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Synthesis and Investigations of the Crystal Structure of a Dinuclear Diazadiene Molybdenum Oxo-Imido Complex with a Unique $N_3Mo(\mu\text{-}O)_2MoN_3$ Core

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Ligand metathesis of the diimido and dioxo precursor complexes $[Mo(X)_2Cl_2(DME)]$ (X = O, N*t*Bu) leads to the mixed oxo-imido derivative $[Mo(NtBu)(O)Cl_2(DME)]$ (**1**). By treatment with Li_2DAD (DAD = 1,4-di-*tert*-butyl-1,4-diazabuta-1,3-diene), **1** is converted into the complex $[Mo(NtBu)(O)(DAD)]_2$ (**2**). The crystal structure determination on a nonmerohedral twin of **2** reveals a dinuclear molecular structure with nearly symmetrical bridging oxygen atoms. The smaller oxo ligand tends to be a better bridging functionality than the imido ligand; the unprecedented $N_3Mo(\mu\text{-}O)_2MoN_3$ configuration is favored over a $ON_2Mo(\mu\text{-}N)_2MoN_2O$ core. Compared to other known molybdenum DAD complexes, **2** reveals some degree of pyramidalization at the nitrogen atoms of the DAD ligand. In accord with the Mo–N, N–C, and C–C bond lengths, complex **2** is best described as an ene-diamido complex of formally six-valent molybdenum.

Introduction

Complexes based on the 1,4-diazabuta-1,3-diene DAD ligand backbone have been the focus of attention for many years. Due to several possible coordination modes and their redox activity, DAD ligands can stabilize metals with a wide range of formal oxidation states.[1] While DAD is a strong π-acceptor ligand that stabilizes low-valent metal centers, the two-electron-reduced DAD ligand, which is best described as an ene-diamido functionality, can be envisaged as a strong π-donor ligand that stabilizes high-valent metal centers. The diversity of substituents at the nitrogen and carbon atoms offers a perfect handle for the fine-tuning of electronic and steric ligand features that may be relevant in catalytic applications. For example, complexes of the late transition metals and diazadiene ligands with bulky electron-withdrawing aryl substituents at the nitrogen atom are extensively used in olefin oligomerization and polymerization.[2]

Following our previous investigations[3] on high-valent N-organoimido complexes of group 6 metals with other strong π-donor ligands, such as cyclopentadienyl, oxo, alkylidene or metallated phosphorus ylide ligands, we set out to explore the unknown chemistry of ene-diamido ligands with imido and oxo complexes. We now report the synthesis of a key oxo-imido complex, $[Mo(NtBu)(O)Cl_2(DME)]$ (**1**), and the conversion into its DAD derivative $[Mo(NtBu)(O)(DAD)]_2$ (**2**) (DAD = 1,4-di-*tert*-butyl-1,4-diazabuta-1,3-diene). Complexes with the functional and structural building block $[CpM(DAD)L_n]$ have been investigated for many years. This is the first report of a group 6 complex with a related $\sigma,2\pi$-donor and π-acceptor ligand regime $[(RN)M(DAD)L_n]$.

Results and Discussion

The oxo-imido complex **1** is formed in good yield by ligand metathesis between the known dioxo $[Mo(O)_2Cl_2(DME)]$[4] and diimido $[Mo(NtBu)_2Cl_2(DME)]$[5a] complexes in DME (Scheme 1). In agreement with the spectroscopic data and with related structurally characterized d^0 oxo-imido complexes,[5b] **1** probably has an octahedral structure with *trans* chloro ligands and the strong π-donor ligands O^{2-} and NR^{2-} in *cis* configuration. Reduction of DAD by lithium in THF affords the ene-diamide Li_2DAD.[6] The latter reacts with **1** to form the ene-diamido title complex **2** in a fair yield of 59%. Complex **2** is a hexane-soluble, dark purple, diamagnetic compound. ^1H and ^{13}C NMR spectra reveal equivalent *tert*-butyl groups at the DAD and imido N atoms, as well as equivalent methine protons at the C_2 bridge of DAD. These data are consistent with either a mononuclear tetrahedral structure or a binuclear species with either a mirror plane or a center of inversion. The EI mass spectra show mononuclear molecular ions $[Mo(NtBu)(O)(DAD)]$ as the highest peaks. To gain further insight into the nature of the title complex, single crystals for X-ray crystal structure determination were grown from a hexane solution.

