

Cesium Molybdenum Alum Prepared from Sodium Hexakis(formato)molybdate(III)

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The mononuclear Mo^{III} aqua ion was first prepared in the early seventies by hydrolysis of $[\text{MoCl}_6]^{3-}$ in a solution of a noncomplexing strong acid (triflic acid ($\text{CF}_3\text{SO}_3\text{H}$) or *p*-toluenesulfonic acid) for several days followed by purification on an ion exchange column.¹⁻⁴ We here report an alternative method for the preparation of $[\text{Mo}(\text{H}_2\text{O})_6]^{3+}$ which is much faster and which does not involve ion exchange. It is based on the new compound sodium hexakis(formato)molybdate(III), $\text{Na}_3[\text{Mo}(\text{HCO}_2)_6]$, which can be hydrolysed in strong acid to give the aqua ion within a few minutes. Whereas the ion exchange method inevitably produces the aqua ion in a dilute solution, this is not the case for the present method by which quite strong solutions (>0.5 M) can easily be made. By preparing $[\text{Mo}(\text{H}_2\text{O})_6]^{3+}$ according to the new method, it has been possible to isolate cesium molybdenum alum, $\text{Cs}[\text{Mo}(\text{H}_2\text{O})_6](\text{SO}_4)_2 \cdot 6 \text{H}_2\text{O}$, which is the first crystalline substance to contain the hexaaquamolybdenum(III) ion. The molybdenum alum belongs to the classical alum series whose other known members from the second long period are the alums of Ru, Rh, and In (see Ref. 5). The failure of some very early attempts^{6,7} to prepare a molybdenum alum may in the light of present knowledge⁸ be ascribed to the absence of *mononuclear* Mo^{III} in the solutions used*.

Since molybdenum(III) is air-sensitive, all experiments have been carried out under dinitrogen using deaerated solutions and Schlenk techniques.

$\text{Na}_3[\text{Mo}(\text{HCO}_2)_6]$: $(\text{NH}_4)_2[\text{MoCl}_5(\text{H}_2\text{O})]^9$ (10 g, 30 mmol) is dissolved in a 7 M solution of sodium formate which is 0.1 M in formic acid (100 ml). After 1 day, a light green precipitate of $\text{Na}_3[\text{Mo}(\text{HCO}_2)_6]$ forms which is then separated from the mother liquor by filtration and washed first with 50 % ethanol, then with 96 % ethanol, and finally with ether. The crystals are dried in a stream of dinitrogen. Yield 12 g, 90 %.

$\text{Na}_3[\text{Mo}(\text{HCO}_2)_6]$ is almost insoluble in saturated sodium formate (approximately 9 M), but can be dissolved in saturated ammonium formate (approximately 10 M) where its UV-vis spectrum has been measured: $(\lambda, \epsilon)_{\text{max}} = (383 \text{ nm}, 115 \text{ l mol}^{-1} \text{ cm}^{-1})$; $(\lambda, \epsilon)_{\text{min}} = (357 \text{ nm}, 97 \text{ l mol}^{-1} \text{ cm}^{-1})$. The absorption band at 383 nm is assigned as the transition ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{2g}$ within the d^3 configuration. This band is located on the low energy foot of an intense absorption which completely obscures the second ligand field transition, ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}$.

Dry $\text{Na}_3[\text{Mo}(\text{HCO}_2)_6]$ may be handled in air for short periods of time. Oxidation is prevented when the salt is stored under dinitrogen.

$[\text{Mo}(\text{H}_2\text{O})_6]^{3+}$: When $\text{Na}_3[\text{Mo}(\text{HCO}_2)_6]$ is dis-

*In recent literature, such hydroxo-bridged species as the di- μ -hydroxobis(tetraaquamolybdenum(III)) ion are commonly named aqua ions. Although it may be justified to name $[\text{Mo}_2(\text{H}_2\text{O})_8]^{4+}$, the Mo^{II} aqua ion, since no such mononuclear species is known and since H_2O is the only ligand present, it seems unfortunate to use this name for species containing ligands which are not water molecules.

solved in strong acid, the complex anion is quickly hydrolysed. If the acid is non complexing, the hydrolysis results in the formation of the Mo^{III} aqua ion whose characteristic UV-vis spectrum^{3,4} can be recorded 3 minutes after the addition of the acid.

