SHORT COMMUNICATION

Synthesis and Crystal Structure of a Tetranuclear Molybdenum(II) Silylamido Cluster

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Dedicated to Prof. Christian Robl on the Occasion of his 65th Birthday

Abstract. Treatment of molybdenum(II) chloride with the difunctional silylamide $Li_2Me_2Si(NPh)_2$ led to the formation of the tetranuclear cluster compound $[Mo_4\{Me_2Si(NPh)_2\}_4]$. According to the X-ray crystal structure determination, the central core of the cluster consists of four molybdenum atoms in a nearly rectangular arrangement. There are two μ_4-κ-N,N,N',N'-$Me_2Si(NPh)_2^{2-}$ ligands capping the Mo_4 rectangle and two μ_2-$Me_2Si(NPh)_2^{2-}$ ligands located at opposite edges. The alternating Mo–Mo distances of 218.1(1) and 279.5(1) pm indicate the presence of a cyclobutadiyne type cluster with alternating Mo–Mo triple and single bonds.

Introduction

Currently there are only few reports in literature on molybdenum(II) complexes with difunctional silylamide ligands. In 2006, *Tsai* et al. described the first derivative, $[Mo_2\{Me_2Si(NDipp)_2\}_2]$ (Dipp = 2,6-diisopropylphenyl), which was obtained from sodium amalgam reduction of the corresponding Mo^{III} complex $[Mo_2Cl_2\{Me_2Si(NDipp)_2\}_2]$.[1] The X-ray structure determination revealed a central Mo_2 unit which is supported by two μ-κ-N,N' bridging $Me_2Si(NDipp)_2^{2-}$ ligands. As part of our research on thioether functionalized silylamide ligands, we recently reported on dinuclear Mo^{II} complexes $[Mo_2\{R_2Si(NC_6H_4-2-SR')_2\}_2]$ (R, R' = Me, Ph).[2] In these cases, the thioether groups are involved in molybdenum coordination and, depending on the type of the residues R and R', the silylamide units act as κ-N,N' bridging or chelating ligands. In the course of these stud-

ies we were now interested in the coordination behavior of the $Me_2Si(NPh)_2^{2-}$ ligand, which differs from the above mentioned types by the absence of additional donor groups and lower steric requirements of the phenyl groups, compared with the Dipp residues.

Results and Discussion

Treatment of a suspension molybdenum(II) chloride in THF with $Li_2Me_2Si(NPh)_2$ at –78 °C immediately led to the formation of a dark brown colored reaction mixture. After stirring at room temperature overnight, all volatiles were removed under reduced pressure and the residue was treated with toluene to extract the reaction product from the residue. Complex **1** was isolated from the toluene solution by slow addition of *n*-hept-
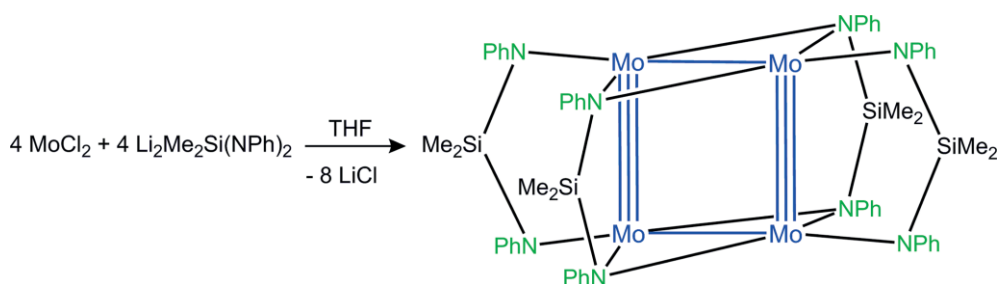
Scheme 1. Synthesis of the tetranuclear Mo^{II} cluster **1**.

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ane. The initially formed dark brown crystals were toluene solvates of the composition **1**·toluene. Additionally, solvent free crystals of compound **1** precipitated after several months (Scheme 1).

Complex **1** is soluble in toluene, benzene and THF and less soluble in *n*-alkanes like *n*-heptane. On contact with air the product decomposes instantly.

