



## NOTE

### Novel Route for Preparation of Molybdenum Dioxydichloridehydrate

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(Received: 14 May 2010;

Accepted: 29 December 2010)

AJC-9438

The reaction of mixtures of selenium and iodine trichloride with molybdenum oxytetrachloride in a sealed evacuated glass ampoule placed in a horizontal tube furnace. After heating for 72 h at 140 °C the experiment resulted in the formation of luminous yellowish, moisture sensitive crystals that subliming at the colder parts of the glass ampoule. The XRD analysis of yellowish crystals showed that the crystal system is orthorhombic, lattice type primitive, space group *pmn2*. Lattice constants are  $a = 9.16 \text{ \AA}$ ,  $b = 3.92 \text{ \AA}$ ,  $c = 6.97 \text{ \AA}$ . The results were compared with the values of Inorganic Structure Data Base and it was found that yellowish crystals have certainly  $\text{MoO}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$  formula. The method of preparation is quite new and the product is pure and has excellent large shining crystals.

**Key Words:** Molybdenumoxytetrachloride, Iodinetrichloride, Transport agent, IR spectra.

Chalcogen trihalide cations can be synthesized by Lewis acid-base reaction between chalcogen-tetrahalides and halides or oxyhalides of metals as suitable halogenide acceptores. For example the reaction of  $\text{TeCl}_4$  with  $\text{MCl}_5$  ( $M = \text{Ta}, \text{Nb}, \text{Sb}$ ) yielded  $\text{TeCl}_3(\text{TaCl}_6)$ ,  $\text{TeCl}_3(\text{NbCl}_6)$  and  $\text{TeCl}_3(\text{SbCl}_6)$ <sup>1</sup>.  $\text{TeCl}_4$  reacted with  $\text{MoOCl}_3$  and then  $\text{TeCl}_3(\text{MoOCl}_4)$  was obtained<sup>2</sup>. Also, compounds such as  $(\text{TeCl}_3)_2(\text{MoCl}_6)$  and  $(\text{TeCl}_3)_3(\text{MoCl}_7)$  were obtained by reacting  $\text{TeCl}_4$  with  $\text{MoOCl}_4$  in 1:2 and 1:3 molar ratios respectively<sup>2,3</sup>. The reactions of  $\text{SeBr}_4$  with  $\text{AlBr}_3$ ,  $\text{TeI}_4$  with  $\text{AlI}_3$  and  $\text{TeBr}_4$  with  $\text{ZrBr}_4$  produced  $\text{SeBr}_3(\text{AlBr}_4)$ ,  $\text{TeI}_3(\text{AlI}_4)$  and  $\text{TeBr}_3(\text{Zr}_2\text{Br}_9)$ , respectively<sup>4,5</sup>. The reaction of  $\text{SeCl}_4$  with  $\text{MCl}_4$  ( $M = \text{Hf}, \text{Zr}, \text{Mo}$ ) obtained<sup>6,7</sup>  $(\text{SeCl}_3)_2(\text{HfCl}_6)$ ,  $(\text{SeCl}_3)_2(\text{ZrCl}_6)$  and  $(\text{SeCl}_3)_2(\text{MoCl}_6)$ .

Beck *et al.*<sup>8</sup> recently used another method in which mixtures of sulphur and  $\text{ICl}_3$  have been used instead of  $\text{SCl}_4$  in the reaction with  $\text{MoOCl}_4$  which resulted in  $\text{SCl}_3(\text{MoOCl}_4)$ . In a similar attempt to synthesis  $\text{SeCl}_3(\text{MoOCl}_4)$  from the reaction mixtures of selenium and  $\text{ICl}_3$  with  $\text{MoOCl}_4$  we have obtained yellowish crystals of  $\text{MoO}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$  and dark red oil with  $\text{Se}_2\text{Cl}_2$  formula and found that  $\text{ICl}_3$  acts as a transport agent in the chemical vapour transport reaction.

