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Highest Oxidation States

The Elusive Halides VCl_5, $MoCl_6$, and $ReCl_6$**

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It is common knowledge that fluorine can stabilize high oxidation states. Well-known examples include ReF_7 and PtF_6. Even more striking is the recent generation of HgF_4 in a neon matrix at 4 K.[1] Compounds such as AuF_6, PdF_5, and PdF_6 could also exist under matrix-isolation conditions. In contrast, the realm of high-valent metal chlorides is not only smaller than that of fluorides, it is fraught with reports that are either incorrect or highly questionable. This is certainly the situation with the three chlorides addressed in this work, VCl_5, $MoCl_6$, and $ReCl_6$.

VF_5 is a well-known compound. It is a strong oxidant, which suggests that VCl_5 might be unstable with respect to Cl_2 and the well-characterized liquid VCl_4, the highest known chloride of vanadium. Note that the homologous compounds $NbCl_5$ and $TaCl_5$ were prepared decades ago and are well-characterized. In 1969 and 1970, the reaction of $VOCl_3$ with PCl_5 was reported to produce "VCl_5" with an unbelievably high melting point of 260–265 °C.[2] It was quickly shown by others that the product was actually a mixture of $PCl_4^+VCl_5^-$ and $PCl_4^+VOCl_4^-$.[3]

We attempted to prepare VCl_5 by two different routes. The first was irradiation of a VCl_4/Cl_2 solution at low temperature, similar to the procedure reported for the synthesis of metastable $AsCl_5$.[4] However, upon irradiation, the orange color of the VCl_4/Cl_2 solution became black, and VCl_5 could not be detected spectroscopically: The Raman spectrum of the product exhibited only an extremely intense fluorescence background and the ^{51}V NMR spectrum showed no signals other than a trace amount of $VOCl_3$.

The second approach was the reaction of VF_5 with BCl_3 at −78 °C. The reaction mixture became dark violet and precipitated black crystals. The structure of VCl_5 is shown in Figure 1. It is a chloride-bridged dimer, similar to the structures of Re_2Cl_{10},[5] Nb_2Cl_{10},[6] Ta_2Cl_{10},[7] W_2Cl_{10},[8] and Sb_2Cl_{10}.[4] A Raman spectra could not be obtained, again because of an intense fluorescence background. However, a ^{51}V NMR spectrum recorded at low temperature exhibited a new resonance at $\delta = 984.6$ ppm ($\delta(VOCl_3) = 0$). The new compound vanadium pentachloride melts at −10 °C with decomposition. It is even less stable in solution and decomposes above −40 °C.

WCl_6 and UCl_6 are the only known binary hexachlorides. They are very stable, and melt without decomposition at 275 and 177.5 °C, respectively. In 1967, it was reported that small amounts of $MoCl_6$ could be prepared by refluxing H_2MoO_4 in $SOCl_2$ or by chlorinating molybdenum metal.[9] It was also reported that $MoCl_6$ could be sublimed. However, the only characterization reported was X-ray powder diffraction, and it is known that β-WCl_6[10] and β-$MoCl_4$[11] crystallize in the same space group type and have very similar lattice constants. In view of the facts that we could not reproduce these results, and that genuine $MoCl_6$ prepared in this work (see below) cannot be sublimed, it is likely that the microcrystalline product prepared in the 1967 work was β-$MoCl_4$. It is certainly possible that $SOCl_2$ could have acted as a reducing agent.

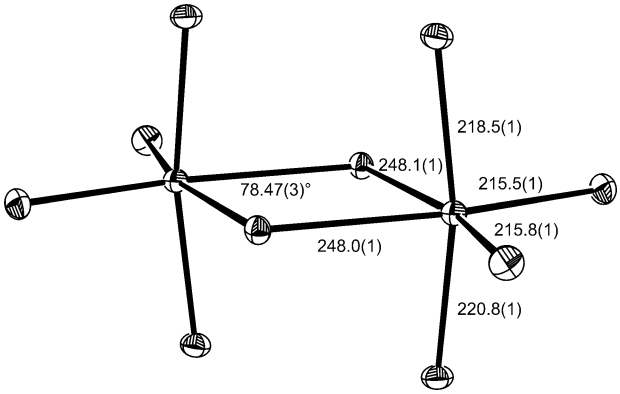

Figure 1. Structure of VCl_5 in the solid state, ORTEP representation, ellipsoids set at 50% probability. Bond lengths are given in pm.

