Preparation, Characterization and Crystal Structure of Some New Molybdenum(III) Amines Coordinated with Macrocyclic Tetraamine Ligands

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$[MoCl_3(thf)_3]$ (thf = tetrahydrofuran) reacts with 1,4,8,11-tetraazacyclotetradecane (cyclam) and *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (cyc*a*) in tetrahydrofuran, to give compounds containing *cis*-tetraaminedichloromolybdenum(III) cations. The compounds have been characterized by their UV-VIS spectra, and also by structure determinations. *cis*-$[Mo(cyclam)Cl_2]Cl$ crystallizes in the space group $P2_1/c$ with a = 7.553(3), b = 14.367(6), c = 14.716(4) Å, β = 101°. 67(3) and Z = 4. The crystals of *cis*-$[Mo(cyca)Cl_2]CF_3SO_3 \cdot 2H_2O$ are triclinic, space group $P\bar{1}$, with a = 9.485(12), b = 10.546(7), c = 15.160(8) Å, α = 83.97(5), β = 75.14(8), γ = 66.14(8)° and Z = 2. In both complexes the macrocyclic ligand is folded to give *cis* complexes, with a distorted octahedral coordination of molybdenum(III). The *cis*-$[Mo(cyclam)Cl_2]^+$ ion possesses a two-fold symmetry axis, with the five- and six-membered chelate rings in gauche and chair conformations, respectively. In the cyc*a* complex one half of the ring system resembles that of the cyclam complex, but the other half has the six-membered ring in a twisted boat conformation and the five-membered ring in a gauche conformation which is the mirror image of the other five-membered ring. The Mo-Cl and Mo-N bond lengths are in the range 2.421(1) to 2.441(4) Å, and 2.197(3) to 2.246(5) Å, respectively. The equilibrium constant for the reaction:

$$cis\text{-}[Mo(cyclam)Cl_2]^+ \rightleftharpoons cis\text{-}[Mo(cyclam)Cl(OH_2)]^{2+} + Cl^-$$

is 0.061(4) M in 1 M CF_3SO_3H at 25 °C.

Macrocyclic ligands play an increasingly important role in coordination chemistry, and tetraamine complexes of 1,4,8,11-tetraazacyclotetradecane (cyclam; cf. Fig. 1) and derivatives of this ring system have been studied for a large number of metal ions. Amine complexes of molybdenum have long been conspicuous by their absence, and it was not until recently that cyclic triamines such as 1,4,7-triazacyclononane,[1] 1,4,7-trimethyl-1,4,7-triazacyclononane[2] and 1,5,9-triazacyclododecane[3] were found to react with hexacarbonylmolybdenum(0) to give [Mo(triamine) $(CO)_3$]. Oxidation of these compounds gave rise to amine complexes in various other oxidation states, including +II to +VI. *meso*- and *rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (cyc*a* and cyc*b*, respectively; cf. Fig. 1) have been found to react analogously with $[Mo(CO)_6]$, and products with three-coordinated nitrogen atoms have been isolated.[4] Oxidation of these molybdenum (0) species failed, however, to give well-defined amine complexes in a higher oxidation state.

The present work decribes the preparation and structure of the first tetraaminemolybdenum(III) complexes of the macrocyclic ligands of Fig. 1, starting from trichlorotris-(tetrahydrofuran)molybdenum(III).

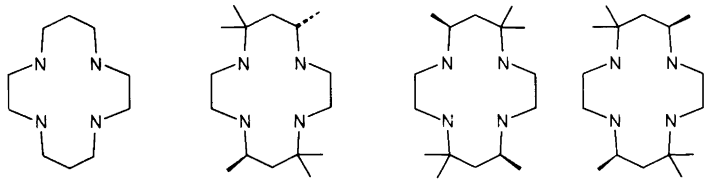

Fig. 1. 1,4,8,11-tetraazacyclotetradecane, and *meso*- and *rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane.

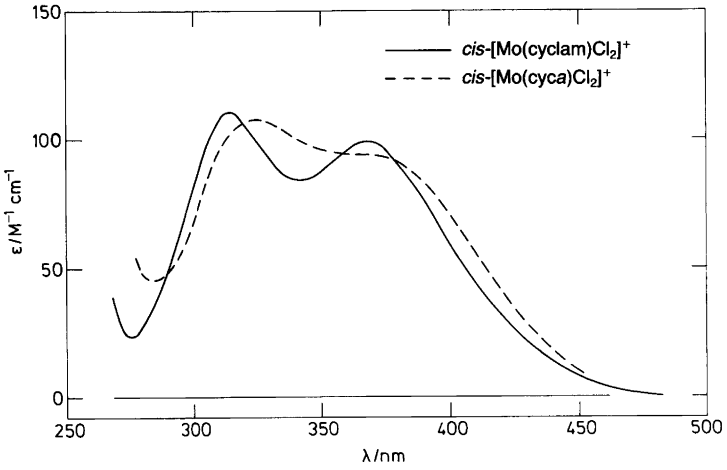

Fig. 2. Absorption spectra of *cis*-$[Mo(cyclam)Cl_2]^+$ and *cis*-$[Mo(cyca)Cl_2]^+$ in 1 M HCl at 25 °C.

