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A New Synthetic Route to Hexachloromolybdate(III). An X-Ray Structure of $(NH_4)_3[MoCl_6]$

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Synopsis. Ammonium hexachloromolybdate(III) $(NH_4)_3[MoCl_6]$ was obtained by a tin metal reduction of ammonium molybdate in high yield (80%). The X-ray structure was determined. Crystal data: tetragonal system, space group $P4_2/m$, $a=8.822(3)$ Å, $c=7.271(2)$ Å, $V=565.9(3)$ Å^3, $Z=2$, $R(R_W)=3.35(5.47)$. Two independent Mo-Cl distances (2.439(2) and 2.451(1) Å) exist.

Hexachloro- and aquapentachloro-molybdate(III) complexes are important for understanding the basic chemistry of Mo(III) and for preparing other Mo(III) complexes (e.g. $[Mo(H_2O)_6]^{3+}$).1) Some chemical and physical studies on $[MoCl_6]^{3-}$ ion have also been reported.2)

Several methods have been used to obtain $[MoCl_6]^{3-}$ and/or $[MoCl_5(H_2O)]^{2-}$: 1) electrolytic reduction of MoO_3 in concentrated hydrochloric acid;3) 2) oxidation of tetrakis(μ-acetato)dimolybdenum, $Mo_2(O_2CCH_3)_4$, in concentrated hydrochloric acid;4) 3) reduction of $MoCl_5$ by $SnCl_2$;5) and 4) substitution reaction of Mo(III) complexes.6) Method 1 requires an electrolytic apparatus and complicated procedures, and the yield is not very high. Though method 2 is simpler than method 1 and gives good yield, the starting material, $Mo_2(O_2CCH_3)_4$, is rather expensive compared to molybdate and must be prepared from $Mo(CO)_6$. The starting material for the method 3, $MoCl_5$, is also expensive.

We report here a very facile preparative method of ammonium salt of hexachloromolybdate(III). Although the X-ray structure of $K_3[MoCl_6]$ had been determined (R=11%),7) it is worthwhile, we thought, to determine the structure of $[MoCl_6]^{3-}$ more precisely; the X-ray structure of $(NH_4)_3[MoCl_6]$ is also described.

Experimental

Preparation of Ammonium Hexachloromolybdate(III), $(NH_4)_3[MoCl_6]$. A five-gram (4.05 mmol) quantity of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ was dissolved in concentrated HCl (100 mL) in an Erlenmeyer flask. Then, tin metal (shot, 20 g) was added to the flask, and the loosely stoppered flask heated in a boiling-water bath for ca. 8 min with vigorous stirring. The color of the solution turned to deep red brown via yellow green, deep green, and red brown. After further heating for 3 min, NH_4Cl (5.0 g) was added to the flask and dissolved by additional heating (2 min). The solution was then cooled in an ice-bath for 1 min and filtered with a sintered-glass filter. The filtrate in an Erlenmeyer flask was ice-cooled and a fairly vigorous stream of gaseous hydrogen chloride was bubbled through the solution until saturation; the flask was tightly stoppered. The solution was kept in a refrigerator for one day; red crystals were collected by filtration and washed with methanol, then dried in a vacuum desiccator: Yield 6.9 g (ca. 68%). Anal. Calcd for $(NH_4)_3[MoCl_6]$: Mo, 26.44; N, 11.58; H, 3.33%. Found: Mo, 26.4; N, 11.45; H, 3.38%. The filtrate contained an appreciable amount of Mo(III) species. Upon the addition of ethanol (ca. 25 mL), followed by HCl gas introduction, the filtrate gave an additional product after several day's storage in a refrigerator; yield ca. 1.2 g (12%).

Table 1. Atom Coordinates for $(NH_4)_3[MoCl_6]$

Atom	x	y	z
Mo	0.5	0.0	0.0
Cl(1)	0.7670(2)	0.0716(2)	0.0
Cl(2)	0.4436(1)	0.1892(1)	0.2373(1)
N1	0.5	0.5	0.0
N2	0.0838(7)	0.2638(7)	0.0

Structure Determination of $(NH_4)_3[MoCl_6]$. Crystal data: F. W.=362.77, tetragonal, space group $P4_2/m$, $a=8.822(3)$, $c=7.271(2)$ Å, $V=565.9(3)$ Å^3, $Z=2$, $d_{calcd}=2.129$ g cm^{-3}, $d_{obsd}=2.12$ g cm^{-3}, crystal size/mm=0.20×0.18×0.17, λ (Mo $K\alpha$)=0.71073 Å, μ (Mo $K\alpha$)=25.1 cm^{-1}. The intensities were measured on Rigaku AFC-6A: scan method, ω ($2\theta<30°$), ω-2θ ($2\theta>30°$); scan speed, 2 deg min^{-1}; scan range, 1.20°+0.5 tan θ°; background measurement, 5 s; max 2θ value, 60°; total no. of reflections, 994; no. of unique data ($|F_o|\geq 8\sigma|F_o|$), 735; no. of variables, 30. No correction was made for absorption. The structure was solved by SHELXS-868) and refined by full matrix least-squares methods. The function minimized was $\sum w(|F_o|-|F_c|)^2$, where $w=1/[\sigma^2(|F_o|)+g|F_o|^2]$; $g=0.001$. The final $R(R_W)$ value was 3.35(5.47), where $R_w=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}$. No attempt was made to locate the hydrogen atoms. The atomic coordinates are listed in Table 1.9) The computations were performed, as described before.10)

