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## Rhenium Trichloride Dioxide, ReO<sub>2</sub>Cl<sub>3</sub>\*\*

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Rhenium(VII) is widespread, for example, in  $\text{ReO}_4^-$  and  $\text{ReF}_7$ . Of the binary rhenium chlorides, the highest is  $\text{ReCl}_5$ ; a postulated  $\text{ReCl}_6$  was also revealed to be  $\text{ReCl}_5$ .<sup>[1,2]</sup> However, hexavalent rhenium is found in  $\text{ReOCl}_4$ .<sup>[3]</sup> The only known rhenium(VII)–chlorine compound is  $\text{ReO}_3$ Cl, which can be prepared in several ways and in large quantities.<sup>[4,5]</sup> A compound richer in chlorine would be  $\text{ReO}_2$ Cl<sub>3</sub>; interestingly, no examples of chloride oxides of composition  $\text{AO}_2$ Cl<sub>3</sub> (A = nonmetal or metal) have yet been reported. In contrast, several of the corresponding oxide fluorides  $\text{AO}_2$ F<sub>3</sub> (A = Cl, I, Re, Os, Tc) have been described.

In the 1930s, attempts were made to prepare ReO<sub>2</sub>Cl<sub>3</sub> (for example, through the reaction of rhenium with  $O_2$  and  $Cl_2^{[6]}$ ; however, they are now known to have been unsuccessful. The properties of the product obtained at that time are not consistent with those of ReO<sub>2</sub>Cl<sub>3</sub>, presented herein. We were also unable to confirm the results of a 1974 publication, in which the isolation of ReO<sub>2</sub>Cl<sub>3</sub> by vacuum sublimation from the reaction of ReO<sub>3</sub>Cl with ReOCl<sub>4</sub>, WOCl<sub>4</sub>, or MoOCl<sub>4</sub> was reported.<sup>[7]</sup> We attempted to reproduce the most promising reaction, that of ReO<sub>3</sub>Cl with WOCl<sub>4</sub>, and did indeed obtain a red-brown sublimate, as previously described. However, this product was unambiguously characterized as ReO<sub>3</sub>Cl·ReOCl<sub>4</sub> by single-crystal X-ray diffraction.<sup>[8,9]</sup> The reaction conditions, namely heating at 100 or 180 °C for several hours, are also inconsistent with the thermal properties of our ReO<sub>2</sub>Cl<sub>3</sub>, which decomposes at lower temperatures.

In attempts to produce a largely uncoordinated  $\text{ReO}_3^+$  ion by chloride-ion abstraction from  $\text{ReO}_3\text{Cl}$ , we treated  $\text{ReO}_3\text{Cl}$ with  $\text{AlCl}_3$  [Eq. (1)]. This reaction was already tried in 1979, but only the adduct  $\text{ReO}_3\text{Cl}\cdot\text{AlCl}_3$  was identified by elemental analysis at that time.<sup>[10]</sup> We observed a slow reaction at room temperature in CFCl<sub>3</sub>, with the formation of an orangecolored solution of  $\text{ReO}_2\text{Cl}_3$  ( $\text{ReO}_3\text{Cl}$  is colorless, and  $\text{AlCl}_3$  is nearly insoluble). At elevated temperatures,  $\text{ReOCl}_4$  is formed, as evidenced by the intense dark red color of the solution. Alternatively,  $\text{Re}_2\text{O}_7$  can be treated with  $\text{AlCl}_3$  to produce  $\text{ReO}_2\text{Cl}_3$  [Eq. (2)]. Moreover, the use of  $\text{BCl}_3$  instead of  $\text{AlCl}_3$  is advantageous, as the reaction proceeds homogenously without solvent, and  $\text{ReO}_2\text{Cl}_3$  can be recrystallized

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directly from the excess  $BCl_3$  [Eq. (3)]. The orange-colored product solutions contain  $ReO_2Cl_3$ , as well as small amounts of  $ReOCl_4$ . Purification can be accomplished by fractional crystallization.

