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Preparation and Characterization of a Novel Macrocyclic Molybdenum(III) Amine Complex. *cis*-[Mo([15]aneN$_4$)Cl$_2$]Cl·2H$_2$O ([15]aneN$_4$ = 1,4,8,12-Tetraazacyclopentadecane)

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Introduction

Molybdenum(III) compounds are frequently characterized by poor stability toward air-oxidation and hydrolysis or a combination of these two processes. Therefore, the coordination chemistry of molybdenum(III) has been less exploited compared to that of the congeneric chromium(III). In particular, the very few well characterized molybdenum(III) amines are conspicuous in this respect. We have attempted the preparation of molybdenum(III) amine complexes as this is a relatively unexplored area of coordination chemistry. Furthermore, it should enable a comparison of the physical and chemical properties of analogous chromium(III) and molybdenum(III) compounds. In this paper we report the preparation and characterization of a novel macrocyclic molybdenum(III) amine complex. The only well-characterized molybdenum(III) amine complexes reported hitherto have been prepared by Wieghardt *et al.*[1] and by Hyldtoft *et al.*,[2] and only recently was the first well-characterized molybdenum(III) ammine complex isolated.[3] Our approach to the preparation of molybdenum(III) amines is different from that adopted by Wieghardt *et al.*,[1] who have prepared molybdenum(III) complexes with the macrocycle 1,4,7-triazacyclononane and derivatives of this ligand. They initially prepared a molybdenum(0) amine MoL(CO)$_3$ (L is a tridentate amine ligand) by reaction of Mo(CO)$_6$ and the free amine ligand. This compound was oxidized to a molybdenum(III) complex (or higher oxidation states) with various different oxidants. Instead, we have decided to use a molybdenum(III) precursor and tried to obtain the amine complexes by the appropriate ligand substitutions. In this way, a search for a suitable oxidant that selectively oxidizes the molybdenum(0) precursor to molybdenum(III) is avoided. Furthermore, we hope by this procedure to gain more insight into the coordination chemistry of molybdenum(III).

It has been our intention to obtain *trans*-tetraaminemolybdenum(III) complexes. As it has previously been found that 1,4,8,11-tetraazacyclotetradecane ([14]aneN$_4$) only yielded a *cis*-complex with Mo^{III},[2] we hoped that the larger macrocyclic ligand [15]aneN$_4$ would facilitate the formation of a *trans*-complex. However, as the UV–vis spectroscopic results were indicative of a *cis*-complex and no other *cis*-complexes had been reported with the ligand [15]aneN$_4$, we decided to perform a single-crystal X-ray diffraction investigation. Previously, *trans*-complexes have been reported with nickel(II) viz., *trans*-Ni([15]aneN$_4$)Cl$_2$ and *trans*-Ni([15]aneN$_4$)(NCS)$_2$.[4]

Table 1. Crystallographic Data for *cis*-[Mo([15]aneN$_4$)Cl$_2$]Cl·2H$_2$O

chem formula	MoC$_{11}$H$_{30}$O$_2$N$_4$Cl$_3$	MW	452.69
a/Å	7.741(3)	space group	$P\bar{1}$
b/Å	9.754(2)	*T*/K	122
c/Å	12.285(3)	λ(Mo K*α*)/Å	0.710 73
α/deg	88.85(2)	D$_{calc}$/g·cm^{-3}	1.521
β/deg	81.73(2)	*μ*/cm^{-1}	11.43
γ/deg	82.39(2)	*R*[a]	0.025
V/Å^3	909.85	*R*$_w$[b]	0.035
Z	2		

[a] $R = [(\Sigma||F_o| - |F_c||)/\Sigma|F_o|]$. [b] $R_w = [\{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{1/2}]$.

Experimental Section

All operations were carried out in a protective atmosphere of dinitrogen using standard Schlenk-line techniques.

Synthesis. Tetrahydrofuran (THF) was dried for several days with 3-Å molecular sieves prior to use. [15]aneN$_4$[5] and *mer*-MoCl$_3$(THF)$_3$[6] were obtained by literature methods. The identity and the purity of the amine were checked by ^{1}H and ^{13}C NMR as well as microanalyses for C, H, and N. *mer*-Mo(THF)$_3$Cl$_3$ was checked by X-ray powder diffraction ($P2_1/c$, monoclinic, a = 8.903 Å, b = 12.837 Å, c = 15.391 Å, β = 92.34°, and Z = 4)[3] and analyses for Mo, C, H, N, and Cl.