The ^1H NMR spectrum of compound **1** (in C_6D_6) displays two singlet signals at $\delta = 0.68$ and 0.08 ppm, which are assigned to the $SiMe_2$ groups of the differently coordinating silyl

amide units (v. i.). In accordance with this observation, the ^{29}Si NMR spectrum consists of two singlet signals at $\delta = 39.2$ and -11.2 ppm, respectively.

Crystal Structure

In order to get a more detailed insight into the molecular structure of compound **1**, X-ray single crystal structure determinations on the solvate **1·toluene** and solvent free **1** were performed. Due to the superior quality of the solvent free form of **1** the further discussion will be based on this. However, there are no significant differences regarding the molecular structure of [Mo$_4${Me$_2$Si(NPh)$_2$}$_4$] in both forms. Details of the crystal structure determination are collected in Table 1. Compound **1**

Table 1. Crystallographic data for compound **1**.

	[Mo$_4${Me$_2$Si(NPh)$_2$}$_4$] (**1**)
Empirical formula	C$_{56}$H$_{64}$Mo$_4$N$_8$Si$_4$
Formula weight /g·mol^{-1}	1345.27
Crystal system	triclinic
Space group	$P\bar{1}$
a /pm	1156.03(4)
b /pm	1321.21(5)
c /pm	1949.41(7)
α /°	90.759(3)
β /°	93.788(3)
γ /°	109.562(3)
Volume /pm^3	2797.5(2) · 10^6
Z	2
Temperature /K	200
Calculated density /g·cm^{-3}	1.597
Absorption coefficient μ /mm^{-1}	1.007
Crystal size /mm^3	0.442 × 0.268 × 0.112
θ range for data collection /°	1.98–25.00
Reflections collected/unique	21642 / 9784
R(int)	0.0604
Data / restraints / parameters	9784 / 0 / 649
Goodness-of-fit on F^2	0.984
R_1 [$I > 2\sigma(I)$]	0.0397
wR_2 (all data)	0.1091

forms triclinic crystals, which belong to the space group $P\bar{1}$. The crystal structure consists of discrete molecules [Mo$_4${Me$_2$Si(NPh)$_2$}$_4$] without any unusually short intermolecular contacts. The unit cell comprises two crystallographically independent [Mo$_4${Me$_2$Si(NPh)$_2$}$_4$] molecules (each with crystallographic $\bar{1}$ symmetry), which differ only slightly regarding the conformation of the peripheral NPh groups. This might be due to some packing effects in the crystal structure. Overall, the bond lengths and angles in both molecules [Mo$_4${Me$_2$Si(NPh)$_2$}$_4$] are practically identical.

The molecular structure of [Mo$_4${Me$_2$Si(NPh)$_2$}$_4$] (Figure 1) consists of a nearly rectangular Mo$_4$ core which displays two short and two long Mo–Mo separations. The central Mo$_4$ unit is capped by two μ$_4$-κ-*N,N,N′,N′*-Me$_2$Si(NPh)$_2$$^{2-}$ ligands which reside below and above the Mo$_4$ plane. Additionally, there are two μ$_2$-Me$_2$Si(NPh)$_2$ units bridging the short edges of the Mo$_4$ core. The alternating long (279.5(1) pm) and short (218.1(1) pm) Mo–Mo distances within the Mo$_4$ rectangle hint for the formation a cyclobutadiyne type cluster. This type is quite rare in Mo^{II} chemistry and up to now, only few comparable clusters have been reported. There are two clusters of the type [Mo$_4$Cl$_8$(PR$_3$)$_4$].

