Keywords: enzyme inhibitors · farnesyltransferase · peptidomimetics · signal transduction · tumour therapy

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$Rb_{10}Mo_{36}S_{38}$: A Novel Reduced Molybdenum Sulfide Containing the Highest Nuclearity Metal Transition Cluster in a Solid-State Compound

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Reduced molybdenum chalcogenides are characterized by Mo–Mo bonds that lead to the formation of clusters with different geometries and nuclearities. The most frequently observed cluster is the octahedral Mo_6, which is present in the Chevrel – Sergent ternary compounds MMo_6X_8 (M = Na, K, Ca, Sr, Ba, rare-earth metals, Sn, Pb…).[1] Clusters with higher nuclearities result essentially from the uniaxial *trans* face sharing of octahedral Mo_6 units. This condensation process is well exemplified by the series of compounds $M_{2n-2}Mo_{6n}X_{6n+2}$ (M = Rb, Cs; X = S, Se, Te)[2] where n ranges between 2 to 5 and infinity. The first member ($n = 1$) corresponds to the binary Mo_6X_8,[3] which constitutes the host structure of the MMo_6X_8 compounds. The final member is the one-dimensional compound $M_2Mo_6X_6$,[4] containing infinite chains of *trans*-face-sharing Mo_6 octahedra $|Mo_{6/2}|^1_\infty$. In addition to their novel interesting structures, Mo condensed cluster compounds also show unusual physical properties. Indeed, the sulfides and selenides generally present superconducting or metal – insulator transitions at low temperature. Thus, studies of the normal and superconducting states of $Cs_2Mo_{12}Se_{14}$ ($n = 2$)[2b] and $Rb_4Mo_{18}Se_{20}$ ($n = 3$)[2c] by measuring the conductivity and magnetization of single crystals and powder samples have shown that these compounds can be classified among the "exotic" superconductors.[5] The quasi-one-dimensional superconductor $Tl_2Mo_6Se_6$ presents extreme type II and non-Bardeen – Cooper – Schrieffer behavior. On the other hand, the anisotropy of the electronic properties in the latter compound is one of the largest ever observed in a superconductor, with a ratio of the conductivities parallel and perpendicular to the infinite chains ($\sigma_\parallel/\sigma_\perp$) of about 1000, and a ratio of the upper critical fields ($H_{c2\parallel}/H_{c2\perp}$) of about 26.[5]

We present here the crystal structure of the sixth member of the $M_{2n-2}Mo_{6n}X_{6n+2}$ family: $Rb_{10}Mo_{36}S_{38}$. The Mo_{36} cluster present in this new compound constitutes the largest observed in solid-state chemistry to date.

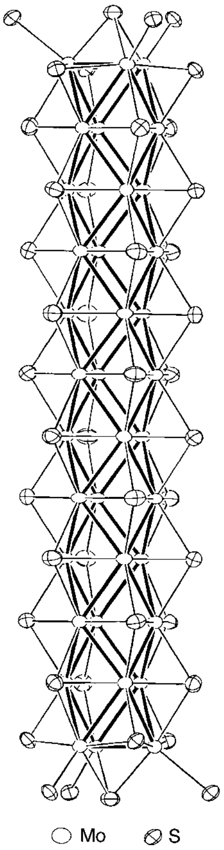

Figure 1. Schematic representation of the $Mo_{36}S_{44}$ cluster unit (ORTEP drawing).

The new Mo_{36} cluster is shown in Figure 1 with the 44 sulfur atoms of its environment, the whole forming a $Mo_{36}S_{44}$ cluster unit. Of these 44 sulfur atoms, 38 are inner ligands and the remaining 6 are outer ligands. The local symmetry of the $Mo_{36}S_{44}$ cluster unit is the same ($\bar{3}$ or S_6) as that of the monomeric Mo_6S_8 unit. The Mo_{36} core can be seen as the result of the uniaxial *trans* face sharing of 11 octahedral Mo_6 clusters.[6] It can alternatively be described as a stack of 12 staggered Mo_3 triangles.

The metal – metal distances lie between 2.637(1) and 2.744(1) Å, and the metal – chalcogen distances between 2.394(2) and 2.602(2) Å. As noticed previously for all phases containing $Mo_{6n}S_{6n+2}$ entities,[2] Mo–Mo bonds between Mo_3 triangles spread over a larger range (2.662(1) – 2.744(1) Å) than those within triangles (2.637(1) – 2.662(1) Å). In average, both types of distances tend to those found in the infinite chains of the $M_2Mo_6S_6$ sulfides. This trend is also reflected by the average distance between the Mo_3 triangles of 2.22 Å in $Rb_{10}Mo_{36}S_{38}$, compared to 2.402 and 2.213 Å for the first member Mo_6S_8 and the final member $M_2Mo_6S_6$, respectively.

