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First Convenient Route to Classical Molybdenum(III) Ammine Complexes. Preparation and Characterization of *fac*-$Mo(NH_3)_3(CF_3SO_3)_3$

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Introduction

In a comparison of the coordination chemistry of the congeneric chromium(III), molybdenum(III), and tungsten(III), it is immediately conspicuous that only relatively few classical molybdenum(III) complexes are known and, in continuation of this trend, those of tungsten(III) are very rare. This situation is even more pronounced focusing on ammine complexes. The wealth of chromium(III) ammines is known to all coordination chemists. Contrary to this, only very few reports on molybdenum(III) ammines have appeared in the literature. A survey of this literature[1,2] reveals that most syntheses are carried out in sealed bombs with liquid ammonia and the products are usually only poorly characterized, probably because of very high oxygen and moisture sensitivity of the compounds obtained. Apparently, only Bowen and Taube[2] have reported a molybdenum(III) ammine, $Mo(NH_3)_4(H_2O)(HCOO)^{2+}$, prepared in aqueous ammonia solution. However, this compound has only been obtained in solution and characterized by UV–vis spectroscopy.

We report the first easily reproducible synthetic route to a classical molybdenum(III) ammine complex, *fac*-$Mo(NH_3)_3(CF_3SO_3)_3$. The experiments carried out with molybdenum(III) have at the same time been conducted in an entirely similar way with the analogous chromium(III) compounds and were found to give analogous compounds in comparable yields.

We have found *fac*-$Mo(NH_3)_3(CF_3SO_3)_3$ to provide the first easily accessible route into the coordination chemistry of molybdenum(III) ammines as the coordinated triflate can easily be substituted by other ligands according to[3]

$$fac\text{-}Mo(NH_3)_3(CF_3SO_3)_3 \xrightarrow[\text{thf/ethanol}]{\text{LiX}} fac\text{-}Mo(NH_3)_3X_3$$

$$X = Cl, Br, I$$

We are currently further investigating the potential of this new molybdenum(III) ammine in the preparation of other classical molybdenum(III) ammine complexes.

Experimental Section

All operations involving molybdenum(III) were carried out under a protective atmosphere of dinitrogen using conventional Schlenk-line techniques. Ammonia (99.995%) was purchased from Alfax and used without further purification, tetrahydrofuran (thf) was dried for several days with 3-Å molecular sieves prior to use, and trifluoromethanesulfonic acid was obtained from 3M. *mer*-$Cr(thf)_3Cl_3$[4] and *mer*-$Mo(thf)_3Cl_3$[5] were prepared according to the published procedures and identified from elemental analyses and their X-ray powder diffraction (XRPD) patterns. The space groups and unit cell parameters of these two compounds are listed in Table I.

XRPD. X-ray powder diagrams were recorded in air by slow scanning on a Philips vertical goniometer equipped with a θ-compensating divergence slit and a diffracted beam graphite monochromator utilizing Cu K-$L_{2,3}$ radiation (IUPAC recommended designation for Cu Kα radiation.[6])

UV–Vis Spectra. Diffuse reflectance spectra were recorded with a Perkin-Elmer Lambda 2 spectrometer equipped with a diffuse reflectance attachment and interfaced with a PC.

Syntheses. ***fac*-$Mo(NH_3)_3(CF_3SO_3)_3$.** A 3.0-g amount (7.17 mmol) of *mer*-$Mo(thf)_3Cl_3$ was suspended in 150 mL of thf. Ammonia was passed through the solution while it was being refluxed. In this way the orange suspension gradually turned brownish, and after 20 min the addition of ammonia was stopped. The brownish-yellow compound was isolated by filtration, washed twice with 25 mL of thf, and dried in vacuum (*ca.* 1 mbar) for 2 h. The X-ray powder diagram consisted of some rather broad lines (indicating very small crystallites) due to the molybdenum compound(s) and some sharp lines that could all be ascribed to a small amount of ammonium chloride. About 1.8 g of material was obtained by this procedure. (Anal. Found: Mo, 35.3; N, 16.57; H, 4.42; Cl, 39.08; C, 0.1. Calcd for $Mo(NH_3)_3Cl_3$: Mo, 37.87; N, 16.58; H. 3.58; Cl, 41.97).

The product obtained as outlined above was transferred to a 25-mL Schlenk flask, 20 mL of trifluoromethanesulfonic acid was added with stirring, and the flask was evacuated to *ca.* 1 mbar for 2 h. The solution obtained thereby was filtered into a 250-mL Schlenk flask (in none of our experiments was left any material on the filter), and 200 mL of diethyl ether was cautiously added. In this way a fine yellow precipitate was obtained and isolated by filtration. This was washed twice with 15 mL of diethyl ether and dried in vacuum (*ca.* 1 mbar) for 30 min. Yield: 1.0 g (23% from *mer*-$Mo(thf)_3Cl_3$). Anal. Found: Mo, 15.9; C, 5.95; N, 6.98; H, 1.63. Calcd for $MoC_3H_9N_3F_9S_3O_9$: Mo, 16.1; C, 6.06; N, 7.07; H, 1.53.