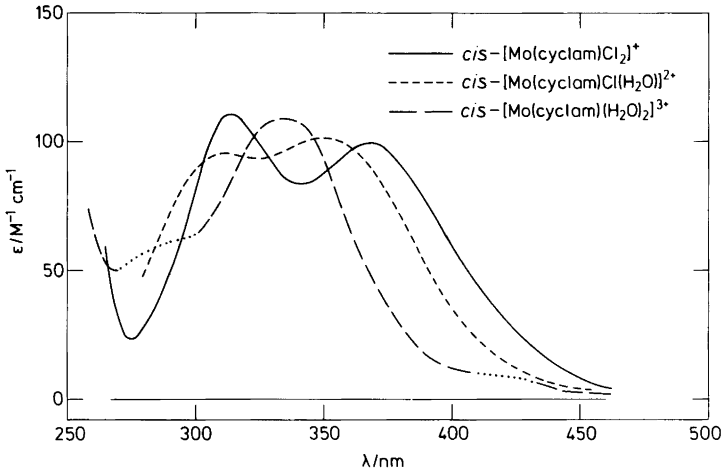

Fig. 3. Absorption spectra of *cis*-$[Mo(cyclam)Cl_2]^+$ in 1 M HCl, *cis*-$[Mo(cyclam)Cl(H_2O)]^{2+}$ as calculated from the equilibrium measurements and *cis*-$[Mo(cyclam)(H_2O)_2]^{3+}$ in 1 M CF_3SO_3H at 25 °C. Dotted curves around 280 nm and 420 nm for the *cis*-$[Mo(cyclam)(OH_2)_2]^{3+}$ spectrum show ranges where the spectral properties are most sensitive to oxidation (see text).

Results and discussion

Chemical properties. Trichlorotris(tetrahydrofuran)molybdenum(III) reacts with the cyclic tetraamines of Fig. 1 to give compounds containing the *cis*-tetraaminedichloromolybdenum(III) ion. Absorption spectra of the cyclam and cyc*a* compounds in 1 M hydrochloric acid are shown in Fig. 2. These spectra depend on the chloride concentration in a manner conistent with the equilibrium:

$$cis\text{-}[Mo(cyclam)Cl_2]^+ + H_2O \rightleftharpoons cis\text{-}[Mo(cyclam)(OH_2)Cl]^{2+} + Cl^-$$

for which $K^{-1} \approx 16.3(1.1)$ M^{-1} at 25 °C in 1.0 M (H, Cs)(Cl, CF_3SO_3). This value is somewhat larger than K_1 for the system $[Mo(OH_2)_6]^{3+} + Cl^-$, which is ≈ 11 M^{-1},[5] but this trend is normally observed on going from classical complexes to complexes containing macrocyclic ligands.

Coordinated chloride may be removed by reaction with neat trifluoromethanesulfonic acid, which provides a route to the diaqua complex. Absorption spectra of the chloride- and water-containing species are given in Fig. 3. The absorbance around 275 nm is an extremely sensitive indicator for oxidation, and a low absorption coefficient was only obtained when the solutions were reduced with amalgamated zinc. On oxidation, the minimum disappears simultaneously with the appearance of an absorption band around 425 nm. This occurs both for the diaqua and the dichloro complex, but the former complex is apparently more susceptible to oxidation as judged from the spectral changes. Qualitatively, the reaction seems to be analogous to dioxygen reduction by hexaaquamolybdenum(III).[6]

Spectral properties. A comparison of the UV-vis absorption spectra of the present molybdenum(III) species (Figs 2 and 3) with those of hexaaquamolybdenum(III)[7] and hexachloromolybdate(III)[8] leads to an assignment of the absorption bands around 370 nm and 310 nm as originating from components of the $^4T_2(O_h) \leftarrow {}^4A_2(O_h)$ and $^4T_1(O_h) \leftarrow {}^4A_2(O_h)$ transitions, respectively. A weak transition around 650 nm in the *cis*-$[Mo(cyclam)Cl_2]^+$ complex may be assigned to a spin-forbidden transition. The average transition energy of the components of the first spin-allowed absorption band for a *cis*-tetraaminedichloro complex with a d^3 electronic configuration is to a good approximation given by 2/3 Δ(amine) + 1/3 Δ(Cl^-). Taking Δ(Cl^-) $\approx 1.9_2$ μm^{-1}

gives Δ(cyclam) $\approx 3.1_5$ μm^{-1} and Δ(cyc*a*) $\approx 3.1_3$ μm^{-1}, respectively. This former value is substantiated by Δ (cyclam) $\approx 3.2_1$ μm^{-1} obtained from the *cis*-[Mo(cyclam)$(OH_2)_2]^{3+}$ spectrum and $\Delta(OH_2) \approx 2.5_1$ μm^{-1}. Summarizing: the usual order in the spectrochemical series: Δ(amine) > $\Delta(OH_2)$ > $\Delta(Cl^-)$ is seen also for a molybdenum(III) center.

