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Short Note

Crystal Structure of Na_3MoCl_6

Martin Beran and Gerd Meyer *

Department für Chemie, Universität zu Köln, Greinstraße 6, D-50939 Köln, Germany;
E-Mail: beran@uni-koeln.de

* Author to whom correspondence should be addressed; E-Mail: gerd.meyer@uni-koeln.de;
Tel.: +49-221-470-3262; Fax: +49-221-470-5083.

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Abstract: The ternary chloride Na_3MoCl_6 is obtained as red crystals from a disproportionation reaction of molybdenum dichloride, $\{Mo_6\}Cl_{12}$, in an acidic $NaCl/AlCl_3$ 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) 10^6 pm^3) is that of Na_3CrCl_6: within a hexagonal closest-packing of chloride ions two thirds of the octahedral voids are filled between the AB double layers with Na^+/Mo^{3+}, and between the BA layers with Na^+.

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 $\{M_x\}$ 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 $MoCl_2$, obtained by a synproportionation reaction, features a crystal structure [1,2] which contains octahedral molybdenum clusters $\{Mo_6\}$ 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, $\{Mo_6\}Cl^i{}_8Cl^a{}_2Cl^{a\text{-}a}{}_{4/2}$.

$$2MoCl_5 + 3Mo \rightarrow 5MoCl_2$$

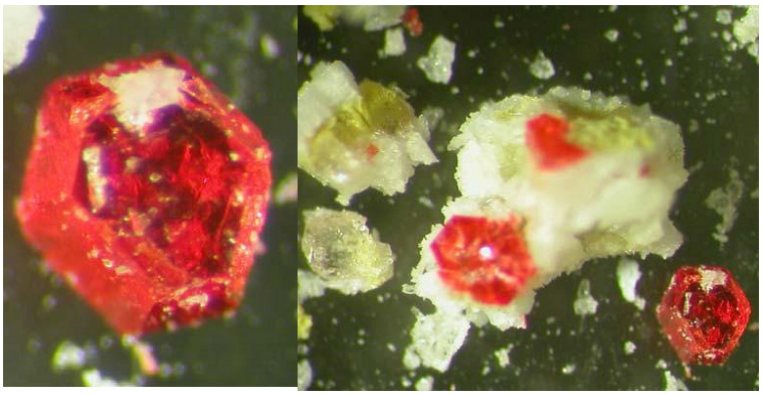
In attempts to synthesize ternary chlorides containing the $[\{Mo_6\}Cl_{14}]^{2-}$ cluster-complex anion in a molten-salt system, $MoCl_2$ faced a disproportionation reaction and red crystals of $Na_3[MoCl_6]$ were obtained.

2. Results and Discussion

Red single crystals of Na_3MoCl_6 were obtained from the attempted dissolution of $MoCl_2 = \{Mo_6\}Cl^i{}_8Cl^a{}_2Cl^{a-a}{}_{4/2}$ in a $NaCl/AlCl_3$ flux (45:55 mol%, close to the eutectic [3]) at 350 °C in a sealed Pyrex ampoule. In this melt the $\{Mo_6\}$ 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.

$$\{Mo_6\}Cl_{12} + 12\ NaCl\ (\text{from xs. } NaCl/AlCl_3) \rightarrow 4\ Na_3[MoCl_6] + 2\ Mo$$

Figure 1. Red single crystals of Na_3MoCl_6.

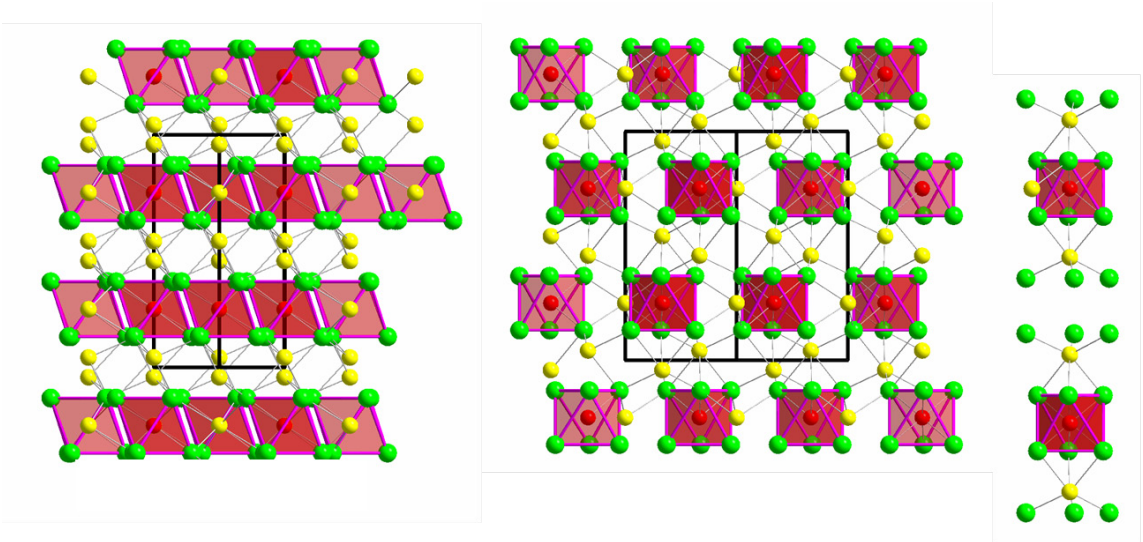


Na_3MoCl_6 crystallizes with the Na_3CrCl_6 type of structure [4], trigonal, space group *P*-31c (No. 163) with a = 687.1(1), c = 1225.3(2) pm, Z = 2. Previous data from powder diffraction, a = 692.0(8),
c = 1222.2(5) pm, agree sufficiently well. It was also assumed that Na_3MoCl_6 and Na_3VCl_6 are isotypic with Na_3CrCl_6 [4]. Other hints at the existence of Na_3MoCl_6 are from preparative investigations or from phase diagram determinations where the crystal structure was apparently of no concern [5,6].