***cis*-[Mo([15]aneN$_4$)Cl$_2$]Cl·2H$_2$O.** A 2.0-g (9.3-mmol) sample of [15]aneN$_4$ was mixed with 4.15 g (11.2 mmol) of *mer*-Mo(THF)$_3$Cl$_3$, and 60 mL of THF was added. Thereby, an orange suspension was obtained. It was stirred for 4 h during which it gradually changed color to olive green. This suspension was filtered, and the product was washed twice with 15 mL of THF and dried under vacuum. The brownish product, which analyzed very close to MoC$_{11}$H$_{26}$N$_4$Cl$_3$, was dissolved in 30 mL of boiling 1 M HCl and filtered. This occasionally left a small amount of an unidentified blue material on the filter. To the resulting yellow-green filtrate with a slight reddish tinge was added 30 mL of a saturated LiCl solution and the solution left at 5 °C overnight. In this way light green crystals were obtained, separated by filtration and washed twice with 10 mL of 99.9% ethanol. Upon recrystallization from 2 M HCl crytals appropriate for a single-crystal diffraction experiment were obtained. The yield of the recrystallized product was approximately 1.0 g (24% from *mer*-Mo(THF)$_3$Cl$_3$).

cis-[Mo([14]aneN$_4$)Cl$_2$]Cl was obtained according to the published procedure[2].

Spectra. The spectrometer setup was a Perkin-Elmer Lambda 2 interfaced with a PC. UV–vis spectra were recorded under an atmosphere of dinitrogen, and amalgamated zinc was added immediately before filling the cuvette in order to eliminate potential traces of oxidized species.

X-ray Crystallography

Due to the air-sensitivity of the light-green cis-[Mo([15]aneN$_4$)Cl$_2$]Cl·2H$_2$O, a prismatic crystal (0.2 × 0.2 × 0.5 mm^3) was quickly selected, mounted on a goniometer head, and transferred to a CAD4 diffractometer, where it was cooled to 122 K with an Enraf-Nonius liquid dinitrogen gas-flow device. Keeping the crystal in a stream of gaseous dinitrogen also prevented oxidation of the compound. The temperature was monitored with a thermocouple placed a few centimeters above the crystal in the exhaust pipe; it remained constant (±1 °C) throughout the data collection performed with graphite-monochromated Mo Kα radiation. The space group and unit cell dimensions were determined from the 2θ values of 22 reflections (19.9° < θ < 24.24°). The ω–2θ scan mode and scan range were selected from an analysis of the reflection profiles. The intensities of the standard reflections were recorded every 10 000 s and the crystal orientation was checked after every 300 reflections. These measurements certified that no missetting or deterioration of the crystal had taken place during the data collection. Reflections were measured

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Table 2. Positional Parameters and Isotropic Displacement Parameters, B_{eq}

atom	x	y	z	B_{eq},[a] Å^2
Mo	0.40746(1)	0.18917(1)	0.21268(1)	0.7556(7)
Cl1	0.56132(3)	0.21606(2)	0.02877(2)	1.367(3)
Cl2	0.63246(3)	0.00368(2)	0.25337(2)	1.636(3)
Cl3	0.13825(3)	0.69763(2)	0.54609(2)	1.584(3)
O1	−0.0163(1)	0.57160(9)	0.35244(6)	1.98(1)
O2	0.1385(2)	0.2936(1)	−0.16713(8)	2.81(2)
N1	0.53102(9)	0.32818(7)	0.30950(6)	1.087(8)
N4	0.26248(9)	0.16180(8)	0.37792(6)	1.119(9)
N8	0.2599(1)	0.04037(7)	0.14329(6)	1.157(9)
N12	0.22706(9)	0.37982(7)	0.18410(6)	1.031(8)
C2	0.4227(1)	0.34960(9)	0.41976(7)	1.38(1)
C3	0.3645(1)	0.2126(1)	0.45938(7)	1.42(1)
C5	0.2195(1)	0.02019(9)	0.40792(7)	1.41(1)
C6	0.1131(1)	−0.03583(9)	0.32822(8)	1.47(1)
C7	0.2186(1)	−0.07746(9)	0.21700(8)	1.48(1)
C9	0.1067(1)	0.0987(1)	0.08733(8)	1.62(1)
C10	0.0050(1)	0.2348(1)	0.13283(8)	1.60(1)
C11	0.1004(1)	0.3607(1)	0.10618(7)	1.44(1)
C13	0.3175(1)	0.50244(9)	0.14549(8)	1.40(1)
C14	0.4207(1)	0.55684(9)	0.22829(9)	1.52(1)
C15	0.5778(1)	0.45995(9)	0.25702(9)	1.46(1)

