Note

The nitrido complex (NEt$_4$)[MoCl$_3$(N)(OH)(MeCN)]

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Abstract

The title compound tetraethylammonium-[(acetonitrile)trichlorohydroxonitridomolybdate(VI)] (**1**) is the product of the reaction of the nitrido complex MoCl$_3$(N) with (NEt$_4$)Cl·H$_2$O in acetonitrile. The acetonitrile and the nitrido ligand are arranged *trans*, while the chloro and the hydroxo group form the equatorial plane of the pseudo-octahedral molybdenum coordination polyhedron. Complex **1** may be regarded as a presumably first step in the hydrolysis of [MoCl$_4$(N)]$^-$ and supplements earlier results showing that [MoCl$_4$(N)]$^-$ can be hydrolized to form [MoCl$_4$(O)]$^-$. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Molybdenum complexes; Nitrido complexes; Crystal structures; Hydrolysis

1. Introduction

Studies of the properties of high-valent metal–nitrido complexes are receiving constant attention [1–7]. The chloro(nitrido)molybdenum complexes X[Mo^{VI}Cl$_4$(N)] (X = NMe$_4$, AsPh$_4$ [8,9], PPh$_4$ [10]) and (NEt$_4$)$_2$-[Mo^{VI}Cl$_5$(N)] and (NEt$_4$)$_2$[Mo^{V}Cl$_4$(N)] [11] are known. The crystal structures of (AsPh$_4$)[Mo^{VI}Cl$_4$(N)] and (PPh$_4$)[Mo^{VI}Cl$_4$(N)] have been elucidated [8,10]. In addition, the structure of (PPh$_3$Me)$_2$[Mo^{V}Cl$_4$(N)] is available, but the pyramidal [Mo^{V}Cl$_4$(N)]$^{2-}$-anion was found disordered around a center of inversion [12].

2. Experimental

The infrared spectrum was measured on a Perkin–Elmer 783 IR spectrometer. Magnetic measurements were carried out on a Johnson Matthey magnetic susceptibility balance (MSB-Auto, Gouy balance) or on a Varian O-300 NMR spectrometer according to the method of Evans [13]. Acetonitrile was dried over CaH$_2$, refluxed and distilled under argon.

MoCl$_5$ (10 g, 36.6 mmol) was stirred for four days in acetonitrile (MeCN, 60 ml). The solution slowly turned brown with the formation of a brown precipitate of MoCl$_4$(MeCN)$_2$ [8,11]. The solvent was removed in vacuo and the remaining solid stirred for 5 h with toluene (60 ml). Then the toluene was decanted and the settled solid dried in vacuo. From this MoCl$_4$(MeCN)$_2$ (9.03 g, 28.2 mmol) and NaN$_3$ (1.84 g, 28.3 mmol) were dissolved in MeCN (40 ml). Upon stirring of the mixture a rapid gas evolution started which ended after 1 h. A dark orange–red solution and a white precipitate (NaCl) were obtained. The solution was decanted and immediately treated with (NEt$_4$)Cl···H$_2$O (4.7 g, 28.3 mmol). The hygroscopic and partly wet (NEt$_4$)Cl had been dried at 100°C for 2 h. Soon the solution turned red–brown and a white precipitate developed. After stirring for 35 h, the solution was filtered and concentrated to about 20 ml. After 2 days at room temperature a yellow solid had precipitated and the solution was filtered again. Cooling to −15°C yielded 5.9 g (51%) of dark-red prismatic crystals. The crystals turn opaque upon drying due to loss of the coordinated MeCN solvent molecule. IR (KBr, cm^{-1}): 3350 w br, 2990 m, 2040 s (CN), 1690 m, 1460 s, 1400 m, 1310 m, 1265 w, 1185 s, 1175 sh, 1055 m, 1035 m, 1005 m, 945 s, 915 s, 790 s, 705 s, 510 w, 380 m, 330 s. *Anal.* of the

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Table 1
Crystallographic data

Empirical formula	$C_{10}H_{24}Cl_3MoN_3O$
Formula weight	404.61
Temperature (K)	173(2)
Wavelength (Å)	0.71073
Crystal system	orthorhombic
Space group	*Pbca*
a (Å)	14.406(7)
b (Å)	14.8820(10)
c (Å)	16.0540(12)
V (Å^3)	3441.8(17)
Z	8
D_{calc} (g cm^{-1})	1.562
Absorption coefficient (mm^{-1})	1.222
$F(000)$	1648
Crystal size (mm^3)	$0.45 \times 0.40 \times 0.40$
θ Range for data collection (°)	3.14 to 25.96
Index ranges	$-17 \leftarrow h \leftarrow 17$,
	$-18 \leftarrow k \leftarrow 0$,
	$-19 \leftarrow l \leftarrow 19$
Reflections collected	12849
Independent reflections	3356 [$R_{(int)} = 0.0393$]
Absorption correction	empirical via Ψ scan
Max., min. transmission	1.000, 0.946
Data/restraints/parameters	3355/0/233
Goodness-of-fit on F^2	1.179
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0419$, $wR_2 = 0.1133$
R indices (all data)	$R_1 = 0.0494$, $wR_2 = 0.1253$
Largest difference peak and hole (e Å^{-3})	1.133 and -1.330

