

Short Communication

## Crystal Structure of Na<sub>3</sub>MoCl<sub>6</sub>

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**Abstract:** The ternary chloride Na<sub>3</sub>MoCl<sub>6</sub> is obtained as red crystals from a disproportionation reaction of molybdenum dichloride, {Mo<sub>6</sub>}Cl<sub>12</sub>, in an acidic NaCl/AlCl<sub>3</sub> melt at 350 °C. The crystal structure (trigonal, *P*-31c, *a* = 687.1(1), *c* = 1225.3(2) pm, *Z* = 2, *V* = 501,0(1) 10<sup>6</sup> pm<sup>3</sup>) is that of Na<sub>3</sub>CrCl<sub>6</sub>: within a hexagonal closest-packing of chloride ions two thirds of the octahedral voids are filled between the AB double layers with Na<sup>+</sup>/Mo<sup>3+</sup>, and between the BA layers with Na<sup>+</sup>.

**Keywords:** molybdenum; chloride; sodium; synthesis; crystal structure

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### 1. Introduction

In their lower oxidation states, the early transition metals of the fourth and fifth periods tend to form metal clusters {M<sub>x</sub>} for two reasons. One, 4*d* and 5*d* orbitals are larger than 3*d* orbitals and are, thus, capable of forming metal-metal bonds. Two, the sublimation enthalpies of the metals are high; part of it is saved when metal clusters are retained. The virtually simple binary halide MoCl<sub>2</sub>, obtained by a synproportionation reaction, features a crystal structure [1,2] which contains octahedral molybdenum clusters {Mo<sub>6</sub>} which are surrounded by eight inner (i) and six outer (a) chloride ligands; four of the latter bridge to neighboring clusters producing a layer structure, according to the *Niggli* formulation, {Mo<sub>6</sub>}Cl<sub>8</sub><sup>i</sup>Cl<sub>2</sub><sup>a</sup>Cl<sub>4/2</sub><sup>a-a</sup>.



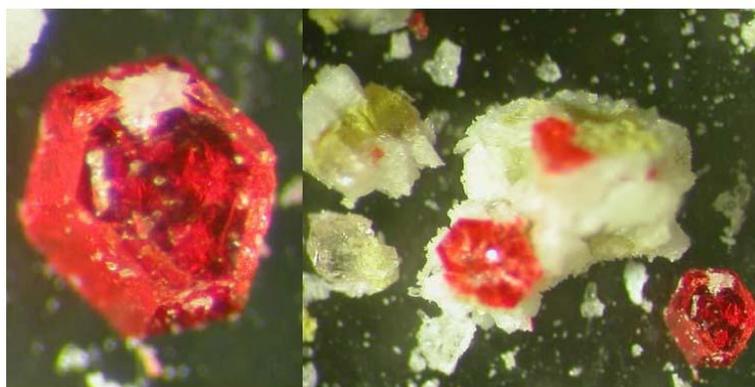
In attempts to synthesize ternary chlorides containing the  $[\{\text{Mo}_6\}\text{Cl}_{14}]^{2-}$  cluster-complex anion in a molten-salt system,  $\text{MoCl}_2$  faced a disproportionation reaction and red crystals of  $\text{Na}_3[\text{MoCl}_6]$  were obtained.

## 2. Results and Discussion

Red single crystals of  $\text{Na}_3\text{MoCl}_6$  were obtained from the attempted dissolution of  $\text{MoCl}_2 = \{\text{Mo}_6\}\text{Cl}_8\text{Cl}_2\text{Cl}^{a-a}_{4/2}$  in a  $\text{NaCl}/\text{AlCl}_3$  flux (45:55 mol%, close to the eutectic [3]) at 350 °C in a sealed Pyrex ampoule. In this melt the  $\{\text{Mo}_6\}$  cluster must have been disrupted during a disproportionation reaction, under the influence of the acidic flux. Hexagonal red crystals were embedded in essentially white crystalline material (Figure 1); some black powder (molybdenum) could also be recognized.