[a] $B_{eq} = (4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + 2ab(\cos\gamma)\beta_{12} + 2ac(\cos\beta)\beta_{13} + 2bc(\cos\alpha)\beta_{23}]$.

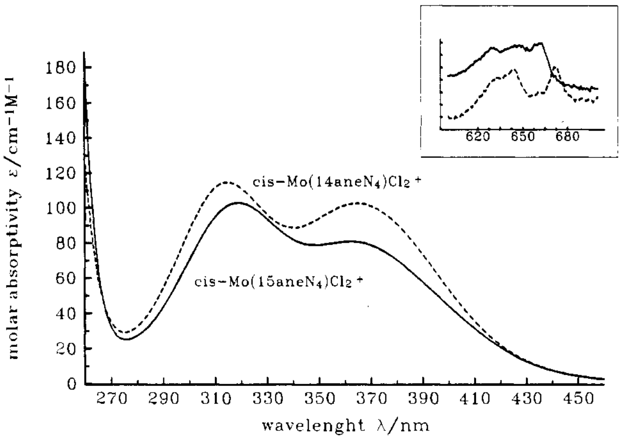

Figure 1. UV–vis spectra of *cis*-$[Mo([14]aneN_4)Cl_2]^+$ (- -) and *cis*-$[Mo([15]aneN_4)Cl_2]^+$ (—) in 1 M HCl at 20 °C. The insert illustrates the very weak transitions observed between 600 and 700 nm. For both of the compounds the molar absorptivity of these transitions were approximately 1 $cm^{-1}M^{-1}$.

in the hemisphere ±*h*±*kl* in the θ range 1–52°. A summary of the data collection and refinement results are given in Table 1.

The structure was solved by Patterson and heavy-atom Fourier methods. It was refined by a full-matrix least-squares analysis minimizing $\sum w(\Delta F)^2$. Data reduction included corrections for background, Lorentz, and polarization effects, but no correction for absorption. The fact that it was possible to locate even the hydrogen atoms before anisotropic displacement parameters were introduced we attribute to the high resolution of the diffraction data. In the final cycles of the least-squares refinement, the non-hydrogen atoms were refined with anisotropic displacement parameters and both the positional and isotropic thermal parameters of the hydrogen atoms were varied. The crystallographic computations were performed with the SDP program package.[7] Atomic scattering factors, including corrections for anomalous dispersion, were taken from ref 8 and used as provided by the software. The final positional parameters are listed in Table 2. The final difference electron densities had values between −1.3 and +1.3 e/Å^3 with the largest peaks and holes close to the molybdenum atom. The maximum shift in the last refinement cycle was 0.05σ. An inspection of the list of structure factors showed that no correction for extinction was required.