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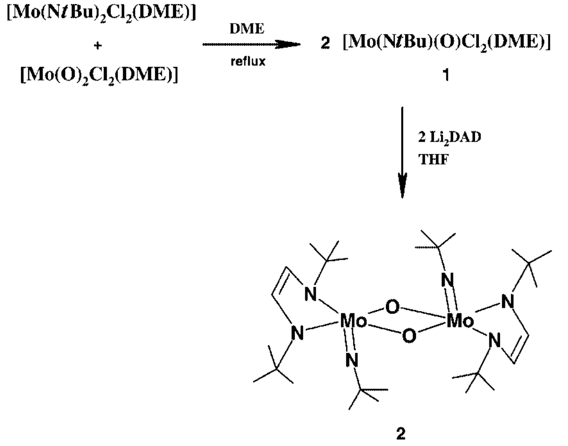


Scheme 1. Preparation of oxo-imido complex **2** using key compound **1**.

Data Collection and Structure Refinement

A crystal with the dimensions 0.35 × 0.15 × 0.15 mm was mounted on a glass fiber by using the "oil drop method". Data were collected at T = 193 K with a STOE IPDS area detector system using graphite monochromated Mo-K_α radiation. The crystal is orthorhombic with a = 19.913(2), b = 18.437(2), c = 9.547(2) Å and happens to be a nonmerohedral twin with only minor overlap of the reflections. Only one orientation matrix was used during the integration of the intensities. Overlapping reflections were ignored. This procedure led to 13576 integrated intensities, with 2877 independent (R_{int} = 12.26%) and the completeness was 90% for $\Theta_{\max}$ = 25°. No absorption correction was applied ($C_{28}H_{58}Mo_2N_6O_2$: M = 702.68, μ = 7.46 cm^{-1} for Z = 4). Structure solution (direct methods) and refinement in the space group *Pnma* were performed by using the SHELX-97 programs,[7] with all non-hydrogen atoms anisotropic, and hydrogen atoms with fixed isotropic temperature factors determined with a riding model. In the final stage of the refinement, two residual peaks in the difference Fourier map (distance 3.09 Å) were interpreted as disorder positions of atoms Mo(1) and Mo(2) (noncrystallographic transformation close to x, y, $5 - z$). The ratio of the occupancies [all atoms of the main part versus atoms Mo(3) and Mo(4)] were refined to 0.907:0.093. No disordered positions of the light atoms were located, final residuals: wR_2 = 11.28% (for all unique reflections), conventional R_1 = 4.86% [for 1346 reflections with $I > 2\sigma(I)$], and 205 refined parameters.

Molecular Structure of 2

The molecular structure of **2** in the crystal is shown by Figure 1, with selected bond lengths and angles in Table 1. Figure 2 displays the disorder and inner coordination spheres. The title complex **2** is binuclear in the solid state. Both molybdenum atoms are tetragonal pyramidal and coordinated by five atoms: an axial imido nitrogen atom, two basal nitrogen atoms of the DAD ligand, and two oxygen atoms of the central planar $Mo_2(\mu\text{-}O)_2$ core. All six basal atoms $N_2O_2N_2$ lie in the same plane. Both imido ligands adopt an *anti* collinear orientation. There is a crystallographic mirror plane defined by the two metal centers and the two Mo–N(imido) vectors. Although there is no inversion symmetry unit, the $Mo_2(\mu\text{-}O)_2$ core can be considered to be symmetrical on the basis of the bond lengths and their standard deviations; the Mo–O bond lengths are 1.959(5) and 1.952(5) Å. These bond lengths correlate with the value for Mo–O single bonds, e.g. in **A**,[8] they are approximately 1.95 Å (Scheme 2).