The earliest one, [Mo$_4$Cl$_8$(PEt$_3$)$_4$], was described in 1978 by *McCarley* et al.[3] and later the related clusters [Mo$_4$Cl$_8${P(OMe)$_3$}$_4$][4] and [Mo$_4$Cl$_6$(OMe)$_2$(dppm)$_2$] (dppm: bis(diphenylphosphanyl)methane)[5] were reported by *Cotton* et al. In the [Mo$_4$Cl$_8$(PR$_3$)$_4$] type clusters each of the molybdenum atoms is bound to a Cl atom and a PR$_3$ group as terminal ligands. Additionally there are two μ$_2$-bridging Cl atoms which support the Mo–Mo single bond at the long edges of the Mo$_4$ rectangle while the Mo–Mo triple bonds remain unsupported. [Mo$_4$Cl$_6$(OMe)$_2$(dppm)$_2$] displays μ-Cl and μ-OMe bridges over the Mo–Mo single bonds and additionally, the Mo-Mo triple bonds are bridged by bidentate dppm ligands. Typically, [Mo$_4$Cl$_8$(PR$_3$)$_4$] type clusters exhibit Mo-Mo distances of
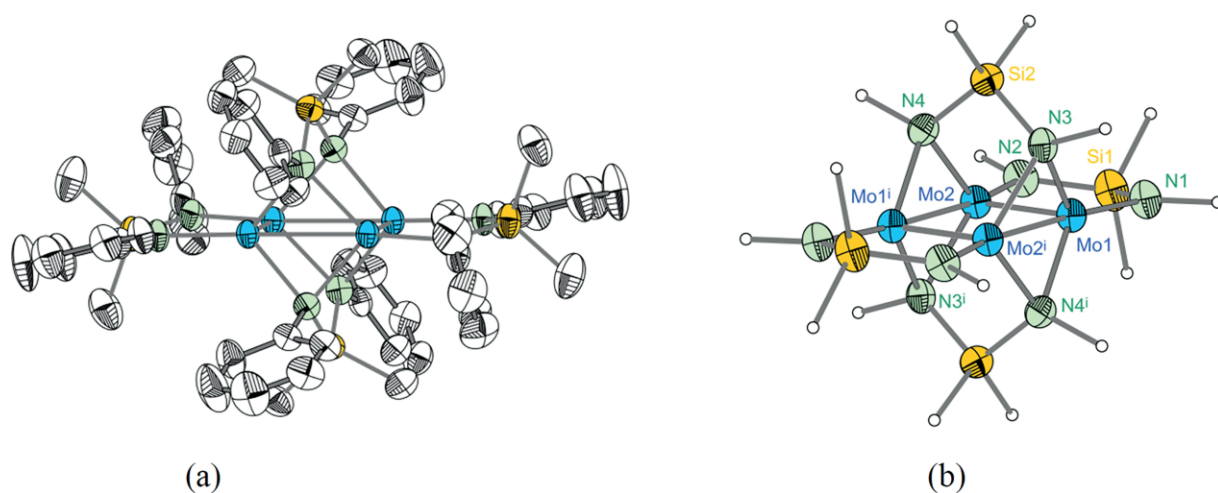

Figure 1. (a) Molecular structure of compound **1** in the crystal (molecule 1). Thermal ellipsoids are shown at the 50 % probability level, hydrogen atoms are omitted for clarity. (b) Central Mo$_4$ core with numbering scheme. Selected bond lengths /pm and angles /°: Mo(1)–Mo(2) 218.1(1), Mo(1)–Mo(2)^i 279.5(1), Mo(1)–N(1) 204.8(3), Mo(1)–N(3) 214.4(3), Mo(1)–N(4)^i 213.7(3), Mo(2)–N(2) 200.7(3), Mo(2)–N(4) 215.3(3), Mo(2)–N(3)^i 217.8(3), Si(1)–N(1) 176.0(4), Si(1)–N(2) 174.2(4), Si(2)–N(3) 175.1(3), Si(2)–N(4) 174.6(3), Mo(2)–Mo(1)–Mo(2)^i 88.9(1), Mo(1)–Mo(2)–Mo(1)^i 91.1(1), N(2)–Si(1)–N(1) 107.2(2), N(3)–Si(2)–N(4) 101.5(2), Mo(1)–N(3)–Mo(2)^i 80.6(1), Mo(1)–N(4)^i–Mo(2)^i 81.3(1), symmetry operator i: 1 −*x*, 1 −*y*, 2 −*z*.
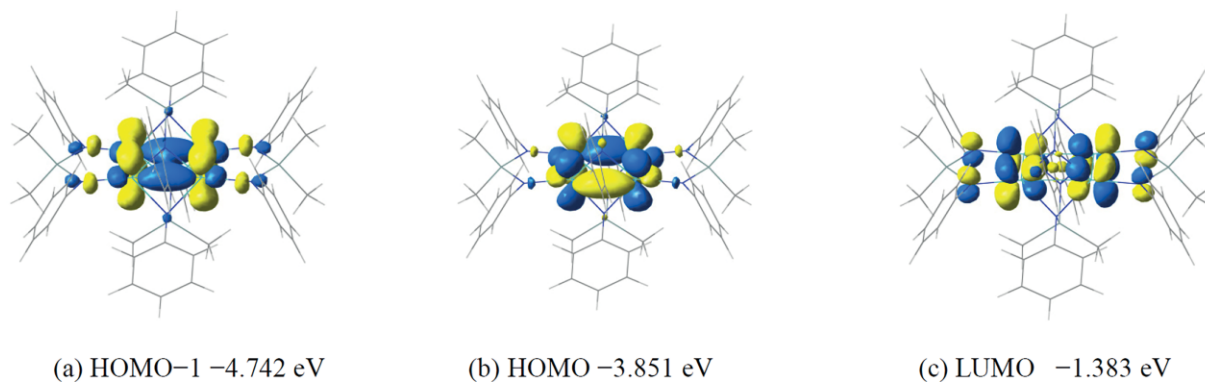
(a) HOMO−1 −4.742 eV   (b) HOMO −3.851 eV   (c) LUMO −1.383 eV