***fac*-$Cr(NH_3)_3(CF_3SO_3)_3$.** This compound was prepared by a procedure exactly as the one above using *mer*-$Cr(thf)_3Cl_3$ as a starting material. Yield: 18% from *mer*-$Cr(thf)_3Cl_3$. Furthermore, *fac*-$Cr(NH_3)_3(CF_3SO_3)_3$ was prepared by the procedure reported in the literature by Andersen *et al.*[7] The density of the compound was determined by He pychnometry in order to determine the number of formula units in the unit cell.

Results and Discussion

Synthesis. We have been able to prepare a new classical molybdenum(III) ammine according to the following reaction scheme

$$mer\text{-}M(thf)_3Cl_3 \xrightarrow[\text{2. neat triflic acid}]{\text{1. }NH_3\text{/thf}} fac\text{-}M(NH_3)_3(CF_3SO_3)_3$$

$$M = Cr, Mo$$

We believe this is the first easily reproducible synthetic route to a molybdenum(III) ammine as all operations can be carried out in conventional Schlenk equipment, i.e. without the use of liquid ammonia, and the product is obtained as a pure crystalline compound that can be conveniently stored under dinitrogen for at least several months. Furthermore, we have found this compound to be a versatile precursor in the preparation of new classical molybdenum(III) ammine complexes.[3]

Structure. Figure 1 illustrates the X-ray powder diagrams of *fac*-$Mo(NH_3)_3(CF_3SO_3)_3$ and *fac*-$Cr(NH_3)_3(CF_3SO)_3$ (the diagrams obtained from the chromium compounds prepared by the two different routes are almost exactly identical). All the lines in the diagram of *fac*-$Cr(NH_3)_3(CF_3SO_3)_3$ could be satisfactorily

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Table I. Space Group and Unit Cell Parameters for *mer*-Mo(thf)$_3$Cl$_3$ and *mer*-Cr(thf)$_3$Cl$_3$[a]

	mer-Mo(thf)$_3$Cl$_3$	*mer*-Cr(thf)$_3$Cl$_3$
space group	$P2_1/c$	$P2_1/c$
Z	4	4
a/Å	8.903(4)	8.733(7)
b/Å	12.837(5)	12.80(3)
c/Å	15.391(5)	15.12(1)
β/deg	92.34(3)	92.06(4)
V/Å^3	1758(1)	1689(4)
fw	418.62(2)	374.68(1)
D_{calc}/g·cm^{-3}	1.582(1)	1.473(4)

[a] The X-ray powder diagrams were identified by comparison with that of *mer*-Sc(thf)$_3$Cl$_3$.[9]

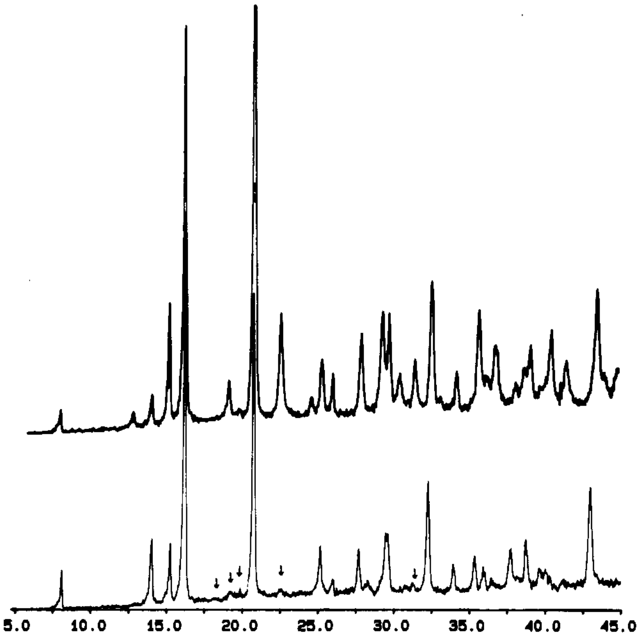

Figure 1. X-ray powder diagrams of *fac*-Mo(NH$_3$)$_3$(CF$_3$SO$_3$)$_3$ (bottom) and *fac*-Cr(NH$_3$)$_3$(CF$_3$SO$_3$)$_3$ (top). Arrows indicate lines belonging to an unidentified impurity.

