NaWCl_6$	0.88
$KWCl_6$	1.02
	0.86[a]
$RbWCl_6$	0.88
	0.94
$CsWCl_6$	1.17
	1.00
	0.87[b]
	1.10
$(C_6H_5)_4AsWCl_5$	1.21

[a] Bomb preparation. [b] Low Cl^- analyses.

It should be pointed out that μ_{eff} values for M_2WCl_6 compounds prepared from our $MWCl_6$ compounds checked closely with values reported by Peacock.[3] A value of 1.44 B.M. was obtained for K_2WCl_6, and of 1.47 B.M. for Cs_2WCl_6.

The ultraviolet spectra of all our $MWCl_6$ compounds were very similar. The positions of observed peaks were: 2340, 2550 (sh), 2800 (sh), 3050 (sh), 3150, 3650 Å. Two such spectra are shown in Fig. 1. The upper curve is for a much more concentrated pellet than the lower one. In fact, it is necessary to run at least two concentrations in order to see all of the peaks and shoulders. For example, in concentrated pellets the 2340 Å. peak cannot be seen at all, it is so strong. On the other hand, the 3650 Å. peak can be resolved only in a concentrated pellet, it is so weak. Most certainly the latter band is very much the weakest in the spectra. Unfortunately, the ordinate scale of absorbance is arbitrary and we regret our inability to estimate extinction coefficients. All band positions except the one at 3650 Å. correspond closely, with only slight shifts, to those of Peacock's[3] M_2WCl_6 compounds. For the W(V) d^1 ion in an octahedral field, one single d–d transition should be observed, corresponding to $^2T_{2g} \rightarrow {}^2E_g$. It seems likely that the lowest energy transition we observed, at 3650 Å. or 27,400 cm.$^{-1}$, can be assigned to this transition. Since this band is the only one not having a counterpart in the WCl_6^{2-} compounds, the remaining bands are probably charge-transfer bands, which should be quite similar for the WCl_6^- and WCl_6^{2-} compounds.

Two d–d bands should have been observed for the WCl_6^{2-} compounds, corresponding to the transitions $^3T_{1g} \rightarrow {}^3T_{2g}$ and $^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$. The value of approximately 19,000 cm.$^{-1}$ which we observed for our WCl_6^{2-} compounds is not unreasonable for the former transition, and the latter probably should be located at somewhat higher energies than the 27,400 cm.$^{-1}$ band observed in WCl_6^-. It is possible that the band at 3200 Å. reported by Peacock[3] corresponds to the $^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$ transition, or that the d–d transition is hidden under a charge-transfer band in the same region of the spectrum.

The band in the visible region in our M_2WCl_6 compounds appeared at 5200–5250 Å., as opposed to the position reported by Peacock[3] of 5500 Å. Also, he refers to the fact that $WCl_5(OH)^{2-}$ salts exhibit a band at 5100–5200 Å.[10] However, we feel confident that the M_2WCl_6 compounds prepared from $MWCl_6$ are not partially hydrolyzed, on the basis of analysis, of no O–H bands in the infrared, and of the identity of our powder patterns with those of Peacock's compounds.

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The Identification and Characterization by X-Ray Diffraction of a New Binuclear Molybdenum(VI) Oxalate Complex[1]

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The crystal and molecular structures of the compound $K_2\{[MoO_2(C_2O_4)(H_2O)]_2O\}$ have been determined by a three-dimensional, single crystal X-ray diffraction study. This compound had previously been formulated as a molybdenum(V) compound, having one less oxygen atom per dimeric anion. An explanation for the discrepancy in stoichiometry is suggested. The centrosymmetric complex anion contains two (distorted) octahedrally coordinated Mo(VI) atoms with a rigorously linear and symmetrical Mo–O–Mo bridge. The various Mo–O bond lengths and O–Mo–O bond angles vary considerably, but all of the variations appear to correlate very well with simple considerations of interatomic repulsions and Mo–O bond orders. The tendency of ligands coordinated *trans* to multiple Mo–O bonds to have abnormally long bonds to the metal is again observed. The Mo–O (terminal) bonds are 1.69 ± 0.02 Å. and the Mo–O (bridge) bonds are 1.876 ± 0.002 Å.

Introduction

Molybdenum in the V and VI oxidation states forms a considerable number of oxo complexes. Few of them have been unequivocally characterized structurally, but it is important to do so in many cases. It is especially important where it appears that the compound is a diamagnetic one containing Mo(V), for this necessarily means that the true molecular formula is some even multiple of the simplest one containing only one molybdenum atom. The point of particular interest in such compounds is the structural arrangement whereby the Mo(V) atoms succeed in pairing their electron spins so as to produce a diamagnetic compound.

The only X-ray structural investigation of a diamagnetic Mo(V) complex which appears to have been reported[2] deals with the diethyl xanthate compound, $[(C_2H_5OCS_2)_2MoO]_2O$, which is found to contain a linear Mo–O–Mo bridge; it was further shown that, by a simple molecular orbital treatment, pairing of the electron spins through this bridge should take place. Each Mo atom is surrounded by a distorted octahedron of ligand atoms.

The structures of two oxo–Mo(VI) complexes have also been reported. The compound diethylenetriaminetrioxomolybdenum(VI) has been shown to have a mononuclear, distorted *cis*-octahedral structure,[3] while the oxalato complex, $NaNH_4[MoO_3(C_2O_4)]\cdot 2H_2O$, has been reported[4] to consist of infinite Mo–O–Mo–O– chains with a distorted octahedron about each Mo atom provided by two oxo oxygen atoms and two oxygen atoms of a chelate oxalate ion. The Mo–O–Mo bridges are bent and unsymmetrical (Mo–O, 2.23, 1.87 Å.) while the two terminal Mo–O bonds are rather long (1.815, 1.850 Å.), in comparison with those in the other two compounds, *viz.*, 1.64 Å. in the xanthate compound and 1.73 Å. in the diethylenetriamine complex.

Another way in which two Mo(V) atoms might be

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(1) Supported by a grant from the National Institutes of Health.

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