Figure 2. Frontier molecular orbitals of [Mo$_4$\{Me$_2$Si(NPh)$_2$\}$_4$].

287.8–290.1 pm for the Mo–Mo single bonds and 221.0–222.6 pm for the Mo–Mo triple bonds.

In the case of [Mo$_4$Cl$_6$(OMe)$_2$(dppm)$_2$] the Mo–Mo single bond lengths (281.4 pm) are markedly reduced due to the presence of μ-OMe bridges while the Mo–Mo triple bonds (222.4 pm) remain nearly unchanged in comparison with the [Mo$_4$Cl$_8$(PR$_3$)$_4$] clusters. In compound **1** a further reduction of the Mo–Mo bond lengths is observed. In the case of the Mo–Mo single bonds the decrease is around 2 pm and the Mo–Mo triple bonds are shortened by around 3.7 pm in comparison with [Mo$_4$Cl$_6$(OMe)$_2$(dppm)$_2$]. It may be assumed that this shrinkage of the Mo–Mo distances is caused by the lowering of the Mo coordination number (three in compound **1** versus four in the [Mo$_4$Cl$_8$(PR$_3$)$_4$] type) on one hand and the particular geometric requirements of the rigid μ$_4$-κ-*N,N,N′,N′*- and the μ$_2$-Me$_2$Si(NPh)$_2$$^{2-}$ chelating ligands on the other hand. On the whole, the observed Mo–Mo distances are within the expected range.

Usually, in dinuclear molybdenum complexes the Mo–Mo single bonds vary from 262–324 pm, depending on the bridging or non-bridging character of the ligands.[6] In the case of dinuclear molybdenum complexes Mo$_2$R$_6$ with Mo–Mo triple bonds a CSD database search revealed Mo–Mo distances in a range from 213.4 to 227.1 pm with a median value of 221.6 pm (lower quantile: 220.0 pm, upper quantile: 222.7 pm, 86 entries).[7] The compounds [Mo$_2$(CH$_2$Ph)$_6$] (217.5 pm)[8] with terminal ligands and [Mo$_2$\{PhB(NEt)$_2$\}$_3$] (216.1 pm)[9] with bridging ligands may serve as representative examples. Different from this coordination pattern observed in the [Mo$_4$Cl$_8$(PR$_3$)$_4$] type clusters, both the Mo–Mo triple bonds in compound **1** are bridged by μ$_2$-Me$_2$Si(NPh)$_2$$^{2-}$ ligands and the Mo$_4$ rectangle as a whole is stabilized by two μ$_4$-κ-*N,N,N′,N′*-Me$_2$Si(NPh)$_2$$^{2-}$ bridging ligands.