$$\operatorname{ReO}_{3}\operatorname{Cl} + \operatorname{AlCl}_{3} \to \operatorname{ReO}_{2}\operatorname{Cl}_{3} + (\operatorname{AlOCl})_{x}$$
(1)

$$\operatorname{Re}_{2}O_{7} + 3\operatorname{AlCl}_{2} \rightarrow 2\operatorname{Re}O_{2}\operatorname{Cl}_{2} + 3(\operatorname{AlOCl})_{2}$$
(2)

$$\operatorname{ReO}_3\operatorname{Cl} + \operatorname{BCl}_3 \to \operatorname{ReO}_2\operatorname{Cl}_3 + (\operatorname{BOCl})_r$$
 (3)

The large orange crystals of  $\text{ReO}_2\text{Cl}_3$  are easily distinguished from the dark red needles of  $\text{ReOCl}_4$  and its adducts, and from the colorless platelets of  $\text{ReO}_3\text{Cl}$ . According to the single-crystal structure determination,  $\text{ReO}_2\text{Cl}_3$  is composed of cyclic chlorine-bridged { $\text{ReO}_2\text{Cl}_3$ } dimers with nearly perfect  $D_{2h}$  symmetry (Figure 1). The *cis* orientation of the



**Figure 1.** Molecular structure of ReO<sub>2</sub>Cl<sub>3</sub> (ORTEP representation, with thermal ellipsoids set at 50% probability). Selected interatomic distances [pm] and angles [°], along with their calculated values (italics), are indicated.

two double-bonded oxygen atoms at each rhenium center is typical for dioxo compounds of transition metals. Terminal chlorine atoms complete the (distorted) octahedral environments of the rhenium atoms. The melting point of 35-38 °C is reached without decomposition. Further heating results in decomposition and dark coloring. A congruent boiling point is not observed. Upon longer storage at room temperature, progressively more ReOCl<sub>4</sub> is formed.

The vibrational spectra of the solid are in accord with the  $D_{2h}$  molecular structure and, thus, with the mutual exclusion rule. The structure and vibrational spectra of ReO<sub>2</sub>Cl<sub>3</sub> can be reproduced well with a density functional theory (DFT) calculation.<sup>[11]</sup> If the calculated energy values are assumed to be similarly trustworthy, an energy of dimerization of  $\Delta H = -0.3 \text{ kcal mol}^{-1}$  is obtained for the equilibrium  $2 \operatorname{ReO}_2 \operatorname{Cl}_3(C_S) \rightleftharpoons \operatorname{Re}_2 \operatorname{O}_4 \operatorname{Cl}_6(D_{2h})$ . This low value indicates that the monomer could be observed as well. Indeed, the compound seems to be monomeric in CCl<sub>4</sub> or Cl<sub>2</sub> solutions, as the Raman spectra of dissolved ReO<sub>2</sub>Cl<sub>3</sub> are considerably different from that of the solid. The calculated structure of monomeric ReO<sub>2</sub>Cl<sub>3</sub> is trigonal bipyramidal, with the doublebonded oxygen atoms in equatorial positions (Scheme 1). A square-pyramidal structure, and a trigonal-bipyramidal structure with the double-bonded oxygen atoms in the axial



# Communications



**Scheme 1.** Calculated structures of monomeric  $\text{ReO}_2\text{Cl}_3$ . Selected interatomic distances [pm] and angles [°] are indicated.

positions are transition states with considerably higher energies.