All the chemicals used were of analytical grade. The IR spectra were recorded on a Perkin-Elmer model 377 spectrometer using KBr pellets. Melting points were measured using an electrothermal Buchi 512 melting point apparatus. Molebdenum was determined by spectrophotometric method using an AA-670 Shimadzu atomic absorption-flame emission spectrophotometer.

$\text{MoOCl}_4$  and  $\text{ICl}_3$  were prepared separately according to a modified procedure<sup>9,10</sup>.

**Preparation of molybdenum dioxydichloridehydrate:** A glass ampoule of 25 cm length and inner diameter 1.5 cm were filled with 316 mg of  $\text{MoOCl}_4$ , 444 mg of  $\text{ICl}_3$  and 125 mg of selenium. The glass ampoule was evacuated and simultaneously sealed by heating with a burner flame. The glass ampoule was placed in horizontal electrically heated furnace. It was heated for 5 h at 140 °C. Then a temperature gradient of 140 °C to 100 °C with a rate of 0.01 °C/min was applied. After 2 days, near to the tip of the glass ampoule, there were sublimed large, big, yellow, shining crystals with a faint green tint.

**Crystal structure of molybdenum dioxydichloridehydrate:** Crystals were filled into glass capillary tube which closed by flame-sealing for X-ray crystallography. The X-ray diffraction analysis of yellowish crystals showed that the lattice constants were:  $a = 9.16 \text{ \AA}$ ,  $b = 3.92 \text{ \AA}$ ,  $c = 6.97 \text{ \AA}$ . Then this result was compared with the value of the inorganic structure data base and it was found that the yellowish crystals had certainly  $\text{MoO}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$  formula.

In an attempt for the preparation of the chalcogen trihalide cations from the reaction mixture of selenium and iodine trichloride with  $\text{MoOCl}_4$  instead of any compound with seleniumtrichloride cation, yellowish crystals of  $\text{MoO}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$  and dark red oil with  $\text{Se}_2\text{Cl}_2$  formula were obtained. The reaction path way can be as follow:



It is clear that at 140 °C at first some iodine trichloride dissociate to chlorine and iodine monochloride. Then selenium reacts with fresh chlorine and forms selenium(I)chloride. In this condition MoOCl<sub>4</sub> reacts with moisture water vapour molecules forming crystals of MoO<sub>2</sub>Cl<sub>2</sub>. Then MoO<sub>2</sub>Cl<sub>2</sub> absorbs vapour of water with the help of iodine trichloride as transporting agent and converts to yellowish crystalline compound of MoO<sub>2</sub>Cl<sub>2</sub>·H<sub>2</sub>O which are separated from the vapour phase in the cold side of the glass ampoule.

Huang *et al.*<sup>11</sup> have grown single crystals of RuS<sub>2</sub> by an oscillating chemical vapour transport using ICl<sub>3</sub>. In another experiment, in the reaction of MoOCl<sub>4</sub> with vapour of water without iodine trichloride with the previous conditions, the crystalline product of MoO<sub>2</sub>Cl<sub>2</sub>·H<sub>2</sub>O was not formed. This is a good proof for acceptance of iodine trichloride acts too as transport agent in our reaction.

MoO<sub>2</sub>Cl<sub>2</sub>·H<sub>2</sub>O was prepared by Schroeder and Schulz<sup>12</sup> from dry HCl gas passed over MoO<sub>3</sub> through a quartz tube at 600 °C, showed that had orthorhombic crystal system, lattice constants of a = 9.23 Å, b = 3.89 Å, c = 9.10 Å and space group *pmn*2<sub>1</sub>. The structure of MoO<sub>2</sub>Cl<sub>2</sub>·H<sub>2</sub>O are built up by chains of irregular octahedron around Mo atom with two chlorine atoms, one oxygen atom and one water molecule as terminal ligands and two bridging oxygen atoms (Fig. 1).