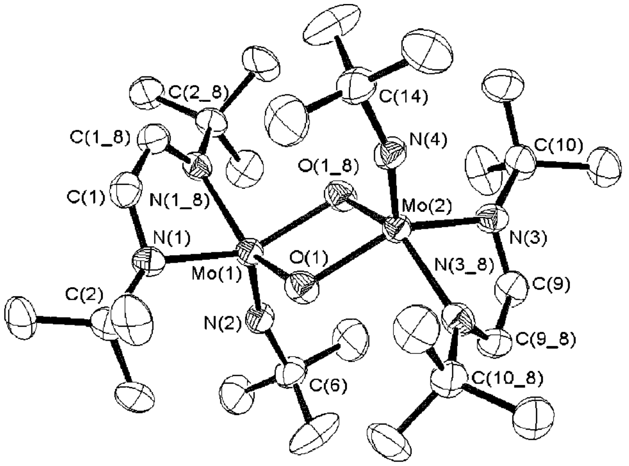


Figure 1. Molecular structure of **2**.

To date, no other structurally characterized example of an $N_3Mo(\mu\text{-}O)_2MoN_3$ coordination polyhedron is known, therefore a direct comparison cannot be made (CCSD search, September 2005). However, a similar framework has been found in a dinuclear thiolato(oxo) complex of the type $S_2(O)Mo(\mu\text{-}O)_2Mo(O)S_2$ (**A**). In contrast to **2**, the two square pyramids with their apical Mo–O vectors are in a *syn* configuration to each other in **A**.

Several molybdenum DAD complexes have been described in the literature, with examples given by **B**–**E**.[9–12] Type **B**[9] represents a four-electron Lewis base adduct of the diazadiene ligand that is coordinated to a formally six-valent molybdenum center, which is characterized by perfectly planar N atoms and long Mo–N distances of ca. 2.40 Å, short N–C distances of ca. 1.27 Å, and long C–C distances of ca. 1.48 Å. It is anticipated, for a metal of d^0 electron configuration that there is no M→L back-bonding in **B**. This is demonstrated by negligible differences between the discussed bond lengths in free DAD[13] and those in **B** (Table 2). However, due to its low-lying π* orbitals, neutral DAD can easily be reduced by more electron-rich metal centers to form the coordinated radical anion [DAD]$^{-}$[14] and the ene-diamido [DAD]$^{2-}$ ligands.[1,6,10,11,15,16] Examples of molybdenum complexes with a fully reduced DAD moiety are **C**[10] and **D**.[11] The structural parameters of their MN_2C_2 units are similar to that of the phenylene-1,2-diamido system **E**[12] (Table 2). Typically, flat[15] and folded[16] ene-diamido units (MN_2C_2) are known. In folded conformations, the metal is located out of the N_2C_2 plane (E^{NCCN}), as indicated by the distance $d(M\text{–}E^{NCCN})$, which

Table 1. Selected inner core bond lengths [Å] and angles [°] of **2**.