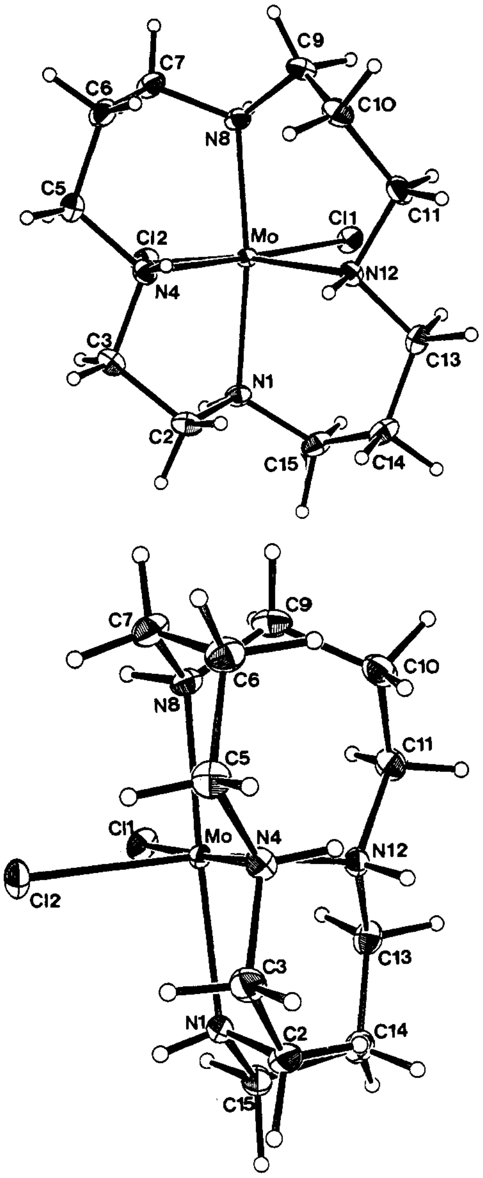

Figure 2. ORTEP drawings showing the atomic labeling of the cation *cis*-$[Mo([15]aneN_4)Cl_2]^+$ (a, top) and, in perspective, illustrating the conformation of the macrocyclic ligand $[15]aneN_4$ (b, bottom). These two figures are immediately comparable with those of ref 2.

Results and Discussion

The reaction of *mer*-$Mo(THF)_3Cl_3$ with $[15]aneN_4$ in THF yields a *cis*-tetraaminodichloro complex in an entirely analogous way to that previously reported for $[14]aneN_4$, and the methyl-substituted derivatives *cyca* and *cycb* (*meso*- and *rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane).[2] These reactions all proceed with rather low yields (<25%), and it is not yet clear which other products are formed in the reactions. Recently, a similar reaction has been reported with $[15]aneN_4$ and $Cr(dmf)_3Cl_3$ (dmf = *N,N'*-dimethylformamide) in boiling dmf.[9] This reaction proceeded to form *trans*-$[Cr([15]aneN_4)Cl_2]Cl$ in high yield. This difference might either be ascribed to the larger size of molybdenum(III) or the higher temperature achievable in dmf.

In Figure 1 the UV–vis spectra of *cis*-$[Mo([15]aneN_4Cl_2]Cl$ and *cis*-$[Mo([14]aneN_4)Cl_2]Cl$ are compared. Both spectra showed the same behavior when the solution was exposed to the atmosphere where the minimum at approximately 275 nm disapeared and a new band around 425 nm was observed.

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Table 3. Selected Bond Lengths (Å), Bond Angles (deg) and Torsion Angles (deg) for *cis*-[Mo(1,4,8,12-tetraazacyclopentadecane)Cl_2]Cl·$2H_2O$

	Bond Lengths		
Mo–Cl1	2.4241(2)	Mo–N4	2.2030(7)
Mo–Cl2	2.4363(2)	Mo–N8	2.2155(7)
Mo–N1	2.2147(7)	Mo–N12	2.2265(7)
	Bond Angles		
Cl1–Mo–Cl2	91.47(1)	Cl2–Mo–N12	171.48(2)
Cl1–Mo–N1	101.91(2)	N1–Mo–N4	79.61(3)
Cl1–Mo–N4	178.45(2)	N1–Mo–N8	170.22(3)
Cl1–Mo–N8	87.84(2)	N1–Mo–N12	84.18(3)
Cl1–Mo–N12	88.18(2)	N4–Mo–N8	90.65(3)
Cl2–Mo–N1	87.56(2)	N4–Mo–N12	91.68(3)
Cl2–Mo–N4	88.89(2)	N8–Mo–N12	97.09(3)
Cl2–Mo–N8	91.40(2)		

Torsion Angles	
N1–C2–C3–N4	−58.48(9)
N4–C5–C6–C7	73.04(10)
C5–C6–C7–N8	−74.91(10)
N8–C9–C10–C11	72.85(11)
C9–C10–C11–N12	−83.55(10)
N12–C13–C14–C15	64.82(11)
C13–C14–C15–N1	−61.89(11)