$\text{CsMo}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$: $\text{Na}_3[\text{Mo}(\text{HCO}_2)_6]$ (3 g, 7 mmol) is added to a solution of Cs_2SO_4 (2 g, 5.5 mmol) in 2 M trifluoromethanesulfonic acid or *p*-toluenesulfonic acid (30 ml). The resulting greenish yellow solution is cooled in ice and after approximately 8 h, bright yellow crystals of the alum are collected. The crystals are washed with 96 % ethanol. Yield 1.2 g, 70 % based on Cs_2SO_4 . During the crystallisation, the solution gradually turns darker, probably due to oligomerization. The rate of this process is kept low by the cooling which also reduces the solubility of the alum. The UV-vis spectrum of the initial greenish yellow reaction mixture does not differ from the spectra of more dilute solutions of Mo^{III} aqua ions even though these seem less green.

When exposed to air, the alum crystals turn brown within a few hours. Even when kept under dinitrogen in a sealed tube at room temperature, the crystals turn brown and gradually decompose in a couple of weeks' time. The decomposition in the tube may be due to efflorescence in combination with a redox reaction between Mo^{III} and SO_4^{2-} . Anyway, if the solid alum is heated at 100 °C, H_2S is evolved in small amounts. Also, if the alum is heated in 2 M H_2SO_4 or 2 M *p*-toluenesulfonic acid, H_2S can be detected.

In addition to elemental analyses, the molybdenum alum is characterized by its room temperature Guinier powder diagram which is almost identical to that of cesium ruthenium alum.⁵ The cubic (*Pa*3) cell dimension of $\text{CsMo}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$ is $a = 12.51 \text{ \AA}$, which agrees well with the values known for other^{5,10,11} cesium alums. As expected for the d^3 configuration of Mo^{III} , the value is, for example, larger than that of Ru^{III} (12.45 Å), which has a low spin d^5 configuration. A low temperature single crystal structure determination of the cesium molybdenum alum has also been carried out, the results of which will be published later. We will here only mention that it belongs to the β class¹⁰ of alums and the Mo–O distance in $[\text{Mo}(\text{H}_2\text{O})_6]^{3+}$ is 2.09 Å.

The UV-vis spectrum of the Mo^{III} aqua ion is very sensitive to the presence of impurities due to

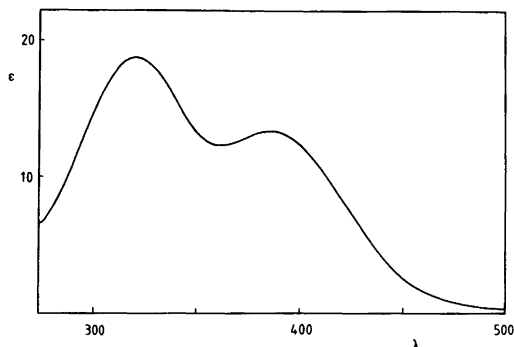


Fig. 1. UV-vis spectrum of an approx. 0.03 M solution of $\text{CsMo}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$ in 2 M $\text{CF}_3\text{SO}_3\text{H}$. The positions of the extrema are the following: $(\lambda, \epsilon)_{\text{max}} = (386 \text{ nm}, 13.3 \text{ l mol}^{-1} \text{ cm}^{-1})$, $(\lambda, \epsilon)_{\text{min}} = (362 \text{ nm}, 12.4 \text{ l mol}^{-1} \text{ cm}^{-1})$, and $(\lambda, \epsilon)_{\text{max}} = (320 \text{ nm}, 19.0 \text{ l mol}^{-1} \text{ cm}^{-1})$. The minimum below 300 nm is extremely sensitive to oxidation of the solution and it cannot be ruled out that the spectrum can be further improved in this region.

oxidation^{2,3,4} and the purification arising from crystallization as an alum is therefore useful. By dissolving the alum in 2 M $\text{CF}_3\text{SO}_3\text{H}$, the spectrum given in Fig. 1 is obtained. In comparison with, e.g., *p*-toluenesulfonic acid, $\text{CF}_3\text{SO}_3\text{H}$ has the advantage that it only absorbs moderately between 250 and 300 nm and thus does not obscure the absorption caused by oxidation products. From the energies of the two absorption bands, the values of the spectrochemical parameter Δ and the interelectronic repulsion parameter B can be calculated as 25900 cm^{-1} and 476 cm^{-1} , respectively. Between 560 and 600 nm, a very weak band ($\epsilon < 0.5 \text{ l mol}^{-1} \text{ cm}^{-1}$) is observed. This may be the spin-forbidden transition $^4\text{A}_{2g} \rightarrow ^2\text{T}_{2g}$.

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