Table 1. Coordination geometry around the molybdenum atoms illustrated by bond lengths (Å) and bond angles (°) in the two cations.

	cis-[Mo(cyclam)$Cl_2]^+$	*cis*-[Mo(cyc*a*)$Cl_2]^+$
Mo-Cl1	2.4206(12)	2.437(4)
Mo-Cl2	2.4276(12)	2.441(4)
Mo-N1	2.208(3)	2.206(5)
Mo-N4	2.197(3)	2.246(5)
Mo-N8	2.208(3)	2.199(5)
Mo-N11	2.197(3)	2.213(4)
Cl1-Mo-C12	91.93(3)	85.77(4)
Cl1-Mo-N1	97.18(7)	100.49(9)
Cl1-Mo-N4	177.16(8)	178.26(8)
Cl1-Mo-N8	94.66(8)	93.12(9)
Cl1-Mo-N11	88.52(7)	88.12(9)
Cl2-Mo-N1	95.94(5)	92.43(8)
Cl2-Mo-N4	87.52(8)	95.79(9)
Cl2-Mo-N8	96.21(7)	97.56(9)
Cl2-Mo-N11	176.35(7)	173.44(9)
N1-Mo-N4	80.11(10)	80.22(12)
N1-Mo-N8	162.71(10)	163.67(12)
N1-Mo-N11	87.59(10)	91.01(12)
N4-Mo-N8	88.17(10)	85.93(12)
N4-Mo-N11	92.20(10)	90.29(12)
N8-Mo-N11	80.14(10)	80.39(12)

Description of the structures. Different views of the complex cations *cis*-[Mo(cyclam)$Cl_2]^+$ and *cis*-[Mo(cyc*a*)$Cl_2]^+$ are shown in Figs. 4 and 5, and selected bond distances and angles are given in Tables 1 and 2. The macrocyclic ligand is seen to be folded in both cases to give *cis* complexes with a distorted octahedral coordination around the metal center.

From the data presented it is apparent that within the experimental accuracy, *cis*-[Mo(cyclam)$Cl_2]^+$ possesses a two-fold axis of symmetry with the five- and six-membered chelate rings in gauche and chair conformations, respectively. Since the compound crystallizes in a centric space group, the individual ions have either (λ, λ) or (δ, δ) conformations of the five-membered chelate rings.

It is evident from the data that the *cis*-[Mo(cyc*a*)$Cl_2]^+$ cation does not possess a similar two-fold axis of symmetry. The folding and conformation of that half of the cyc*a* ligand which is spanned by N4-C5···C10-N11 is similar to the stereochemistry observed in the cyclam complex, but the other half of the cyc*a* ligand is different. It has the five-membered chelate ring in the mirror image conformation with a dihedral angle twisted about 10° away from the staggered conformation. The conformations of the two five-membered rings in this complex are therefore (λ, δ) or (δ, λ), as the structure is centrosymmetric. The six-membered ring defined by the N11 and N1 donor atoms is in a conformation that can be classified as a twisted boat. This is grossly different from the usual chair conformation seen for the other six-membered rings, which is normally considered to be the most stable conformation. Model building of the complex with the chelate ring in the usual chair conformation shows, however, that this conformation leads to significant interactions between a methyl group and a chloride ligand, as well as to interactions between two axial

Table 2. Comparison of bond lengths (Å), and torsion angles (°) in the macrocyclic ligands of the two cations.

	cis-[Mo(cyclam)$Cl_2]^+$		*cis*-[Mo(cyc*a*)$Cl_2]^+$	
A-B-C-D	N1-C2-C3-N4	N8-C9-C10-N11	N1-C2-C3-N4	N8-C9-C10-N11
A-B	1.496(4)	1.489(4)	1.490(6)	1.500(6)
B-C	1.516(5)	1.512(4)	1.502(6)	1.509(6)
C-D	1.491(4)	1.489(4)	1.509(6)	1.500(6)
A-B-C	109.4(3)	109.3(3)	111.1(3)	109.3(3)
B-C-D	108.6(3)	109.4(3)	112.8(3)	109.3(3)
A-B-C-D	−57.5(6)	−57.0(6)	49.3(6)	−57.7(6)
A-B-C-D-E	N4-C5-C6-C7-N8	N11-C12-C13-C14-N1	N4-C5-C6-C7-N8	N11-C12-C13-C14-N1
A-B	1.492(4)	1.481(4)	1.535(6)	1.535(5)
B-C	1.521(5)	1.527(5)	1.526(6)	1.541(7)
C-D	1.520(5)	1.522(4)	1.541(7)	1.526(6)
D-E	1.497(4)	1.496(4)	1.515(6)	1.501(5)
A-B-C	112.1(3)	112.2(3)	106.3(3)	110.4(3)
B-C-D	116.3(3)	115.9(3)	121.4(3)	115.9(4)
C-D-E	114.4(3)	113.9(3)	112.2(3)	108.4(3)
A-B-C-D	70.4(7)	70.1(7)	59.5(7)	−46.1(7)
B-C-D-E	−67.2(7)	−67.6(7)	−70.6(7)	93.7(7)