In the presence of small amounts of water, the monohydrate  $ReO_2Cl_3$ ·H<sub>2</sub>O is formed (Figure 2). The ability to



**Figure 2.** Molecular structure of the hydrate  $\text{ReO}_2\text{Cl}_3 \cdot \text{H}_2\text{O}$  (ORTEP representation, with thermal ellipsoids set at 50% probability). Hydrogen atoms are in assumed positions. Selected interatomic distances [pm] are indicated.

form a detectable hydrate, in spite of hydrolytic sensitivity, is common to  $\text{ReO}_2\text{Cl}_3$  and  $\text{ReOCl}_4$ .<sup>[12]</sup> If the reaction temperature is too high, a large amount of  $\text{ReOCl}_4$  is produced as a byproduct, and the adduct  $\text{ReO}_2\text{Cl}_3\cdot\text{ReOCl}_4$  crystallizes. This adduct also contains a { $\text{ReO}_2\text{Cl}_3$ } dimer, in this case with slightly asymmetric chlorine bridges (Figure 3). Two { $\text{ReOCl}_4$ } molecules are coordinated by oxygen atoms from the dimer to form a { $\text{ReO}_3\text{Cl}\cdot\text{ReOCl}_4$ } tetramer.

A preference for a coordination number of 6 is often observed in oxide halides of the transition metals, especially in the oxide fluorides:  $\text{ReO}_2F_3$  exists as a fluorine-bridged



**Figure 3.** Molecular structure of the adduct  $\text{ReO}_2\text{Cl}_3$ ·ReOCl<sub>4</sub> (ORTEP representation, with thermal ellipsoids set at 50% probability). Selected interatomic distances [pm] and angles [ $^{\circ}$ ] are indicated.

polymer, and also as cyclic fluorine-bridged trimers and tetramers;<sup>[13,14]</sup> in ReO<sub>3</sub>F, the rhenium atoms reach a coordination number of 6 through oxygen and fluorine bridges.<sup>[14]</sup> It is anticipated that ReO<sub>2</sub>Cl<sub>3</sub> can be transformed into a ReO<sub>2</sub>Cl<sub>2</sub><sup>+</sup> cation and a *cis*-ReO<sub>2</sub>Cl<sub>4</sub><sup>-</sup> anion.

## **Experimental Section**

ReO<sub>2</sub>Cl<sub>3</sub>: a) ReO<sub>3</sub>Cl (1 mmol, 270 mg), prepared according to reference [4], was combined with excess AlCl<sub>3</sub> (10-15 mmol, 1.3-2 mg). Upon mixing, the color of the solution changed to orange. After 30 min, the components that are volatile at room temperature were transferred under dynamic vacuum into a trap at -196 °C. CFCl<sub>3</sub> (3 mL) was then condensed onto the mixture. By slowly cooling the solution to -78°C, large orange crystals of ReO<sub>2</sub>Cl<sub>3</sub> (ca. 100 mg, 31%) were obtained, which could be easily separated from unreacted ReO<sub>3</sub>Cl (colorless platelets) and ReOCl<sub>4</sub> (dark red needles). M.p. 35-38°C, with color change to red. Elemental analysis (%) found for ReO<sub>2</sub>Cl<sub>3</sub>: Cl 32.95; calcd: 32.74. b) Re<sub>2</sub>O<sub>7</sub> and AlCl<sub>3</sub> were mixed in the molar ratio 1:15 and shaken at room temperature. The product was isolated as described above, but with poorer yield and purity. c) ReO<sub>3</sub>Cl (0.55 mmol, 150 mg) and BCl<sub>3</sub> (256 mmol, 3 g; free of HCl) were condensed into a glass ampoule. The mixture was briefly warmed and mixed at room temperature. Slow cooling of the redgreen BCl<sub>3</sub> solution to -60°C afforded orange crystals of ReO<sub>2</sub>Cl<sub>3</sub> (175 mg, 97%). Longer reaction times and the presence of HCl led to the formation of ReOCl<sub>4</sub>, which crystallizes as red needles that are easily distinguished from ReO<sub>2</sub>Cl<sub>3</sub>.