**Figure 1.** Red single crystals of  $\text{Na}_3\text{MoCl}_6$ .

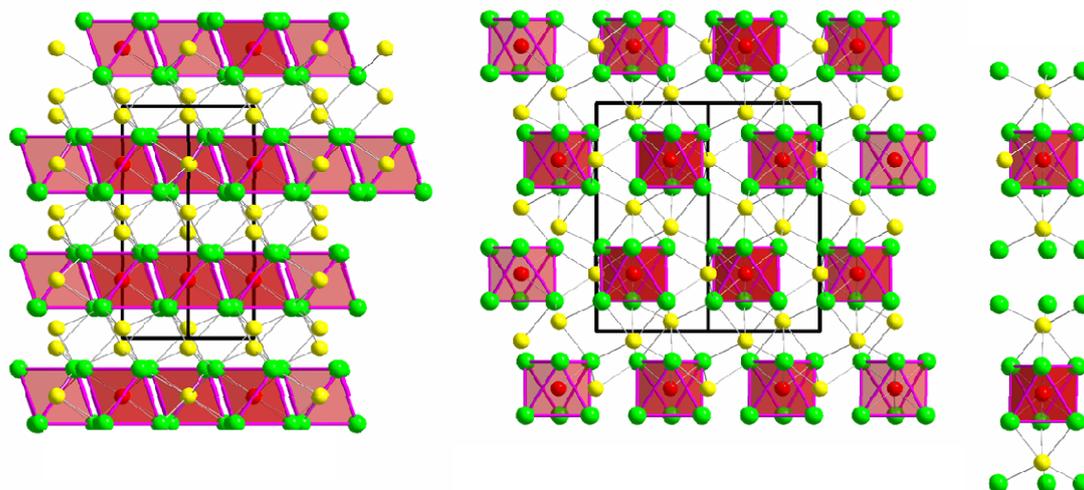


$\text{Na}_3\text{MoCl}_6$  crystallizes with the  $\text{Na}_3\text{CrCl}_6$  type of structure [4], trigonal, space group  $P\bar{3}1c$  (No. 163) with  $a = 687.1(1)$ ,  $c = 1225.3(2)$  pm,  $Z = 2$ . Previous data from powder diffraction,  $a = 692.0(8)$ ,  $c = 1222.2(5)$  pm, agree sufficiently well. It was also assumed that  $\text{Na}_3\text{MoCl}_6$  and  $\text{Na}_3\text{VCl}_6$  are isotypic with  $\text{Na}_3\text{CrCl}_6$  [4]. Other hints at the existence of  $\text{Na}_3\text{MoCl}_6$  are from preparative investigations or from phase diagram determinations where the crystal structure was apparently of no concern [5,6].

The structure of  $\text{Na}_3\text{MoCl}_6$  consists of hexagonally closest-packed layers of chloride anions,  $4\text{H}\dots\text{B} \mid \text{ABAB} \mid \text{A}\dots$ . Octahedral voids between these layers are filled in a way that half of them are filled between double layers BA by  $\text{Na}^+$  cations, and half of the voids are filled by  $\text{Na}^+$  and  $\text{Mo}^{3+}$  in an ordered fashion between double layers AB, see Figure 2. Thus, chains of face-sharing octahedra run parallel  $[001]$  and are filled with  $\text{Na}^+$ ,  $\text{Cr}^{3+}$ ,  $\text{Na}^+$ ,  $\square$ , where  $\square$  denominates a void. Neighboring chains are displaced by  $\frac{1}{2}c$  in the  $[001]$  direction. Therefore, the  $\text{Mo}^{3+}\text{--Mo}^{3+}$  distance is 729.9(1) pm. In the triple octahedron  $(\text{Cl}^-)_3\text{Na}^+(\text{Cl}^-)_3\text{Mo}^{3+}(\text{Cl}^-)_3\text{Na}^+(\text{Cl}^-)_3$ ,  $\text{Mo}^{3+}$  resides in a perfect octahedron when distances are concerned, 245.2(1) pm, 6x, but the octahedron is somewhat compressed along the  $-3$  axis giving rise to Cl-Mo-Cl angles of  $88.71(3)^\circ$  and  $93.75(3)^\circ$ , respectively. The  $\text{Na}^+$  ions are, however displaced from the octahedral center with  $\text{Na}^+\text{--Cl}^-$  distances of 274.8(1) to 291.4(2) pm, 3x