dried crystals: Found: C, 26.83; H, 5.57; N, 7.58; Mo, 25.9. Calc. for $(NEt_4)[MoCl_3(N)(OH)]$: C, 26.43; H, 5.82; N, 7.71; Mo, 26.4%. Calculated for a sample with 78% $[MoCl_3(N)(OH)]^-$ and 22% $[MoCl_4(N)]^-$ (see Section 3) $(NEt_4)[MoCl_{3.22}(N)(OH)_{0.78}]$: C, 26.14; H, 5.65; N, 7.62; Mo, 26.1%.

Crystal, data collection, and refinement parameters are given in Table 1. Data were collected on an Enraf–Nonius Turbo CAD-4 diffractometer with a graphite monochromator. The structure was solved by direct methods (SHELXS-86) and refined by full-matrix least-

squares on F^2 (SHELXL-93) [14]. All non-hydrogen atoms were refined isotropically. The hydrogen atoms of the ethyl and methyl groups were fully refined in their positional parameters. Their isotropic displacement parameters were refined as 1.5 U_{eq} of the carbon atom for methyl and 1.2 $U_{eq}(C)$ for ethyl. The hydroxyl hydrogen was calculated by assuming an idealized OH group with Mo–O–H tetrahedral in a rotating group refinement.

3. Results and discussion

In the attempted synthesis of $(NEt_4)[Mo^{VI}Cl_4(N)]$ in acetonitrile according to Dehnicke and Kolitsch [9] and Young et al. [11] we obtained dark-red crystals in 51% yield which were structurally studied. The single crystal X-ray structure determination indicated that a hydroxo complex of formula $(NEt_4)[Mo^{VI}Cl_3(N)(OH)(MeCN)]$ (**1**) had been obtained. Most likely the hydroxo group originates from a water molecule from $(NEt_4)Cl·H_2O$ which is highly hygroscopic. The water molecule can then react with a chloro ligand of the molybdenum complex under formation of HCl and the hydroxo product **1**.

The magnetic susceptibility measurement of the reaction product at room temperature both in the solid state with a Gouy balance as well as in solution by the method of Evans [13] showed the compound to be diamagnetic. This precludes the formation of the paramagnetic (d^1) Mo(V)-oxo complex as another possible hydrolysis product and supports the formulation of **1** as a (d^0) Mo(VI)–nitrido complex. In addition, nitrogen and oxygen or a Mo–N triple and Mo–O double bond cannot be discerned from X-ray diffraction. The infrared stretching frequencies of both groups also overlap. The M–N(nitrido) band in the IR is assigned to 1055 cm^{-1}. Intentional hydrolysis of **1** leads to the disappearance of this band while other parts of the fingerprint region remain unchanged.

The molecular structure of the title compound **1** is shown in Fig. 1. Selected bond distances and angles are given in Table 2. The three chloro ligands show a meridional arrangement around the metal, with the Mo–Cl bond *trans* to the OH group being slightly elongated (2.461(1) Å instead of 2.389(1) Å). These Mo–Cl distances and the Mo–O(H) distance of 1.963(3) Å fall well into the expected range of 2.389 ± 0.053 and 1.988 ± 0.043 Å, respectively [15]. The Mo–Cl distances from the related $X[MoCl_4(N)]$ compounds are 2.345(5) Å [8] for X = AsPh$_4$ and 2.344(1) Å for X = PPh$_4$ [10].

The acetonitrile ligand is found *trans* to the nitrido group. The Mo–N(nitrido) bond length of 1.680(3) Å in **1** is usual (1.636 ± 0.006 Å) [15]. In comparison, Mo≡N is 1.66(4) Å in $(AsPh_4)[MoCl_4(N)]$ [8] and 1.637(4) Å in $(PPh_4)[MoCl_4(N)]$ [10]. The Mo–N
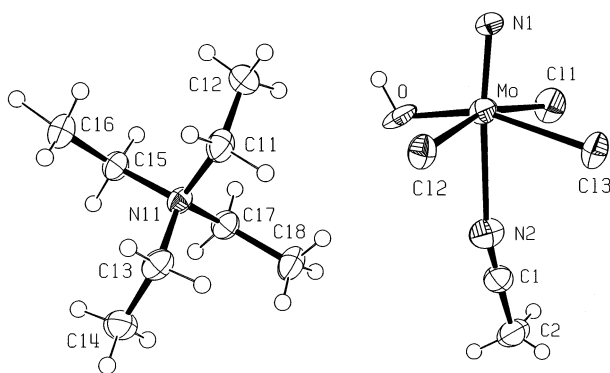

Fig. 1. ORTEP view [25] of the title compound showing the labeling of the non-hydrogen atoms, thermal ellipsoids correspond to 50% probability levels.