We prepared $MoCl_6$ by reacting MoF_6 and BCl_3. The reaction is rapid at room temperature and very slow at −78 °C. At −25 °C shiny black hexagonal plates crystallized. The structure of $MoCl_6$, determined from diffraction data collected at −140 °C is shown in Figure 2. It is isostructural with β-WCl_6 and UCl_6, and like these two structures it is made up of rigorously octahedral $MoCl_6$ molecules. The unit cell contains two independent, nearly identical molecules. The

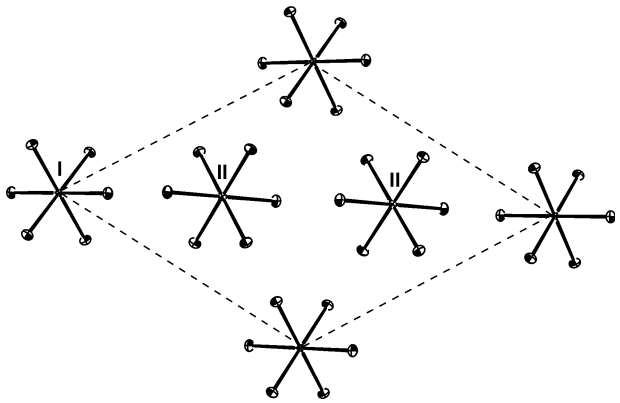

Figure 2. Structure of α-$MoCl_6$, viewed along 001. ORTEP representation, ellipsoids set at 50% probability.

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structures of all three hexachlorides are best described as hexagonal close-packed (HCP) lattices of Cl atoms with the metal atoms in one-third of the O_h holes. In this low-temperature phase of $MoCl_6$, there is always a 25% disorder of the molybdenum atoms within the hexagonal chlorine lattice. For comparison we have obtained the single-crystal structure of α- and β-WCl_6, as the previous structure determinations were carried out on powder data. Both modifications show no disorder.

The $MoCl_6$ crystallization is spontaneous during its formation, and there is no possibility for recrystallization owing to its insolubility at temperatures below 0 °C and its thermal instability at elevated temperatures.

When the single crystal used to collect the diffraction data at −140 °C was warmed to −10 °C, a single-crystal-to-single-crystal phase change occurred. When diffraction data of this new phase were collected again at −140 °C, the HCP lattice of Cl atoms is virtually unchanged. In this β-$MoCl_6$, the molybdenum atoms are now disordered over two positions at $z = 0$ and $z = 0.5$ in a 1:1 manner, while in α-$MoCl_6$ there is a 1:2 distribution at $z = 0$ and $z = 0.5$ (or 5:7, if the 75:25% disorder is taken into account). The interchange of the α- into the β-modification can be envisioned as a shift of the $MoCl_6$ columns along the z axis until complete disorder is achieved. The β-modification has very weak and diffuse reflection which can be fitted into the lattice if a and b are increased by a factor of four each. This superstructure could not be solved. Only when this problem is solved a reliable description for the interconversion between α-$MoCl_6$ and β-$MoCl_6$ might be possible.

Differential scanning calorimetry of samples of $MoCl_6$ revealed a transition at 100 °C that is not observed for samples of $MoCl_5$. Above 100 °C the DSC curves for $MoCl_6$ and $MoCl_5$ are identical. We conclude that solid $MoCl_6$ decomposes rapidly to $MoCl_5$ at about 100 °C. At room temperature, the decomposition of $MoCl_6$, with evolution of Cl_2, required several days.

The d^1 molecule $ReCl_6$, like ReF_6,[11] should exhibit a Jahn–Teller distortion. Calculated structural parameters for molecular $ReCl_6$ (Table 1) show deviations from O_h symmetry as in ReF_6, such as a compression along a fourfold axis, that are so small that they are unlikely to be observed in single-crystal structural determinations, and may, in any case, be dynamic. This is indeed the case for crystalline ReF_6.[18] The synthesis of $ReCl_6$ has been controversial. The first report, the reaction of rhenium metal with Cl_2 at 600 °C,[12] was later challenged by different groups.[13–16] More recently, it was reported that $ReCl_6^-$ can be electrochemically oxidized to $ReCl_6$.[17]

Table 1: Experimental[19] and calculated[20] bond lengths in $MoCl_6$ and $ReCl_6$, compared to WCl_6.