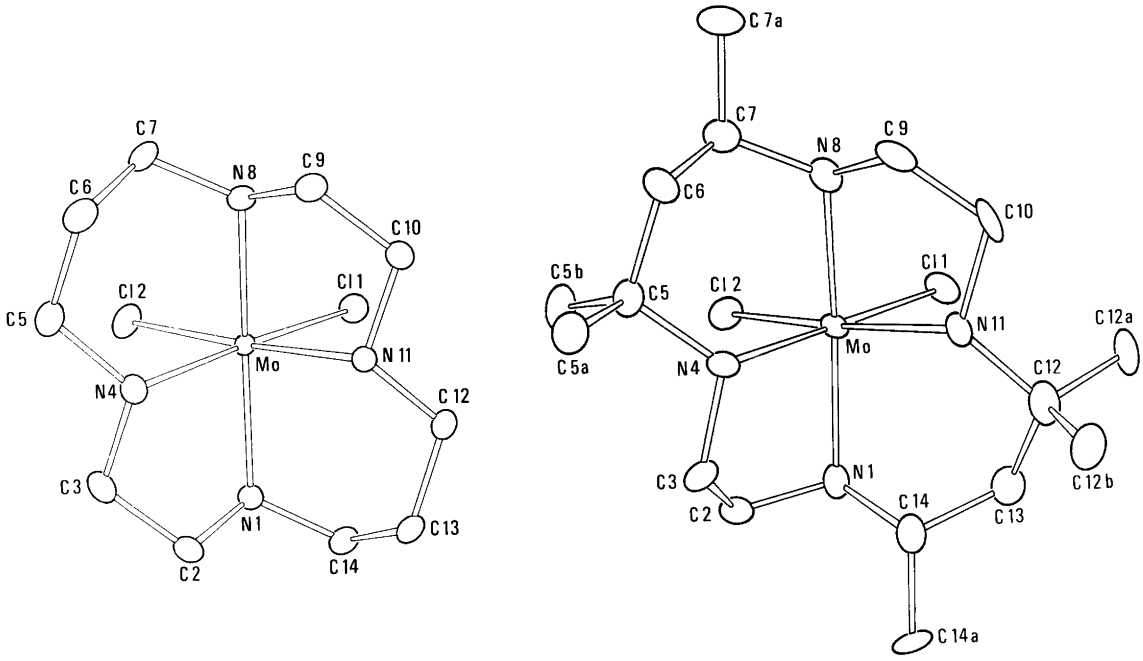

Fig. 4. ORTEP drawings showing the atomic labelling of the two cations *cis*-[Mo(cyclam)Cl_2]$^+$ (left) and *cis*-[Mo(cyc*a*)Cl_2]$^+$ (right).

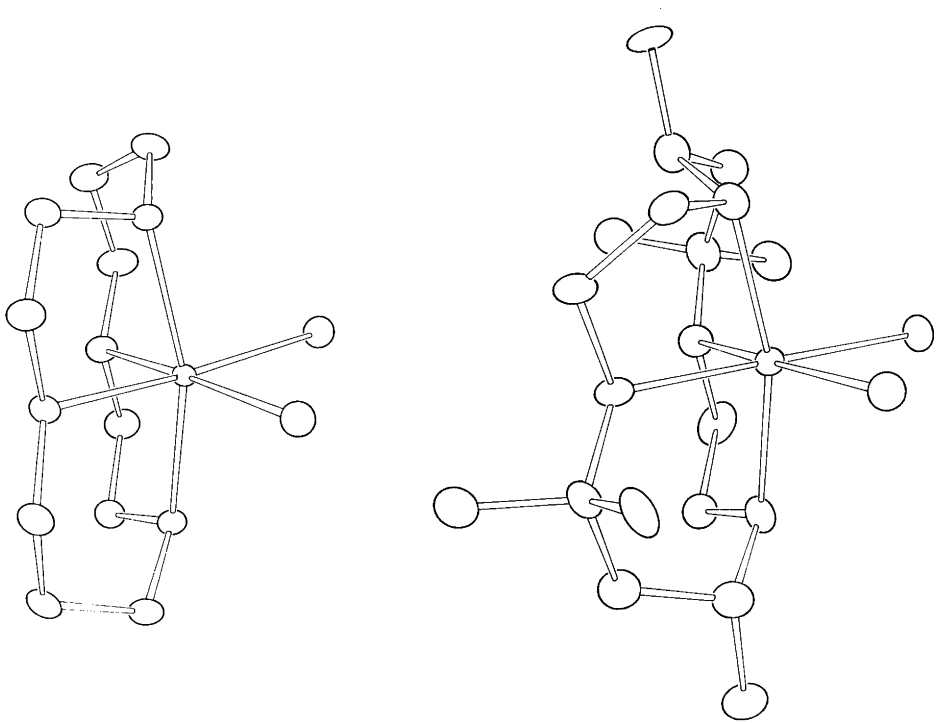

Fig. 5. Perspective ORTEP drawings showing the conformations of the macrocyclic ligands in *cis*-[Mo(cyclam)Cl_2]$^+$ (left) and *cis*-[Mo(cyc*a*)Cl_2]$^+$ (right).

Table 3. Molecular dimensions (Å and °) of the $CF_3SO_3^-$ ion in *cis*-[Mo(cyc*a*)Cl_2]$CF_3SO_3 \cdot 2H_2O$.

C-S	1.805(6)		
S-O(1S,2S,3S)	1.451(4)	1.452(4)	1.423(4)
C-F(1,2,3)	1.324(6)	1.354(5)	1.338(6)
S-C-F(1,2,3)	113.7(3)	110.7(3)	110.5(3)
C-S-O(1S,2S,3S)	103.4(2)	102.6(2)	104.4(2)

methyl groups. Both types of interactions are reduced in the twisted boat conformation.