C(1)–N(1)	1.333(11)	N(1)–Mo(1)–N(1_8)	80.4(5)
C(1)–C(1_8)	1.420(20)	N(2)–Mo(1)–Mo(2)	111.0(3)
C(2)–N(1)	1.493(13)	O(1_8)-Mo(1)–Mo(2)	38.4(2)
C(6)–N(2)	1.464(13)	O(1)–Mo(1)–Mo(2)	38.4(2)
C(9)–N(3)	1.345(11)	N(1)–Mo(1)–Mo(2)	119.7(2)
C(9)–C(9_8)	1.389(17)	N(1_8)-Mo(1)–Mo(2)	119.7(2)
C(10)–N(3)	1.501(13)	N(4)–Mo(2)–O(1)	106.2(3)
C14–N(4)	1.471(14)	N(4)–Mo(2)–O(1_8)	106.2(3)
Mo(1)–N(2)	1.716(8)	O(1)–Mo(2)–O(1_8)	77.1(3)
Mo(1)–O(1_8)	1.959(5)	N(4)–Mo(2)–N(3)	110.4(3)
Mo(1)–O(1)	1.959(5)	O(1)–Mo(2)–N(3)	143.3(3)
Mo(1)–N(1)	2.036(8)	O(1_8)–Mo(2)–N(3)	90.0(3)
Mo(1)–N(1_8)	2.036(8)	N(4)–Mo(2)–N(3_8)	110.4(3)
Mo(1)–Mo(2)	3.062(1)	O(1)–Mo(2)–N(3_8)	90.0(3)
Mo(2)–N(4)	1.718(8)	O(1_8)–Mo(2)–N(3_8)	143.3(3)
Mo(2)–O(1)	1.952(5)	N(3)–Mo(2)–N(3_8)	80.1(4)
Mo(2)–O(1_8)	1.952(5)	N(4)–Mo(2)–Mo(1)	110.8(3)
Mo(2)–N(3)	2.017(8)	O(1)–Mo(2)–Mo(1)	38.6(1)
Mo(2)–N(3_8)	2.017(8)	O(1_8)-Mo(2)–Mo(1)	38.6(1)
Mo(3)–Mo(4)	3.085(16)	N(3)–Mo(2)–Mo(1)	120.9(2)
		N(3_8)-Mo(2)–Mo(1)	120.9(2)
N(2)–Mo(1)–O(1_8)	106.2(3)	C(1)–N(1)–C(2)	118.4(7)
N(2)–Mo(1)–O(1)	106.2(3)	C(1)–N(1)–Mo(1)	104.3(6)
O(1_8)–Mo(1)–O(1)	76.8(3)	C(2)–N(1)–Mo(1)	134.5(5)
N(2)–Mo(1)–N(1)	111.4(3)	C(6)–N(2)–Mo(1)	161.5(8)
O(1_8)–Mo(1)–N(1)	142.2(3)	C(9)–N(3)–C10	117.1(7)
O(1)–Mo(1)–N(1)	89.4(3)	C(9)–N(3)–Mo(2)	103.6(6)
N(2)–Mo(1)–N(1_8)	111.4(3)	C(10)–N(3)–Mo(2)	134.8(5)
O(1_8)–Mo(1)–N(1_8)	89.4(3)	C(14)–N(4)–Mo(2)	161.1(8)
O(1)–Mo(1)–N(1_8)	142.2(3)	Mo(2)–O(1)–Mo(1)	103.1(2)

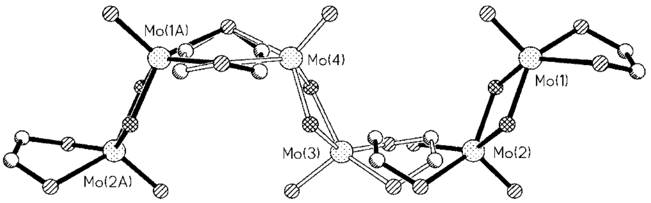
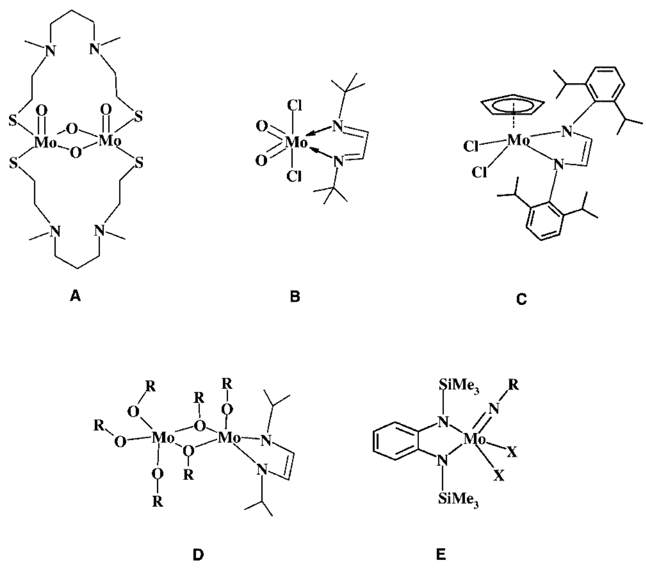