However, this change was somewhat slower for the [15]aneN$_4$ complex, which was stable for *ca.*$^1/_2$ h in air (<5% change in the spectrum). On air-oxidation the spectral changes can be summarized as follows: the green solution gradually turns yellow and becomes colorless within 24 h. These changes can probably be ascribed to an oxidation first to molybdenum(V) and then further to Mo(VI). However, these oxidation products have not been further characterized. The comparison of two spectra in Figure 1 shows a *cis*-dichloro configuration also of the [15]aneN$_4$ complex. The two absorption bands at 319 nm and 363 nm can therefore be assigned as originating from components of the $^4T_1(O_h) \leftarrow {}^4A_2(O_h)$ and $^4T_2(O_h) \leftarrow {}^4A_2(O_h)$ transitions, respectively. Using the approximation $^2/_3\Delta$([15]aneN$_4$) + $^1/_3\Delta$(Cl$^-$) for the average transition energy of the first band and Δ(Cl$^-$) = 1.9$_2$ μm^{-1} (taken from $MoCl_6^{3-}$)[10] from Hyldtoft *et al.*,[2] thereby Δ([15]aneN$_4$) = 3.1$_7$ μm^{-1} is found to be in good agreement with the results for cyclam and *cyca* (Δ(cyclam) $\approx$ Δ(*cyca*) $\approx$ 3.1 μm^{-1}). At *ca.* 640 nm three weak bands all with $\epsilon < 1$ cm^{-1} M^{-1} are observed for both compounds. These spin-forbidden transitions have not been assigned.

The data used in this low-temperature single crystal X-ray investigated correspond to a very high resolution. Table 2 lists the positional parameters and isotropic displacement parameters of the non-hydrogen atoms, and in Table 3 selected bond lengths and bond and torsion angles are listed. Table 4 contains hydrogen bond distances and angles. The bond lengths and bond angles around and molybdenum are very similar to those of the analogous [14]aneN$_4$ complex. However, the distortion of the coordination sphere from octahedral was less pronounced in the [15]aneN$_4$ complex (e.g., the angle N1–Mo–N8 is 162.7 and 170.2° for [14]aneN$_4$ and [15]aneN$_4$, respectively). ORTEP[11] drawings of the cation viewed from two different angles are shown in Figure 2, and it is evident from this figure that the coordination sphere of molybdenum(III) is rather distorted from octahedral apparently because of the steric requirements of the macrocyclic ligand [15]aneN$_4$. The average Mo^{III}–N bond length is 2.215(1) Å and the Mo–Cl bond lengths are 2.424(1) and 2.436(10 Å, respectively. Table 3 shows selected torsion angles, and from these it is apparent that the three six-membered rings are all in distorted chair conformations and the five-membered ring adopts a gauche conformation. The less distorted coordination sphere of the [15]aneN$_4$ complex compard to that of the [14]aneN$_4$ complex may account for the relatively larger stability toward air-oxidation of the [15]aneN$_4$ complex as we would predict that the oxidation of molybdenum(III) leads to a reduction in the size of molybdenum and therefore, this reaction could be less favorable with the larger macrocyclic ligand.

Table 4. Hydrogen Bond Distances (Å) and Angles (deg)

D–H–A	D–H	D–H–A	H–A	D–A
O1–HW11–Cl3	0.86(3)	162(2)	2.26(3)	3.0868(10)
O1–HW12–Cl3	0.86(2)	171(2)	2.30(2)	3.1514(9)
O2–HW21–O1	1.02(3)	161(3)	1.84(3)	2.8245(13)
O2–HW22–Cl2	0.80(3)	172(3)	2.51(3)	3.2998(10)
N1–H11–Cl3	0.847(16)	138(2)	2.62(2)	3.2995(7)
N4–H41–Cl3	0.89(2)	160(2)	2.38(2)	3.2345(8)
N8–H81–Cl1	0.97(2)	142(2)	2.51(2)	3.2218(7)
N12–H121–O1	0.93(1)	150(2)	2.23(2)	3.0698(11)

We are currently further investigating the formation of molybdenum(III) complexes with ammonia and other amine ligands.

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Supplementary Material Available: Tables giving crystal data and details of the structure determination, atom coordinates, anisotropic displacement parameters, and positional parameters for the hydrogen atoms and a stereoscopic drawing of the unit cell (5 pages). Ordering information is given on any current masthead page.

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