The central atom to donor atom distances in the present cations are all similar to values found in related chloro and amine molybdenum(III) structures. The bond lengths of the two halves of the cyc*a* ligand in the *cis*-[Mo(cyc*a*)Cl_2]$^+$ cation are virtually identical, but larger variations between the bond angles are connected with the different conformations. The four chiral nitrogen atoms in each of these two closely related cations are of identical chirality, and the crystals contain equal numbers of the *R,R,R,R* and *S,S,S,S* isomers.

A pronounced distortion of the ($MoCl_2N_2$)-plane is observed in both cations. In the cyclam complex the distortion is tetrahedral, with N11 and Cl1 0.066 Å above the mean plane while N4 and C12 are 0.064 Å below. The distortion of the cyc*a* complex is not as regular; here Mo, Cl1 and N4 are 0.025, 0.011 and 0.011 Å, respectively, below the mean plane, and Cl2 and N11 both 0.024 Å above. The shift of N1 and N8 away from the normal to the mean plane to give (N1-Mo-N8)-angles around 163° represents another deviation from an idealized octahedral symmetry.

The anion in *cis*-[Mo(cyc*a*)Cl_2]$CF_3SO_3 \cdot 2H_2O$ is found in the usual staggered conformation, with bond lengths and angles in agreement with the values found in other structure determinations (cf. Table 3). The two slightly larger S-O bonds involve the oxygen atoms hydrogen-bonded to water.

It is obvious from Fig. 7 and the data for hydrogen bonds in Table 4 that the crystal packing of *cis*-[Mo(cyc*a*)Cl_2]$CF_3SO_3 \cdot 2H_2O$ is dominated by hydrogen bonding in two dimensions, and that all the possible donor atoms are involved in these bonds. The complex cations are linked by hydrogen bonds between the two coordinated chloride ligands and the nitrogen atoms N1 and N8, forming infinite chains in the direction of the *a*-axis. Similar chains are

Table 4. Hydrogen bond distances (Å) and angles (°) in *cis*-[Mo(cyc*a*)Cl_2]$CF_3SO_3 \cdot 2H_2O$.

D-H···A	Dist(D···A)	Angle(D-H···A)
N1-H···Cl2[a]	3.397(6)	163
N4-H···O2	2.933(6)	161
N8-H···Cl1[b]	3.379(6)	141
N11-H···O2	2.993(6)	167
O1-H···O1S	2.904(6)	175
O1-H···O2S	2.787(6)	176
O2-H···O1S	2.860(6)	153
O2-H···O1	2.729(6)	155

[a](1-*x*, 1-*y*, -*z*), [b](-*x*, 1-*y*, -*z*).

Table 5. Hydrogen bond distances (Å) and angles (°) in *cis*-[Mo(cyclam)Cl_2]Cl.

D-H···A	Dist(D···A)	Angle(D-H···A)
N1-H···Cl3[a]	3.223(3)	151
N4-H···Cl3[b]	3.217(3)	173
N8-H···Cl3[c]	3.242(3)	158
N11-H···Cl3[b]	3.264(3)	164

[a](*x*, 1/2-*y*, 1/2+*z*), [b](*x*, *y*, *z*+1), [c](1+*x*, *y*, 1+*z*).

formed by the anions and the water of crystallization, and these two types of one-dimensional arrays are held together by hydrogen bonds from the N4 and N11 hydrogens to one of the waters of crystallization. By comparison, the significant intermolecular interactions in *cis*-[Mo(cyclam)Cl_2]Cl give a two-dimensional net of hydrogen bonds between the chloride anions and four nitrogen-bound hydrogen atoms on three different cations. This is shown in Fig. 7 and Table 5.

Many other metal complexes containing cyclam as ligand have been investigated. These usually have a *trans* configuration, but *cis* complexes of Cr(III),[9] Co(III),[10] Ni(II),[11] Ru(III)[12] and Pb(II)[13] have also been characterized structurally. The ligand geometry of the present *cis*-[Mo(cyclam)Cl_2]$^+$ ion is similar to that of the previously investigated *cis* complexes. Molecular mechanics calculations have indicated the ideal metal–nitrogen distance to be 2.07 Å in a *trans* cyclam complex.[14] This is significantly smaller than the average molybdenum–nitrogen distance in the present compound, which is about 2.20 Å, and is the

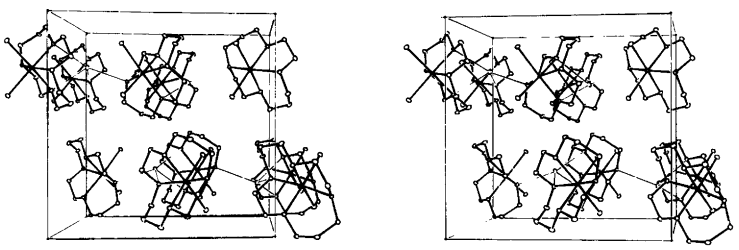

Fig. 6. Stereoscopic pair showing the packing in *cis*-[Mo(cyclam)Cl_2]Cl. The structure is viewed along the crystallographic a^* axis. The hydrogen bonds are drawn as thin lines.