Figure 2. Coordination polyhedra and disorder in the crystal structure of **2**. Open bonds: minor part of disorder, positions of light atoms calculated.

is listed in Table 2. In almost flat conformations, as found in **C** and **D**, the Mo atom is only ca. 0.3 Å out of the plane. Perfectly flat conformations are present in DAD adducts such as **B**. Similarly to those in **B**, the nitrogen atoms of **C** and **D** are close to planar (the sum of angles at the N atoms Σ°N ca. 360°). By comparing the M–N, N–C, and C–C bond lengths, complex **2** is best described as an ene-diamide of d^0-Mo^{VI} and not as a neutral diazadiene adduct of d^2-Mo^{IV}. In contrast to those of **C** and **D**, the Mo atom of **2**



Scheme 2. Related complexes and reference compounds.

Table 2. Comparison of selected bond lengths [Å] and angles [°] in reference compounds.

	Mo–N	N–C	C–C	*d*(M–E^{NCCN})	Σ°N
*t*Bu-DAD	–	1.264–1.267	1.468(2)	–	–
B	2.388–2.399	1.267–1.271	1.476(3)	0	360.0(5)
C	2.081–2.092	1.353(4)	1.363(2)	0.329	360.0(3)
D	1.957–2.075	1.354–1.392	1.344(8)	0.329	359(1)
E	1.996–2.078	1.373–1.407	1.409–1.452	0.085–1.148	356.3–360.0
2	2.017–2.036	1.333–1.345	1.389–1.420	0.951(1)	355.5–357.2

is located 0.951(1) Å out of the N_2C_2 plane, and the sum of angles at the nitrogen atoms, $\Sigma°N = 355.5°$ and 357.2°, respectively, indicates a trend for pyramidalization, which is analogous to that of phenylene-diamido complexes of type **E**. Table 2 shows that the shortening of the Mo–N and C–C bonds is accompanied by a lengthening of the N–C bonds and a higher degree of pyramidalization at the N atoms. Currently we are investigating the scope of this statement by exploring other diazadiene imido complexes of the early transition metals. Preliminary results reveal that the liaison of both DAD and NR ligands at one metal offers access to a growing new class of covalent functional compounds.

Experimental Section

General: All reactions and manipulations were carried out under argon using standard Schlenk techniques. Solvents were refluxed in the presence of an appropriate drying agent and distilled: C_6D_6 and hexane (Na/K alloy), THF and DME (Na/benzophenone), and toluene (Na). Literature methods were employed for the synthesis of starting materials $[Mo(O)_2Cl_2(DME)]$,[4] $[Mo(N\mathit{t}Bu)_2Cl_2(DME)]$,[5] 1,4-di-*tert*-butyl-1,4-diazabuta-1,3-diene (DAD),[17] and Li_2DAD.[6] Melting points (uncorrected) were measured with a Büchi MP B-540 apparatus. C, H, and N analyses were carried out with a Heraeus CHN-Rapid analyzer. Mass spectra were recorded with a Varian MAT CH-7a (EI, 70 eV) instrument. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded with Bruker AMX300 and DRX500 spectrometers; chemical shifts were referenced to the ^1H (δ = 7.15 ppm) and ^{13}C (δ = 128.0 ppm) residual signals of C_6D_6. Infrared spectra were recorded with a Bruker IFS 88 FT instrument, and samples were Nujol mulls between KBr plates.