each. The  $\text{Cr}^{3+}\text{-Cl}^-$  distances in  $\text{Na}_3\text{CrCl}_6$  are with 235.3(2) pm 10 pm smaller, roughly in accord with Shannon's ionic radii for  $\text{Cr}^{3+}$  (CN 6, 62 pm) and  $\text{Mo}^{3+}$  (CN 6, 69 pm) [7].

**Figure 2.** Views of the crystal structure of  $\text{Na}_3\text{MoCl}_6$ . Left: A [1-10] projection showing the hexagonal closest packing of chloride ions (green) and the occupation of octahedral voids by sodium (yellow) and molybdenum (red) ions. Middle: A [110] projection. Right: A sequence of triple octahedra  $\{\text{Cl}_3\text{NaCl}_3\text{MoCl}_3\text{NaCl}_3\}$  as they appear in the [001] direction.



It is interesting to note that the  $\text{Na}_3\text{CrCl}_6$  type of structure is only adopted with  $M = \text{V}, \text{Cr}, \text{Mo}$ , whereas the lighter and larger  $M = \text{Sc}, \text{Ti}, \text{Y}$  [8-11] as well as the lanthanides  $R = \text{Dy-Lu}$  [8,12,13] adopt the cryolite type of structure, Figure 3. The cryolite type of structure ( $\text{Na}_3\text{AlF}_6$  type) is a monoclinic structure in which  $\text{Na}^+$  and  $\text{F}^-$  in a 1:3 ratio form layers between which octahedral voids are occupied by  $\text{Na}^+$  and  $\text{Al}^{3+}$ . The  $\text{Na}_3\text{GdCl}_6$  structure, on the other hand, is a stuffed  $\text{LiSbF}_6$  type structure [14] in which  $\text{Cl}^-$  ions form, again, a hexagonal closest packing and  $\text{Na}^+$  and  $\text{Gd}^{3+}$  occupy octahedral voids. One  $\text{Na}^+$  and  $\text{Gd}^{3+}$  center rather regular octahedra, the remaining two  $\text{Na}^+$  are statistically distributed over the remaining four octahedral voids. There is a close relationship between the cryolite and the  $\text{Na}_3\text{GdCl}_6$  type [11];  $\text{Na}_3\text{GdCl}_6$ , for example, undergoes a reversible first-order phase transition from  $\text{Na}_3\text{GdCl}_6\text{-I}$  (stuffed  $\text{LiSbF}_6$ ) to  $\text{Na}_3\text{GdCl}_6\text{-II}$  (cryolite type) at 205 °C [8].

**Figure 3.**  $\text{Na}_3\text{MCl}_6$  type compounds and their structures. **M** on a colored field denominates existence and defines the crystal structure at ambient temperature. Yellow:  $\text{Na}_3\text{AlF}_6$  (cryolite) type; red:  $\text{Na}_3\text{CrCl}_6$  type; green:  $\text{Na}_3\text{GdCl}_6$  (stuffed  $\text{LiSbF}_6$ ) type.

<b>Sc</b>	<b>Ti</b>	<b>V</b>	<b>Cr</b>			
<b>Y</b>	Zr	Nb	<b>Mo</b>			
La						
	Ce	Pr	Nd	Pm	Sm	<b>Eu</b>
<b>Gd</b>	<b>Tb</b>	<b>Dy</b>	<b>Ho</b>	<b>Er</b>	<b>Tm</b>	<b>Yb</b>
<b>Lu</b>						