Table 6. Crystal data, and data collection and reduction characteristics.

	cis-[Mo(cyclam)Cl_2]Cl	*cis*-[Mo(cyca)Cl_2]$CF_3SO_3 \cdot 2H_2O$
Formula	$MoCl_3N_4C_{10}H_{24}$	$MoCl_2SF_3O_5N_4C_{17}H_{40}$
MW/g mol^{-1}	402.6	636.4
Space group	Monoclinic $P2_1/c$	Triclinic $P\bar{1}$
Cell parameters at 110 K:		
a/Å	7.553(3)	9.485(12)
b/Å	14.367(6)	10.546(7)
c/Å	14.716(4)	15.160(8)
α/°	90.0	83.97(5)
β/°	101.67(3)	75.14(8)
γ/°	90.0	66.14(8)
V/Å^3	1564(2)	1340(2)
D_m/g cm^{-3}	1.64	
D_c/g cm^{-3}	1.710	1.487
Z	4	2
F(000)	820	658
μ(Mo*K*α)/cm^{-1}	13.27	8.0
Crystal size/mm	0.25×0.25×0.10	0.15×0.25×0.25
Scan mode	ω/2θ	ω
Scan range, Δω	1.3 + 0.35 tanθ	3.5
θ-range/°	1–30	1–22
No. of reflections:		
Independent	4550	3457
Observed [$F_{obs} \geq 2\sigma(F)$][a]	3513	2753
No. of parameters	183	298
R[b]	0.038	0.051
1/*w*	$\sigma^2(F) + 0.009\ F^2$	$\sigma^2(F) + 0.0006\ F^2$
R_w	0.045	0.071

[a]σ(*F*) determined from counting statistics. [b]Minimization of $\Sigma(F_{obs} - F_{calc})^2$.

most likely reason why a *cis* configuration is adopted. Suitable methyl substituents increase the probability of forming *trans* complexes, and the literature contains no examples of octahedral *cis* cyc*a* complexes with only monodentate ligands in the remaining coordination sphere. For a molybdenum(III) center this methyl substitution is apparently not sufficient to overcome an unfavourable metal–nitrogen bond distance, and instead the ligand adopts an unfavourable conformation. Previously, a *cis* configuration of a cyc*a* complex has only been seen in a nickel(II) complex which also contained a chelate acetylacetonate anion.[15] In contrast to the present molybdenum(III) complex which has the ligand folded along the N1-N8 axis, the nickel(II) complex is folded along the N4-N11 axis.

Experimental

Preparations. All preparations were carried out under dinitrogen using standard vacuum techniques and Schlenk equipment. [$MoCl_3(thf)_3$][16] and cyclam[17] were prepared according to the literature. cyc*a* · $2H_2O$ and cyc*b* · H_2O were prepared and purified according to the literature.[18] All other reagents were commercial products.

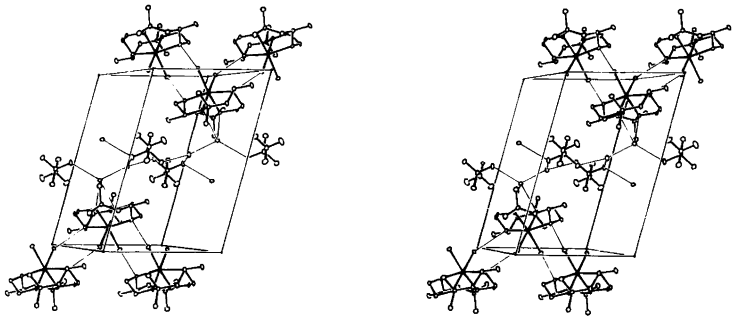

Fig. 7. Stereoscopic pair showing the packing in *cis*-[Mo(cyca)Cl_2]$CF_3SO_3 \cdot 2H_2O$ viewed along the crystallographic *b** axis. Hydrogen bonds are shown as thin lines.

Table 7. Fractional coordinates and equivalent isotropic thermal parameters in units of Å^2 for *cis*-[Mo(cyclam)Cl_2]Cl.

Atom	*x*	*y*	*z*	B_{iso}[a]
Mo	0.18919(3)	0.23969(2)	0.11183(2)	0.782(4)
Cl1	−0.0006(1)	0.13268(6)	0.17604(6)	1.50(1)
Cl2	0.0931(1)	0.37028(6)	0.19472(6)	1.77(1)
N1	0.4423(4)	0.2126(2)	0.2131(2)	1.13(5)
C2	0.5930(5)	0.2650(3)	0.1842(3)	1.39(6)
C3	0.5215(5)	0.3565(3)	0.1402(3)	1.68(6)
N4	0.3711(4)	0.3365(2)	0.0601(2)	1.34(5)
C5	0.2867(6)	0.4237(3)	0.0163(3)	2.02(7)
C6	0.1436(5)	0.4042(3)	−0.0703(3)	1.89(7)
C7	−0.0304(5)	0.3594(2)	−0.0550(3)	1.61(6)
N8	−0.0088(4)	0.2618(2)	−0.0189(2)	1.16(5)
C9	0.0324(5)	0.1969(3)	−0.0908(3)	1.53(6)
C10	0.1017(5)	0.1059(2)	−0.0454(3)	1.46(6)
N11	0.2632(4)	0.1242(2)	0.0291(2)	1.10(5)
C12	0.3327(5)	0.0384(2)	0.0797(3)	1.40(6)
C13	0.5086(5)	0.0555(2)	0.1497(3)	1.47(6)
C14	0.4922(5)	0.1131(3)	0.2345(2)	1.49(6)
Cl3	0.5632(1)	0.21503(6)	0.92384(6)	1.43(1)

[a] $B_{iso} = 8\pi^2/3 \sum_i \sum_j U_{ij}\, a_i \cdot a_j\, a_i^*\, a_j^*$.