Preparation of $[Mo(N\mathit{t}Bu)(O)Cl_2(DME)]$ (1): Under argon, $[Mo(N\mathit{t}Bu)_2Cl_2(DME)]$ (400 mg, 1.00 mmol) and $[Mo(O)_2Cl_2(DME)]$ (290 mg, 1.00 mmol) were dissolved in DME (10 mL) and heated to reflux for 3 days. The volatiles were removed in vacuo, and the yellow-green product was extracted into toluene (30 mL) and crystallized at –40 °C. Yield 500 mg (73%). M.p. 71 °C. $C_8H_{19}NCl_2O_3Mo$ (M = 344.09 $g\,mol^{-1}$): calcd. C 27.93, H 5.57, N 4.07; found C 27.49, H 5.44, N 3.97. ^1H NMR (C_6D_6, 300 MHz, 300 K): δ = 3.41 (s, 6 H, Me), 3.02 (s, 4 H, CH_2), 1.41 (s, 9 H, N*t*Bu) ppm. $^{13}C\{^1H\}$NMR (C_6D_6, 75 MHz, 300 K): δ = 70.6 (s, CH_2), 63.2 (br s, Me), 27.8 (s, N*t*Bu) ppm. IR (KBr): 3160 (m, vbr), 1587 (m), 1405 (w), 1362 (s), 1276 (w), 1259 (w), 1228 (s, br), 1188 (w), 1162 (w), 1137 (w), 1108 (w), 1086 (s), 1044 (s, b), 1005 (vw), 961 (m), 910 (s), 861 (s), 826 (m), 799 (m), 725 (w), 627 (w), 592 (w), 572 (m), 515 (w) cm^{-1}.

Preparation of $[Mo(N\mathit{t}Bu)(DAD)(\mu\text{-}O)]_2$ (2): A solution of Li_2DAD (265 mg, 1.45 mmol) in THF (20 mL) was added dropwise to a solution of **1** (500 mg, 1.45 mmol) in THF (20 mL) at –80 °C. After 10 min at –80 °C, the reaction mixture reached room temperature within 30 min. After 8 h at room temperature, THF was removed at reduced pressure, and the product was extracted with two portions of hexane (30 mL). The analytically pure dark violet compound was obtained by crystallization from hexane at –80 °C. Yield: 300 mg (59%). M.p. 190 °C (dec.). $C_{28}H_{58}N_6O_2Mo_2$ (M = 702.69 $g\,mol^{-1}$): calcd. C 47.86, H 8.32, N 11.96; found C 47.44, H 8.02, N 11.55. EI-MS: m/z (%) = 353 (1) $[M/2^+]$, 338 (2) $[M/2^+ - Me]$, 57 (100). ^1H NMR (C_6D_6, 500 MHz, 300 K): δ = 6.75 (s, 2 H, CH–DAD), 1.51 (s, 18 H, *t*Bu-DAD), 1.38 (s, 9 H, N*t*Bu) ppm. $^{13}C\{^1H\}$NMR (C_6D_6, 125 MHz, 300 K): δ = 119.9 (CH–DAD), 69.9 ($NCMe_3$), 57.6 (CMe_3–DAD), 30.5 (DAD–CMe_3), 30.4 ($NCMe_3$) ppm. IR (KBr): 3038 (w), 1605 (w), 1420 (w), 1358 (m), 1262 (s), 1235 (s), 1219 (s), 1148 (w), 1098 (m, br), 1022 (m, br), 936 (w), 864 (w), 804 (s), 766 (m), 723 (w), 644 (m, br), 567 (m), 525 (w), 492 (w) cm^{-1}.

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