IR (solid, NaCl, polyethylene):  $\tilde{\nu} = 964.1$  (m), 934.9 (s), 371 cm<sup>-1</sup> (s, br); calculated values:<sup>[11]</sup>  $\tilde{\nu} = 1013.6$  (228), 993.3 (206), 371.5 (125), 365.1 (9.6), 348.7 cm<sup>-1</sup> (1.6), and eight other absorptions in the range 278–76 cm<sup>-1</sup>. Raman (solid):  $\tilde{\nu} = 979$  (100), 948 (40), 385 (95), 357 (30), 283 (45), 261 (90), 255 (sh), 180 (sh), 164 (25), 123 (45), 105 (10), 82 cm<sup>-1</sup> (14); calculated values:  $\tilde{\nu} = 1016.5$  (136), 981.9 (76), 366.3 (24.4), 356.1 (0.7), 348.7 (27.2), 266 (24.5), 246.6 (5.4), 245.6 (0.1), 175.1 (0.14), 149.4 (9.7), 122.7 (4.5), 107.2 (2.1), 90.5 (1.1), 46.9 cm<sup>-1</sup> (0.26). Raman (Cl<sub>2</sub> solution):  $\tilde{\nu} = 1000$  (40, p), 950 (5, dp), 539, 546 (Cl<sub>2</sub>), 400 (100, p), 338 (20, p), 309 (10, dp), 264 (30, dp), 215 (2, dp), 195 (15, dp), 158 cm<sup>-1</sup> (30, p); calculated values:  $\tilde{\nu} = 1016.7$  (48.3, p), 982.2 (14.3, dp), 381.8 (20.8, p), 354.4 (0.0, dp), 321.1 (9.3, p), 292.5 (8.1, p), 272.7 (7.5, dp), 263.9 (9.1, dp), 213.2 (0.2, dp), 191 (1.7, dp), 145.7 (4.0, p), 36.5 cm<sup>-1</sup> (1.3, dp). MS: most abundant fragment at  $m/z = 308 [^{187} \text{Re}^{35} \text{Cl}_3 \text{O}]^+$ , as well as isotopomers of  $^{185/187} \text{Re}$  and  $^{35/37} \text{Cl}$ .

Crystal structures: crystals were mounted at -100 °C on a Smart CCD diffractometer; full spheres of data were collected, 1800 frames separated by  $\Delta \omega = 0.3^{\circ}$ ; the structures were solved and refined with the SHELX programs.<sup>[15]</sup> ReO<sub>2</sub>Cl<sub>3</sub>: orange crystal;  $2\theta_{max} = 61^{\circ}$ , 8385 measured, 822 independent reflections; a = 797.3(1), b = 813.2(1), c =774.1(1) pm, Pnnm, Z=4, R=0.014,  $wR_2=0.039$ . ReO<sub>2</sub>Cl<sub>3</sub>·H<sub>2</sub>O: brown needle;  $2\theta_{max} = 61.0^{\circ}$ , 3459 measured, 1657 independent reflections; a = 543.4(2), b = 616.9(2), c = 944.5 pm, a = 93.42(1),  $\beta = 104.39(1), \gamma = 98.0(1)^{\circ}, P\bar{1}, Z = 2, R = 0.067, wR_2 = 0.166.$  $\text{ReO}_2\text{Cl}_3\cdot\text{ReOCl}_4$ : black needle;  $2\theta_{\text{max}} = 83.6^\circ$ , 29579 measured, 7210 independent reflections; a = 615.7(1), b = 1087.7(1), c =1617.0(2) pm,  $\beta = 94.939(4)^{\circ}$ ,  $P2_1/n$ , Z = 4, R = 0.048,  $wR_2 = 0.097$ . 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-416056 (ReO<sub>2</sub>Cl<sub>3</sub>), CSD-416057 (ReO<sub>2</sub>Cl<sub>3</sub>·H<sub>2</sub>O), CSD-416053 (ReO<sub>2</sub>Cl<sub>3</sub>·ReOCl<sub>4</sub>), and CSD-416429 (ReO<sub>3</sub>Cl·ReOCl<sub>4</sub>, P1).

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