Table 8. Fractional coordinates and isotropic thermal parameters in units of Å^2 for *cis*-[Mo(cyca)Cl_2]$CF_3SO_3 \cdot 2H_2O$.

Atom	*x*	*y*	*z*	B_{iso}[a]
Mo	0.27509(5)	0.39415(5)	0.11558(3)	1.09(1)
Cl1	0.1640(2)	0.5737(2)	0.0087(1)	1.79(3)
Cl2	0.4862(2)	0.2841(1)	−0.0166(1)	1.78(3)
N1	0.4224(5)	0.4793(5)	0.1608(3)	1.5(1)
C2	0.5565(6)	0.3528(6)	0.1801(4)	1.6(1)
C3	0.4968(6)	0.2577(6)	0.2449(4)	1.5(1)
N4	0.3701(5)	0.2304(5)	0.2169(3)	1.3(1)
C5	0.4092(6)	0.0763(6)	0.2043(4)	1.5(1)
C5a	0.4305(7)	0.0023(6)	0.2957(5)	1.9(2)
C5b	0.5570(7)	0.0117(6)	0.1299(4)	1.9(1)
C6	0.2670(7)	0.0615(6)	0.1841(4)	1.9(1)
C7	0.2018(7)	0.1319(6)	0.1005(4)	1.9(1)
C7a	0.0912(7)	0.0701(7)	0.0825(5)	2.5(2)
N8	0.1198(5)	0.2880(5)	0.1108(3)	1.5(1)
C9	−0.0224(6)	0.3360(6)	0.1894(4)	1.8(1)
C10	−0.0703(6)	0.4879(6)	0.2063(4)	1.9(1)
N11	0.0669(5)	0.5093(5)	0.2242(3)	1.5(1)
C12	0.0324(7)	0.6576(6)	0.2500(4)	2.0(2)
C12a	−0.0935(7)	0.7646(6)	0.2052(5)	2.3(2)
C12b	−0.0310(7)	0.6718(6)	0.3546(5)	2.2(2)
C13	0.1836(7)	0.6870(6)	0.2196(5)	2.1(2)
C14	0.3344(7)	0.5734(6)	0.2419(4)	1.8(1)
C14a	0.4382(7)	0.6351(6)	0.2687(4)	2.1(1)
S	0.2758(2)	0.7355(2)	0.5553(1)	1.91(4)
O1S	0.1649(4)	0.7088(4)	0.5171(3)	2.4(1)
O2S	0.4244(5)	0.7189(5)	0.4903(3)	2.7(1)
O3S	0.2884(5)	0.6772(5)	0.6433(3)	2.7(1)
C	0.1837(7)	0.9203(7)	0.5746(5)	2.6(2)
F1	0.1615(4)	0.9943(4)	0.4995(3)	3.1(1)
F2	0.0417(4)	0.9552(4)	0.6354(3)	3.6(1)
F3	0.2735(4)	0.9616(4)	0.6101(3)	3.8(1)
O1	0.2829(5)	0.4202(4)	0.4653(3)	2.5(1)
O2	0.1209(4)	0.3111(4)	0.3852(3)	1.8(1)

[a] $B_{iso} = 8\pi^2/3 \sum_i \sum_j U_{ij}\, a_i \cdot a_j\, a_i^*\, a_j^*$.

cis-*[Mo(cyclam)Cl$_2$]Cl*. 3.0 g of [$MoCl_3(thf)_3$] (7.1 mmol) and 1.4 g of cyclam (7.1 mmol) are heated under reflux in 80 ml of thf for 2 h. After cooling to 0 °C, the solid is filtered off, washed with 10 ml of ice-cold thf, and then dried in vacuum. The slightly grey and very air sensitive product is recrystallized by treatment with 50 ml of boiling 1 M HCl for a few minutes, filtering and addition of 50 ml of saturated aqueous NaCl to the warm brown filtrate. On slow cooling of the solution a dark green precipitate is formed. This is filtered off, washed with a little 96% ethanol, and recrystallized twice by dissolution in 50 ml of 1 M boiling HCl, filtering and slowly cooling the solution. This gives light green crystals which are collected by filtration, washed with a little 96% ethanol and dried in vacuum. Yield 0.29 g (10%). Anal. $MoC_{10}H_{24}N_4Cl_3$: Mo, Cl, N, C, H. In solution the compound is oxidized by air in minutes but when dry the solid complex can be handled for short periods of time in air without oxidation.

cis-*[Mo(cyca)Cl$_2$]CF$_3$SO$_3$ · 2H$_2$O*. 3.0 g of [$MoCl_3(thf)_3$] (7.1 mmol) and 2.0 g of anhydrous cyc*a* (7.0 mmol) are heated under reflux for 12 h in 80 ml of thf. cyc*a* · $2H_2O$ apparently does not react with [$MoCl_3(thf)_3$] and it is important to dry the amine at 110 °C for some hours before using it for the reaction. After cooling to 0 °C the suspension is filtered, and the greyish product is washed with 10 ml of thf and dried in vacuum. The crude product is dissolved by treatment with 150 ml of boiling 1 M CF_3SO_3H for a few minutes. The solution is filtered and 100 ml of saturated NaCl are added to the warm pink filtrate. On cooling, a dark green product precipitates. This product is recrystallized twice by dissolution in 50 ml of 1 M boiling CF_3SO_3H, filtration and addition of 1 ml of saturated aqueous NaCl to the filtrate. Yield 0.80 g (18%). Anal. $MoCl_{17}H_4Cl_2F_3SO_5$: Mo, Cl, N, C, H. This complex is more sensitive towards oxidation than the cyclam compound.