The structure of Na_3MoCl_6 consists of hexagonally closest-packed layers of chloride anions, 4H–...B│ABAB│A.... Octahedral voids between these layers are filled in a way that half of them are filled between double layers BA by Na^+ cations, and half of the voids are filled by Na^+ and 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 Na^+, Cr^{3+}, Na^+, □, where □ denominates a void. Neighboring chains are displaced by ½c in the [001] direction. Therefore, the Mo^{3+}–Mo^{3+} distance is 729.9(1) pm. In the triple octahedron $(Cl^-)_3Na^+(Cl^-)_3Mo^{3+}(Cl^-)_3Na^+(Cl^-)_3$, 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)° and 93.75(3)°, respectively. The Na^+ ions are, however displaced from the octahedral center with Na^+–Cl^- distances of 274.8(1) to 291.4(2) pm, 3x

each. The Cr^{3+}–Cl^{-} distances in Na_3CrCl_6 are with 235.3(2) pm 10 pm smaller, roughly in accord with Shannon's ionic radii for Cr^{3+} (CN 6, 62 pm) and Mo^{3+} (CN 6, 69 pm) [7].

Figure 2. Views of the crystal structure of Na_3MoCl_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 $\{Cl_3NaCl_3MoCl_3NaCl_3\}$ as they appear in the [001] direction.



It is interesting to note that the Na_3CrCl_6 type of structure is only adopted with M = V, Cr, Mo, wheras the lighter and larger M = Sc, Ti, Y [8-11] as well as the lanthanides R = Dy–Lu [8,12,13] adopt the cryolite type of structure, Figure 3. The cryolite type of structure (Na_3AlF_6 type) is a monoclinic structure in which Na^{+} and F^{-} in a 1:3 ratio form layers between which octahedral voids are occupied by Na^{+} and Al^{3+}. The Na_3GdCl_6 structure, on the other hand, is a stuffed $LiSbF_6$ type structure [14] in which Cl^{-} ions form, again, a hexagonal closest packing and Na^{+} and Gd^{3+} occupy octahedral voids. One Na^{+} and Gd^{3+} center rather regular octahedra, the remaining two Na^{+} are statistically distributed over the remaining four octahedral voids. There is a close relationship between the cryolite and the Na_3GdCl_6 type [11]; Na_3GdCl_6, for example, undergoes a reversible first-order phase transition from Na_3GdCl_6-I (stuffed $LiSbF_6$) to Na_3GdCl_6-II (cryolite type) at 205 °C [8].

Figure 3. Na_3**M**Cl_6 type compunds and their structures. **M** on a colored field denominates existence and defines the crystal structure at ambient temperature. Yellow: Na_3AlF_6 (cryolite) type; red: Na_3CrCl_6 type; green: Na_3GdCl_6 (stuffed $LiSbF_6$) type.

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

3. Experimental Section

All reactions and handling were carried out under a dry nitrogen atmosphere using dry box equipment (MBraun, Garching, Germany). $MoCl_2$ was prepared by synproportionation of Mo (Chempur, Karlsruhe, Germany, 99.95%) and $MoCl_5$ (Sigma-Aldrich, München, Germany, 99.99%) in a 3:2 molar ratio with a slight excess of $MoCl_5$. $MoCl_2$ was filled into a Pyrex ampoule together with an excess $AlCl_3$ (Sigma-Aldrich, München, Germany, 99.99%) / 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.

Na_3MoCl_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 Na_3MoCl_6 (377.64 g mol^{-1}); diffractometer IPDS-I, Stoe, Darmstadt; Mo-K_α (graphite monochromator, λ = 71.073 pm); T = 293(2) K; $2\theta_{max}$ = 56.3°; 100 images, $0° \leq \varphi \leq 200°$; $\Delta\varphi$ = 2°; indices: $-9 \leq h \leq 9$, $-9 \leq k \leq 9$, $-15 \leq l \leq 16$; transmission (min, max) = 0.0872, 0.1363; ρ_{calc} = 2.503 g cm^{-3}; 4490 reflection intensities measured of which 416 were symmetrically independent, R_{int} = 0.0543, F(000) = 354, μ = 17.76 mm^{-1}. Trigonal, *P*-31c (no. 163), $a = b$ = 687.1(1), c = 1225.3(2) pm, V = 501.0(1) × 10^6 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_{all} = 1.062.

4. Conclusions

Red single crystals of Na_3MoCl_6 were obtained from the solution of the cluster chloride $\{Mo_6\}Cl_{12}$ in a slightly acidic $NaCl/AlCl_3$ melt at 350 °C upon cooling. The crystal structure was first observed for Na_3CrCl_6; in a hexagonal closest-packing of chloride spheres, half of the octahedral voids are occupied by Na^+ and one sixth by Mo^{3+} ions such that these are 729.92(7) pm apart. Mo^{3+}–Cl^- distances (245.2(1) pm) are 10 pm longer than for homologous Cr^{3+}–Cl^-.

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