### 3. Experimental Section

All reactions and handling were carried out under a dry nitrogen atmosphere using dry box equipment (MBraun, Garching, Germany).  $\text{MoCl}_2$  was prepared by synproportionation of Mo (Chempur, Karlsruhe, Germany, 99.95%) and  $\text{MoCl}_5$  (Sigma-Aldrich, München, Germany, 99.99%) in a 3:2 molar ratio with a slight excess of  $\text{MoCl}_5$ .  $\text{MoCl}_2$  was filled into a Pyrex ampoule together with an excess  $\text{AlCl}_3$  (Sigma-Aldrich, München, Germany, 99.99%) /  $\text{NaCl}$  (Chempur, Karlsruhe, Germany, 99.99%) flux, 55:45 mol%. The Pyrex ampoule was sealed under reduced pressure. The following temperature program was applied in a tubular furnace: heated to 623 K with 20 K/h, kept at that temperature for 3 days, then cooled slowly to 298 K (2 K/h). The Pyrex tube was transferred to a dry-box and the contents inspected with the aid of a microscope.

$\text{Na}_3\text{MoCl}_6$  forms well-faceted, polygonal red crystals. Some of these were selected under a microscope and sealed in thin-walled glass capillaries. After their quality had been checked by Laue diffraction patterns, the single crystals were transferred to a single-crystal X-ray diffractometer (Stoe Image Plate Diffraction System, IPDS I) to collect a complete intensity data set at ambient temperature. Structure solution and refinement was performed with the programs SHELXS-97 (direct methods) [15] and SHELXL-97 [16], scattering factors were from International Tables for X-ray Crystallography [17]. Data corrections were carried out for Lorentz and polarization factors and absorption (numerical with the aid of the programs X-RED [18] and X-SHAPE [19]). Further details of the crystal structure determination may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fizkarlsruhe.de), on quoting the depository number ICSD-422981, the authors and the journal citation.

Crystal data for  $\text{Na}_3\text{MoCl}_6$  ( $377.64 \text{ g mol}^{-1}$ ); diffractometer IPDS-I, Stoe, Darmstadt; Mo- $\text{K}\alpha$  (graphite monochromator,  $\lambda = 71.073 \text{ pm}$ );  $T = 293(2) \text{ K}$ ;  $2\theta_{\text{max}} = 56.3^\circ$ ; 100 images,  $0^\circ \leq \varphi \leq 200^\circ$ ;  $\Delta\varphi = 2^\circ$ ; indices:  $-9 \leq h \leq 9$ ,  $-9 \leq k \leq 9$ ,  $-15 \leq l \leq 16$ ; transmission (min, max) = 0.0872, 0.1363;  $\rho_{\text{calc}} = 2.503 \text{ g cm}^{-3}$ ; 4490 reflection intensities measured of which 416 were symmetrically independent,  $R_{\text{int}} = 0.0543$ ,  $F(000) = 354$ ,  $\mu = 17.76 \text{ mm}^{-1}$ . Trigonal,  $P\bar{3}1c$  (no. 163),  $a = b = 687.1(1)$ ,  $c = 1225.3(2) \text{ pm}$ ,  $V = 501.0(1) \times 10^6 \text{ pm}^3$ ,  $Z = 2$ . R values:  $R_1/wR_2$  for 318 reflections with  $[I_0 > 2\sigma(I_0)]$ : 0.0238/0.0671 and for all data: 0.0350/0.0706;  $S_{\text{all}} = 1.062$ .

### 4. Conclusions

Red single crystals of  $\text{Na}_3\text{MoCl}_6$  were obtained from the solution of the cluster chloride  $\{\text{Mo}_6\}\text{Cl}_{12}$  in a slightly acidic  $\text{NaCl}/\text{AlCl}_3$  melt at  $350^\circ\text{C}$  upon cooling. The crystal structure was first observed for  $\text{Na}_3\text{CrCl}_6$ ; in a hexagonal closest-packing of chloride spheres, half of the octahedral voids are occupied by  $\text{Na}^+$  and one sixth by  $\text{Mo}^{3+}$  ions such that these are  $729.92(7) \text{ pm}$  apart.  $\text{Mo}^{3+}\text{-Cl}^-$  distances ( $245.2(1) \text{ pm}$ ) are 10 pm longer than for homologous  $\text{Cr}^{3+}\text{-Cl}^-$ .

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