cis-*[Mo(cycb)Cl$_2$]CF$_3$SO$_3$ · xH$_2$O* can be prepared analogously to the cyc*a* compound, but except for measuring its absorption spectrum it was not investigated further.

cis-*[Mo(cyclam)(CF$_3$SO$_3$)$_2$]CF$_3$SO$_3$*. 0.5 g of *cis*-[Mo(cyclam)Cl_2]Cl is dissolved in 5 ml of neat CF_3SO_3H at room temperature, and dinitrogen is passed through the solution for 1/2 h to remove the Cl^- as HCl.[19] A solid compound is precipitated by addition of 40 ml of ether and isolated by filtration as a white compound. The complex is washed with ether, dried in vacuum, redissolved in CF_3SO_3H and the procedure for removal of chloride repeated. This complex is extremely sensitive towards oxidation and it was not possible to obtain a completely reproducible absorption spectrum (cf. Fig. 3).

Spectrophotometric measurements. UV-VIS absorption spectra were measured at 25 °C on a Cary 118 spectrophotometer equipped with a thermostatted cell holder. Reproducible spectra of the dichloro complexes were only obtained when the solutions were reduced with amalgamated zink immediately before filling the cuvette. The handling of solutions and recording of the spectra took place under dinitrogen.

Hydrolysis. Solutions with molybdenum(III)-concentrations around 4 mM and with total chloride concentrations varying from 12 mM to 1.0 M were made by dissolving the cyclam compound in 1.0 M CF_3SO_3H and adding solid CsCl and water to obtain the desired Cl^- concentration. Solutions were equilibrated at 25 °C with amalgamated zinc. Absorption spectra were recorded between 280 and 460 nm, and data for 10 solutions at 10 nm intervals were used to evaluate K_1 for the loss of the first chloride ligand and the spectrum of the *cis*-[Mo(cyclam)Cl(OH_2)]$^{2+}$ ion.[20]

X-Ray crystallography. Crystals of *cis*-[Mo(cyclam)Cl_2]Cl and *cis*-[Mo(cyc*a*)Cl_2]CF_3SO_3 · $2H_2O$ suitable for diffraction studies were obtained as described above. The compounds were characterized by room-temperature Weissenberg and precession photographs. The data collection at 110 ± 0.5 K for the two structures was performed with an Enraf–Nonius CAD 4 diffractometer equipped with an Enraf–Nonius gas-flow low-temperature device. The crystal data and a summary of the data collection and structure refinement results are listed in Table 6.

The structures were solved by Patterson and Fourier methods, and refined by the method of least squares using the Enraf–Nonius SDP-system.[21] The atomic scattering factors[22] and the anomalous dispersion corrections used for Mo, Cl, S, O, N, C, and F[23] were those contained in the program system.

The final atomic coordinates are listed in Tables 7 and 8, and additional details concerning the two structure determinations are given in the following.

cis-[Mo(cyclam)Cl_2]Cl forms green box-shaped crystals which grow together forming conglomerates. A single crystal was obtained by cutting a conglomerate. It was bounded by the faces {100}, {010} and {001}. The systematically absent reflections, are only consistent with the space group $P2_1/c$. The scan type and range were selected on the basis of a detailed analysis of the reflection profiles. The cell parameters were determined from 16 reflections in the θ-range $10.6 < \theta < 17.3$.

The intensities of three standard reflections were monitored every 10000 s and the orientations of 8 reflections were checked after every 300 reflections. These measurements had no systematic variations, indicating that misalignment or deterioration of the crystal had not occurred during the data collection. The data were corrected for absorption effects with transmission factors in the range 0.7125–0.8283. A difference Fourier map showed clearly the positions of all the hydrogen atoms in the structure. They were given a common fixed thermal parameter of 2.0 Å^2 and their positional parameters were included in the refinement.

After the final refinement cycle the maximum shift of

parameters was 0.75 σ and the maximum peaks in the final difference Fourier map of 1.6 e/Å^3 were found close to the heavy atoms of the structure.

cis-[Mo(cyc*a*)Cl_2]$CF_3SO_3 \cdot 2H_2O$ forms green box-shaped crystals which are rather rapidly oxidized at room temperature, and it was difficult to obtain a crystal of a reasonable quality for the low-temperature diffraction study. The unit cell dimensions were determined from 16 reflections with $12.6 < \theta < 18.7$. The data collection was performed as described for *cis*-[Mo(cyclam)Cl_2]Cl. The intensity control for the three standard reflections showed an isotropic, significant decrease of 23 % during the data collection. The data were corrected for this decay by a rescale function linear in exposure time. A difference Fourier map showed the positions of all the hydrogen atoms in the structure except one bonded to a methyl carbon atom. Due to the limited resolution of the data the hydrogen atoms were not refined but introduced in idealized geometries with a common isotropic thermal parameter of 2.5 Å^2.

The maximum peak in the final difference map was 0.7 e/Å^3 and the maximum shift in the final refinement cycle was 0.04 σ.

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