Table II. Space Groups and Unit Cell Parameters for *fac*-Mo(NH$_3$)$_3$(CF$_3$SO$_3$)$_3$ and *fac*-Cr(NH$_3$)$_3$(CF$_3$SO$_3$)$_3$

	fac-Mo(NH$_3$)$_3$(CF$_3$SO$_3$)$_3$	*fac*-Cr(NH$_3$)$_3$(CF$_3$SO$_3$)$_3$
space group	P^*c^* [a]	$P6cc$ or $P6/mcc$
Z	2	4
a/Å	12.62(1)	12.455(5)
c/Å	6.86(1)	13.611(5)
V/Å^3	945(2)	1829(1)
fw	594.24(2)	550.30(2)
D_{exp}/g·cm^{-3}		1.922(3)[b]
D_{calc}/g·cm^{-3}	2.080(4)	1.998(1)

[a] Five possible space groups: No. 159, 163, 186, 190, or 194. [b] Obtained by He pychnometry. These values are typically 0.5–5% lower than the calculated values.

explained by the space group and unit cell parameters given in Table II. The diagram of *fac*-Mo(NH$_3$)$_3$(CF$_3$SO$_3$)$_3$ contained five very weak lines (marked with arrows) that could not be explained by the space group and unit cell parameters in Table II. This can be ascribed to the air-sensitivity of the compound, which turns black upon exposure to the atmosphere for longer periods (>10 min), and this was proved by recording the powder diagram again immediately after the diagram in Figure 1 had been obtained. In this new diagram only the five marked lines had gained intensity. The hexagonal space group for the chromium(III) and molybdenum(III) compounds combined with four formula units and two formula units in the unit cell, respectively, is a definite proof of the facial coordination geometry as this necessitates a trigonal or hexagonal site symmetry of the complexes.[8] This is in agreement with the previously reported ESR spectroscopic evidence for *fac*-Cr(NH$_3$)$_3$(CF$_3$SO$_3$)$_3$.[7]

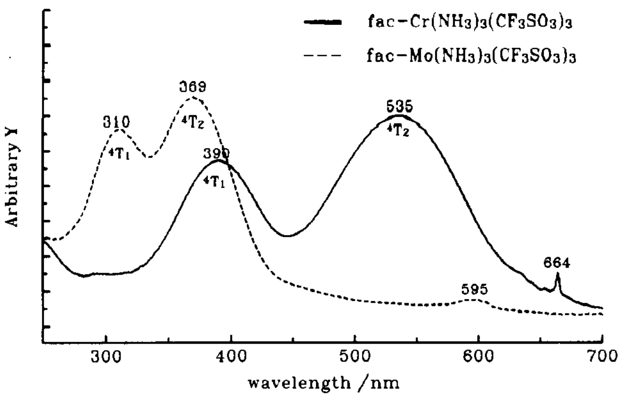

Figure 2. Diffuse reflectance spectra of *fac*-Mo(NH$_3$)$_3$(CF$_3$SO$_3$)$_3$ (···) and *fac*-Cr(NH$_3$)$_3$(CF$_3$SO$_3$)$_3$ (—).

Spectra. The diffuse reflectance spectra of *fac*-Cr(NH$_3$)$_3$(CF$_3$SO$_3$)$_3$ and *fac*-Mo(NH$_3$)$_3$(CF$_3$SO$_3$)$_3$ are illustrated in Figure 2. Since the holohedrized symmetry of both complexes by assumption is close to O_h, the electronic states will in the following be labeled by the irreducible representations of this group. Both spectra exhibit two bands between 250 and 700 nm which have been assigned to the spin–allowed transitions from the $^4A_{2g}$ ground state to the $^4T_{2g}$ and $^4T_{1g}$ excited states. From the low-energy spin-allowed transition for chromium, we find $\Delta_{triflate}(Cr) = 16\,280$ cm^{-1} using the relation[10]

$$\Delta = {}^1/_2\Delta_{NH_3} + {}^1/_2\Delta_{triflate}$$

and $\Delta_{NH_3}(Cr) = 21\,100$ cm^{-1}.[11]

The compound *fac*-Mo(NH$_3$)$_3$Cl$_3$[3] has the lowest energy spin-allowed transition at 406 nm. Using $\Delta_{Cl}(Mo) = 19\,200$ cm^{-1} from MoCl$_6^{3-}$,[12] we find $\Delta_{NH_3}(Mo) = 30\,060$ cm^{-1} and $\Delta_{triflate}(Mo) = 24\,140$ cm^{-1}. The ratios $\Delta_f(Mo)/\Delta_f(Cr)$ found here are all close to 1.5 as it is very often found for other analogous first- and second-row transition metal complexes. The value of $\Delta_{NH_3}(Mo)$ is as expected somewhat lower than the Δ_{amine} values determined from the UV–vis spectra of *cis*-[Mo([14]aneN$_4$)Cl$_2$]$^+$ [13] and *cis*-[Mo([15]aneN$_4$)Cl$_2$]$^+$.[14] This leads to the following spectrochemical series for Mo(III):

$$Cl^- < \text{triflate} < H_2O < NH_3 < NR_2$$

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