Table 2
Selected bond distances (Å) and angles (°)

Bond lengths			
Mo–N1	1.680(3)	Mo–N2	2.420(4)
Mo–O	1.963(3)	Mo–Cl1	2.3888(9)
Mo–Cl2	2.3887(9)	Mo–Cl3	2.4608(12)
N2–C1	1.136(5)		
Bond angles			
N1–Mo–O	103.67(13)	N2–Mo–O	80.82(12)
N1–Mo–Cl1	96.49(10)	N2–Mo–Cl1	79.75(8)
N1–Mo–Cl2	97.34(10)	N2–Mo–Cl2	85.84(8)
N1–Mo–Cl3	96.80(11)	N2–Mo–Cl3	78.70(9)
N1–Mo–N2	174.28(13)	Cl1–Mo–Cl2	164.10(4)
O–Mo–Cl1	91.04(7)	Cl1–Mo–Cl3	85.83(3)
O–Mo–Cl2	93.29(7)	Cl2–Mo–Cl3	84.77(3)
O–Mo–Cl3	159.52(8)	Mo–N2–C1	158.7(3)
N2–C1–C2	177.6(4)		

(nitrile) bond length in **1** of 2.420(4) Å is considerably longer than the given average of 2.147 ± 0.043 Å [15]. This is due to a *trans* effect of the nitrido ligand, i.e. the competition over the σ- and π-bonding orbitals to the metal [16]. Mo–N(nitrile) bonds of similar lengths are found *trans* to an imino group (2.315 Å) [17], *trans* to an oxo ligand (2.49 Å) [18], or *trans* to a phosphazene group (2.390 Å) [19]. Even longer Mo–N(nitrile) bond lengths of about 2.75 Å are encountered *trans* to a Mo–Mo quadruple bond [20].

The position of the hydroxyl hydrogen in Fig. 1 is clearly uncertain since this atom could only be calculated with a rotating group refinement. This problem of localization may be due to the fact that OH cannot form a hydrogen bond. There are no obvious acceptor atoms nearby. The nearest chlorine atom of the neighboring anion is about 5 Å away from the oxygen center. The next nitrido atom can be found 5.2 Å and the next nitrogen of the MeCN group 4.3 Å away from the oxygen atom. Hydrogen bond formation to acceptor ligands within the same anion does not seem feasible because of angular constraints. Possibly, the problematic OH situation with lack of hydrogen bonding is reflected in the asymmetric thermal ellipsoid of the oxygen atom. A similar asymmetric thermal ellipsoid for the oxygen atom of a terminal OH group without hydrogen bonding has been observed in $[(C_5H_5)Mo(OH)(PMe_3)_3]BF_4$ [21]. A possible disorder of oxygen and chlorine positions has been considered. Contamination of **1** with $(NEt_4)[MoCl_4(N)(MeCN)]$, which was the original synthetic target, may be a possibility. And indeed, allowing a partial occupancy of Cl (22%) along the Mo–O bond improves the thermal parameter. Both the chlorine and oxygen atoms can be anisotropically refined with a slight decrease in the R-values. Yet, the bond lengths refine to the rather small values of Mo–Cl = 2.19(1) Å and Mo–O =

1.76(1) Å. Such a contamination or a solid solution of two complexes would be reminiscent to the mixture of $[MoCl_2(O)(PR_3)_3]$ and $[MoCl_3(PR_3)_3]$ that was responsible for the notorious 'bond-stretch isomer' problem [22].

Usually, the Mo-nitrido functionality is not necessarily inert towards protic reagents. However, the chloro or other ligands can be even more reactive. In MoN-(O-t-Bu)$_3$ the tert-butanolato ligands can be replaced by reaction with alcohols with smaller R groups under retention of the nitrido function [23]. Reaction of $MCl_3(N)$ with diols starts with a substitution of a chloro ligand followed by protonation of the nitrido group [24]. Partial hydrolysis of orange–red $(AsPh_4)[Mo^{VI}Cl_4(N)]$ with moist air leads to isotypic green $(AsPh_4)[Mo^VCl_4(O)]$ [8]. The synthesis and structure of **1** supplements these earlier findings, in that **1** may be regarded as a presumably first step in the hydrolysis of $[MoCl_4(N)]^-$.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 130264. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: + 44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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