Up to now, the μ$_4$-κ-*N,N,N′,N′*-coordination mode has been only rarely observed in transition metal silylamide complexes, e.g. [Cu$_8$\{R$_2$SiNPh)$_2$\}$_4$] (R = Me, Ph).[10] Compound **1** exhibits Mo–N separations in the range 200.7(3)–217.8(3) pm. The short bonds (200.7(3) and 204.8(3) pm) are formed by the μ$_2$-Me$_2$Si(NPh)$_2$$^{2-}$ ligands and similar values have been observed for other molybdenum silylamides like [Mo$_2$Cl$_2$\{Me$_2$Si(NDipp)$_2$\}$_2$] (197.6 pm), [Mo$_2$\{Me$_2$Si(NDipp)$_2$\}$_2$] (195.9 pm)[1] and

[Mo$_2$\{Me$_2$Si(NC$_6$H$_4$-2-SR)\}] (R = Me, Ph; 208.0(3)–214.0(3) pm)[2] with tri-coordinate nitrogen atoms. In the case of the μ$_4$-Me$_2$Si(NPh)$_2$ ligands the coordination number of nitrogen is raised up to four and thus the Mo–N distances are markedly increased to a range of 214.4(3)–217.8(3) pm. The Si–N bond lengths are in the range 174.2(4) –176.0(4) for both coordination modes of the silylamide ligands. However, N–Si–N angle in the μ$_2$-ligand is larger (107.2(2)°) than in the μ$_4$-ligand (101.5(2)°).

In order to get a first insight into the electronic structure of compound **1** a DFT calculation on the B3LYP/def2tzvp level of theory was carried out. The geometry optimization (in the gas phase) led to a rectangular Mo$_4$ unit with Mo–Mo distances of 217.6 and 281.0 pm, which are very close to the experimental data. An inspection of the frontier molecular orbitals revealed that the bonding in the Mo$_4$ unit can be derived formally from the interaction of two Mo–Mo quadruple bonds as presented by Cotton et al. in the case of [Mo$_4$Cl$_8$(PR$_3$)$_4$] clusters.[4,5] According to *Cotton* et al. there is a strong interaction between two Mo$_2$ units if the Mo–Mo distance drops below 312 pm. In this case the in-phase combination (δ*+δ*) of the δ* orbitals of the Mo–Mo quadruple bonds becomes to the HOMO of the Mo$_4$ unit and two Mo–Mo single bonds are formed. Additionally the Mo–Mo quadruple bonds are transformed into Mo–Mo triple bonds. Figure 2 displays the frontier orbitals of **1**, which are closely related to those of [Mo$_4$Cl$_8$(PMe$_3$)$_4$]. *Cotton* et al. used the energy difference between the (δ+δ) and (δ–δ) MOs as a measure for the electronic interaction of the Mo$_2$ units. Typically, amidinates of the type [*cis*-Mo$_2$(DAniF)$_2$]$_2$(μ-X)$_4$] (DAniF = *N,N′*-di-*p*-anisylformamidinate; X = Cl, Br, I) with only very weak interactions exhibit rather low ΔE values in the range of 0.21–0.34 eV and for the cyclobutadiyne type cluster [Mo$_4$Cl$_8$(PMe$_3$)$_4$] a ΔE of 3.21 eV was reported.[11] The DFT calculation of compound **1** revealed a ΔE value of 3.36 eV which fits well into this series.

Conclusions

The reaction of molybdenum(II) chloride with Li$_2$Me$_2$Si(NPh)$_2$ led to the unexpected formation of a new type of tetranuclear Mo^{II} silylamido cluster complex. This is in contrast to the recently reported dinuclear complexes

[Mo$_2${R$_2$Si{N-C$_6$H$_4$-2-SR′}$_2$] with Mo–Mo quadruple bonds.[2] [Mo$_4${Me$_2$Si(NPh)$_2$}$_4$] can be described as cyclobutadiyne type cluster with alternating Mo–Mo triple and single bonds analogous to the well known [Mo$_4$Cl$_8$(PR$_3$)$_4$] compounds. Future investigations should give some insights into the influence of the silylamide ligands R$_2$Si(NR′)$_2$$^{2-}$ on the formation of dinuclear versus tetranuclear Mo^{II} complexes.