	M–Cl
α-$MoCl_6$, X-ray	230.4(9) molecule 1
	228.4(9), 231.8(9) molecule 2
β-$MoCl_6$, X-ray	231.1(1)
$MoCl_6$, MP2, calcd	232.3
$ReCl_6$, X-ray	226.3(6)
$ReCl_6$, MP2, calcd	230.6(2×)
	231.5(4×)
α-WCl_6, X-ray	227.5(3)
β-WCl_6, X-ray	228.5(1) molecule 1
	228.5(1), 228.6(1) molecule 2
WCl_6, MP2, calcd	231.8

The F/Cl exchange method which we used to prepare $MoCl_6$ in this work has been used by others to prepare $ReCl_6$,[12,13,15] but apparently only impure samples of the hexachloride were obtained. In this work, we reacted ReF_6 with BCl_3 very slowly at −25 °C, which resulted in the formation of shiny black hexagonal crystals. The structure of $ReCl_6$ is shown in Figure 2. It is isostructural with α-WCl_6. As in the case of crystalline $MoCl_6$, crystals of $ReCl_6$ were always twinned. The structure can be solved when the overlapping reflections were excluded from the refinement.

The crystallinity of $ReCl_6$, like with $MoCl_6$, cannot be improved by recrystallization, which is again due to its insolubility at temperatures below 0 °C and its thermal instability above this temperature.

As expected, molecules of $ReCl_6$ are octahedral to within the uncertainties. Distances are listed in Table 1. Like $MoCl_6$, samples of $ReCl_6$ decomposed to $ReCl_5$ during several days at room temperature with evolution of Cl_2.

Experimental Section

VCl_5: Boron trichloride (3 g, 25.6 mol) was condensed into a PFA tube (PFA = poly(perfluorovinyl ether-*co*-tetrafluoroethylene) at −196°, traces of Cl_2 and HCl were pumped off at −78 °C. VF_5 (300 mg, 2 mol) was condensed in at −196 °C. Warming to −60°C affords a dark violet solution, and slow cooling to −78°C gave black crystals, while much of the VCl_5 remained in solution. X-ray data at −140 °C: $a = 594.2(2)$, $b = 644.6(2)$, 879.2(2) pm, $\alpha = 108.94(1)$, $\beta = 90.95(1)$, $\gamma = 116.08(1)°$, $V = 279.0(2) \times 10^6$ pm^3. $Z = 2$, triclinic, $P\bar{1}$, $R_1 = 0.0309$, $wF_2 = 0.0983$. ^{51}V-NMR ($VOCl_3$), $\delta = 984.6$ ppm; cf. VF_5: $\delta = -802$ ppm.

$MoCl_6$, $ReCl_6$: BCl_3 (3 g, 25.6 mmol) and MoF_6 (300 mg, 1.43 mmol) or ReF_6 (300 mg, 1 mmol) were reacted as described above. Upon warming to −20 °C, the solution turned dark red in both cases. Within 2–3 hours, hexagonal black crystals of $MoCl_6$ were formed that after few more hours turned into black needles. The $ReCl_6$ crystallization requires 12–14 hours, giving hexagonal black plates. α-$MoCl_6$: X-ray data at −140 °C: $a = 1034.1(3)$, $c = 554.0(2)$ pm, $V = 513 \times 10^6$ pm^3, $Z = 3$, trigonal, $P\bar{3}m1$, $R_1 = 0.0383$, $wR_2 = 0.1209$. β-$MoCl_6$: X-ray data at −140 °C: $a = 596.4(1)$, $c = 553.9(1)$ pm, $V = 170.63 \times 10^6$ pm^3, $Z = 1$, hexagonal, $P6_3mcm$, $R_1 = 0.0193$, $wR_2 = 0.0413$. Raman (solid): $\tilde{\nu} = 403$ (10, A_{1g}), 175 cm^{-1} (4, T_{2g}). $ReCl_6$: X-ray data: $a = 597.5(2)$, $c = 1645.3(9)$ pm, $V = 508.7 \times 10^6$ pm^3, rhombohedral, $R\bar{3}$, $R_1 = 0.0282$, $wR_2 = 0.0489$. Raman (solid): $\tilde{\nu} = 404(10)$, 169(3) cm^{-1}.

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[19] Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD 425143 (α-$MoCl_6$), 425144 (β-$MoCl_6$), 425145 ($ReCl_6$), 425146 (VCl_5), 425147 (α-WCl_6), and 425148 (β-WCl_6).
[20] Basis sets used for the MP2 calculations: Mo: 8s7p6d[6s5p3d], core potential for 28 electrons, Re: 8s7p6d[6s5p3d], core potential for 60 electrons, Cl, V: 6-311 + g(d,p).