Results and Discussion

Preparation and Properties. This method employs a reduction of ammonium molybdate by tin metal in a concentrated hydrochloric acid solution, followed by the addition of NH_4Cl, which requires no air-free

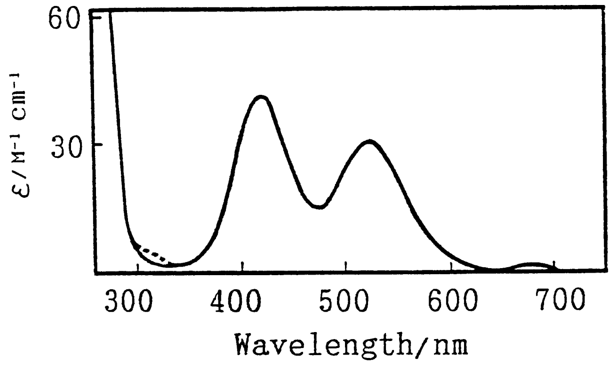

Fig. 1. Electronic spectra of (—) $[MoCl_6]^{3-}$ in concentrated HCl under a dinitrogen atmosphere, (······) as above but with a small amount of air.

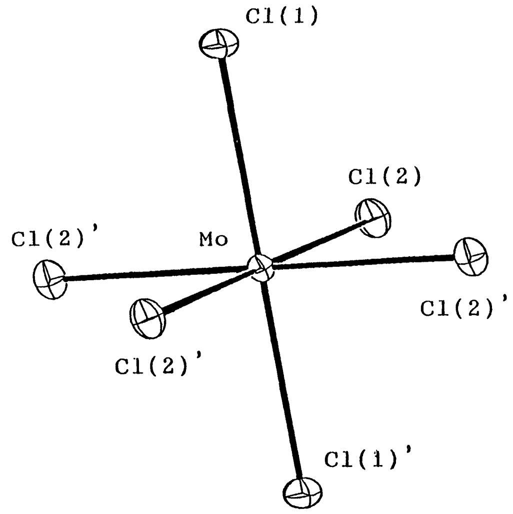

Fig. 2. Perspective vierw of $[MoCl_6]^{3-}$ showing the atom labeling scheme. The primed atoms are related to the unprimed ones by symmetry.

Table 2. Atomic Distances(<4.0 Å) and Angles(deg) for $(NH_4)_3[MoCl_6]$[#]

Mo-Cl(1)	2.439(2)
Mo-Cl(2)	2.451(1)
Cl(1)-N(2)[a)]	3.269(6)
Cl(1)-N(2)[b)]	3.239(6)
Cl(1)-N(2)[c)]	3.647(6)
Cl(2)-N(1)	3.278(1)
Cl(2)-N(1)[c)]	3.379(1)
Cl(2)-N(2)	3.672(6)
Cl(2)-N(2)[c)]	3.343(6)
Cl(2)-N(2)[d)]	3.459(6)
Cl(1)-MO-Cl(2)	91.12(4)
Cl(2)-MO-Cl(2)[e)]	90.53(5)

[#] Symmetry operations a) $x+1.0$, y, z. b) $-x+1.0$, $-y$, z. c) $-y+1.0$, x, $z+0.5$. d) y, $-x$, $z+0.5$. e) $-x$, $-y$, z.

technique; the yield was high (totally 80%). The use of sodium molybdate instead of ammonium molybdate gave a somewhat impure product (probably due to contamination of NaCl). Compounds MoO_3 and H_2MoO_4 dissolve only little in concentrated HCl and are inadequate. The solid is stable in air; the solution, however, is air-oxidised, as has been described previously.[3,4)] Somewhat different electronic spectra have been reported for $[MoCl_6]^{3-}$,[2,11)] and our spectrum (Fig. 1) in the visible region {λ_{max}, nm (ε, $mol^{-1}\,dm^3\,cm^{-1}$) 419 (41.5), 523 (30.6), and 677 (1.5)} obtained in a concentrated HCl solution is very similar to the reported values in Refs. 2a and 11a. A very small amount of air causes a spectrum change at around 310 nm (as shown in a dotted line in Fig. 1); however, the ε values of the three peaks change little.

Structure of $(NH_4)_3[MoCl_6]$. The structure of the anion $[MoCl_6]^{3-}$ is shown in Fig. 2, and the atomic distances and angles are collected in Table 2. Molybdenum atom is located on a symmetry-fixed position with a site symmetry of 2/m; Cl(1) is on a mirror plane. Therefore, only two independent Mo-Cl distances exist. The mean Mo-Cl distance (2.445[8] Å) is nearly identical to that (2.447[24] Å) of $K_3[MoCl_6]$;[7)] each Mo-Cl distance of the latter is relatively widely scattered, though (2.427(5)—2.486(6) Å).

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