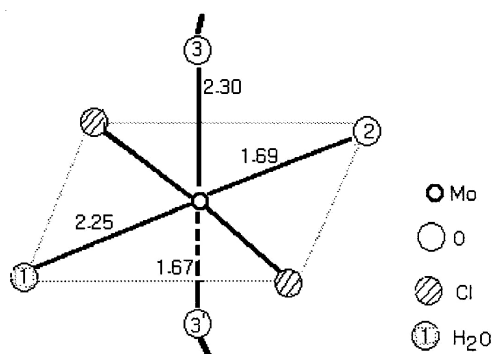


Fig. 1. Schematic presentation of the possibilities of positional distribution of Mo and its ligands in an isolated coordination octahedron in MoO<sub>2</sub>Cl<sub>2</sub>·H<sub>2</sub>O. The bond lengths are given in Å

Table-1 lists the frequencies and assignments of normal modes vibration and it is found that the present results highly correlate with those of Schroeder *et al.*<sup>13</sup>. As can be seen there is a strong band at 3447 cm<sup>-1</sup> which is due to stretching of ν(O···H). In comparison with the corresponding bands in ice which is 3150 cm<sup>-1</sup> frequency is increased to a bout 300 cm<sup>-1</sup>. Thus, it is shown that the hydrogen bonding in MoO<sub>2</sub>Cl<sub>2</sub>·H<sub>2</sub>O

is weaker than H<sub>2</sub>O. Considering the bond length of O···H···Cl (2.987 Å) in MoO<sub>2</sub>Cl<sub>2</sub>·H<sub>2</sub>O which is longer than that of O···H···O (2.987 Å) in ice, is another proof for the weaker hydrogen bonding in MoO<sub>2</sub>Cl<sub>2</sub>·H<sub>2</sub>O. Hydrogen bonding is carried out *via* chlorine atoms. In comparison with MoO<sub>2</sub>Cl<sub>2</sub> evidences, there is no vibration in the case of MoO<sub>2</sub>Cl<sub>2</sub>·H<sub>2</sub>O in the range of metal-oxygen bonds. The frequencies of symmetric and asymmetric vibration bridge O···Mo···O in MoO<sub>2</sub>Cl<sub>2</sub> observed in 867 and 789 cm<sup>-1</sup>, respectively. Besides there appears a strong band in 924 cm<sup>-1</sup> which is due to the isolated Mo···O bond.

TABLE-1  
IMPORTANT IR BANDS (cm<sup>-1</sup>) AND THEIR  
ASSIGNMENTS FOR MoO<sub>2</sub>Cl<sub>2</sub>·H<sub>2</sub>O

Frequencies (cm <sup>-1</sup> )	Assignments
3447 s,b	ν(O···H)
1626 s	δ(HOH)
963 s, 924 s	ν(Mo···O <sub>2</sub> )
762 m,b	ν(Mo···O <sub>3</sub> )
569 s	ν(Mo···OH <sub>2</sub> )
465 w	δ(O···Mo···O)
450 w	δ(O···Mo···Cl)

Regarding Fig. 1 the bands could be assigned as follows. The strong band at 1626 cm<sup>-1</sup> is assigned to the bending vibration of δ(HOH). The strong bands at 963 and 924 cm<sup>-1</sup> are assigned to the stretching vibration of ν(Mo···O<sub>2</sub>) and the other strong bond at 762 cm<sup>-1</sup> is concerned with ν(Mo···O<sub>3</sub>). The strong band at 569 cm<sup>-1</sup> is assigned to ν(Mo···OH<sub>2</sub>). The weak band at 465 cm<sup>-1</sup> is assigned to bending vibration of δ(O···Mo···O) and the other weak band at 450 cm<sup>-1</sup> is due to bending of δ(O···Mo···Cl).

#### ACKNOWLEDGEMENTS

The author thanks to Prof. Beck from University of Bonn for X-ray diffraction studies.

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