Experimental Section

General: All experiments were carried out in flame dried glassware in an argon atmosphere using Schlenk techniques. The solvents were purified by distillation from sodium/benzophenone and moisture and air were excluded. The NMR spectra were recorded with an Agilent Technologies 500 MHz DD2 spectrometer (^{1}H, 500 MHz; ^{13}C, 125 MHz; ^{29}Si, 99 MHz). The chemical shifts were referred relative to tetramethylsilane. C$_6$D$_6$ was freshly distilled from sodium/potassium alloy (23 % Na, 77 %K). IR spectra were recorded on a BRUKER Tensor 27 equipped with a diamond ATR unit. Due to the extremely high air and moisture sensitivity compound **1** was not suitable for elemental analysis. In order to get a chemical analysis, the molybdenum content was determined photometrically (mercaptoacetic acid method) with an Agilent Cary 60.[12] Molybdenum(II) chloride[13] and Me$_2$Si(NHPh)$_2$[14] were prepared by standard literature methods.

X-ray Diffraction: The crystal structures were solved by direct methods (SHELXL) and refined with the SHELXL program.[15] OLEX2 was used as graphical user interface.[16] The hydrogen atoms were positioned geometrically using a riding model. The crystal structure drawings were generated with DIAMOND.[17]

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository number CCDC-2008122 (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

DFT: DFT calculations were carried out with the Gaussian16 (Rev. B.01) program[18] employing the B3LYP hybrid functional[19] with the def2tzvp[20] basis set. The optimized minimum was confirmed by the absence of imaginary vibrational frequencies.

Synthesis of [Mo$_4${Me$_2$Si(NPh)$_2$}$_4$] (1): *n*Butyllithium (8 mL, 2.5 M in *n*-hexane, 20 mmol) was added dropwise into a solution of Me$_2$Si(NHPh)$_2$ (1.21 g, 5 mmol) in THF (20 mL) at –78 °C. After 30 min the reaction mixture was allowed to warm up to room temperature. This solution was added dropwise to a suspension of molybdenum(II) chloride (0.83 g, 5 mmol) in THF (20 mL) at –78 °C. The mixture was allowed to warm up and stirred overnight. Afterwards, the solvent was removed under reduced pressure and toluene (40 mL) was added to precipitate LiCl. After removal of the insoluble parts by filtration, the dark brown solution was layered with *n*-heptane to yield compound **1** as crystalline precipitate. Yield: 1.68 g (1.25 mmol, quantitative). C$_{56}$H$_{64}$Mo$_4$N$_8$Si$_4$: Mo 17.23 % (calcd. 17.93 %). ^{1}**H NMR** (500 MHz, C$_6$D$_6$): δ = 6.76–6.57 (m, 40 H, *o,m,p* NC$_6$H$_5$), 0.68 (s, 18 H, SiMe$_2$), 0.08 (s, 18 H, SiMe$_2$). ^{13}**C NMR** (125 MHz, C$_6$D$_6$): δ = 146.57 (4 C, *i*-NPh), 146.19 (4 C, *i*-NPh), 129.16 (8 C, *m*-NPh), 128.65 (8 C, *m*-NPh), 125.14 (8 C, *o*-NPh), 122.97 (4 C, *p*-NPh), 118.55 (4 C, *p*-NPh), 116.77 (8 C, *o*-NPh), 3.49 (4 C, CH$_3$, SiMe$_2$), –1.77 (4 C, CH$_3$, SiMe$_2$). ^{29}**Si NMR** (100 MHz, C$_6$D$_6$, inept): δ = 39.2(s, μ_2-ligand), –11.2(s, μ_4-ligand). **IR** (ATR): ṽ = 3039(w), 2960(w), 1599(m), 1586(s), 1496(m), 1476(s), 1383(m), 1287(m), 1219(m), 1074(m), 1027(m), 996(m), 913(s, br), 888(vs), 821(vs), 792(vs), 748(vs), 690(vs), 615(m), 508(s), 463(s), 390(s), 248(s) cm^{-1}.

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