Each cluster shares six outer sulfur atoms (a type) with six neighboring clusters to form the three-dimen-

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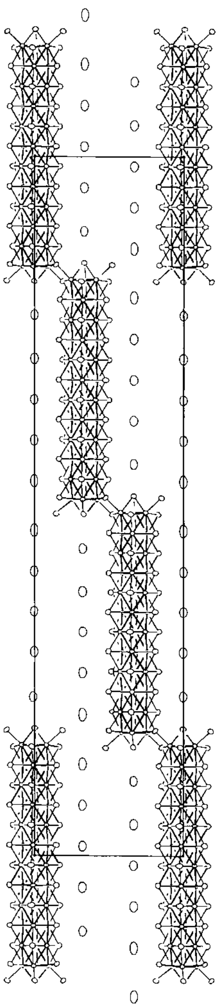

Figure 2. Projection of the crystal structure of $Rb_{10}Mo_{36}S_{38}$ onto the hexagonal (110) plane.

sional Mo–S network with the following connective formula $Mo_{36}S^{i}_{32}S^{i-a}_{6/2}S^{a-i}_{6/2}$ in the notation of Schäfer and von Schnering.[7] This classical interunit linkage for reduced Mo chalcogenides leads to a Mo–Mo distance of 3.113(1) Å between adjacent Mo_{36} clusters and consequently to only weak Mo–Mo interactions. The large cavities between the $Mo_{36}S_{44}$ cluster units are occupied by the Rb^+ cations which form linear finite chains (Figures 2 and 3). The two terminal Rb^+ cations are surrounded by ten S atoms forming a distorted tetracapped trigonal prism, and the remaining Rb^+ cations are surrounded by nine S atoms in a distorted tricapped trigonal prismatic arrangement. The Rb–S distances range from 3.363(2) to 3.936(2) Å, and the spacing between Rb^+ cations from 4.509(3) to 5.430(3) Å.

Calculation of the number of valence electrons on the Mo atoms for the Mo_{6n} clusters show that the valence electron count (VEC) asymptotically tends towards the value of 4.333 found for the $M_2Mo_6X_6$ compounds with increasing cluster size. The VEC of 4.167 in $Rb_{10}Mo_{36}S_{38}$ indicates that Mo_{6n} clusters with $n > 6$ might be possible electronically. This situation differs from that observed in the reduced molybdenum oxides $M_{n-x}Mo_{4n+2}O_{6n+4}$[8] ($n = 2$, $x = 0$ for M = Ca, Sr, Sn, Pb, La–Gd; $n = 3$, $x = 0$ for M = K; $n = 4$ and 5, $x = 1$ for M = Ba and $x = -1$ for M = In) in which *trans*-edge-sharing Mo_{6n} clusters occur. Indeed, members with $n = 5$ have a VEC (3.26) of the same magnitude as those in the infinite chain present in the series $M_xMo_4O_6$, which range from 3.25 for $NaMo_4O_6$[9a] to 3.45 for $Sn_{0.9}Mo_4O_6$.[9b] Consequently, clusters Mo_{4n+2} with $n > 5$ should be unstable with respect to the infinite chain compounds.

The principle of face-sharing condensation of octahedral M_6 clusters is also observed in metal organic compounds with cobalt,[10] nickel,[11] and rhenium.[12] However, in the latter systems, the maximum number of octahedral M_6 clusters involved is four in $Ni_{15}X_{15}(PPh_3)_6$ (X = S, Se).

Finally, magnetic susceptibility measurements made on a cold-pressed powder of $Rb_{10}Mo_{36}S_{38}$ between 300 and 2 K did not reveal superconductivity.

Experimental Section

Preparation of $Rb_{10}Mo_{36}S_{38}$: The starting materials MoS_2, Rb_2MoS_4, and Mo were all in powder form. Before use, the Mo powder was reduced under H_2 atmosphere at 1000 K over 10 h in order to eliminate any trace of oxygen. The MoS_2 was prepared by the reaction of molten S with reduced Mo in a ratio of 2:1 in an evacuated (10^{-2} Pa) and sealed silica tube, and heated to 1073 K for 2 d. Rb_2MoS_4 was obtained by treatment of Rb_2MoO_4 with CS_2 gas at 723 K for 2 d under an argon flow. Rb_2MoO_4 was synthetized from an equimolar ratio of MoO_3 and Rb_2CO_3 with heating in an alumina vessel at 1073 K for 2 d. After the synthesis, all reactants were kept and handled in a purified argon-filled glovebox. Single crystals of $Rb_{10}Mo_{36}S_{38}$ were obtained by high-temperature solid-state reaction of MoS_2, Rb_2MoS_4, and Mo in the molar ratio 2.3:1:4.5. These powders were mixed, ground together in a mortar, and then cold-pressed using a hand press. The pellet was then loaded in a molybdenum crucible, which was sealed under a low argon pressure using an arc welding system. The crucible was heated at a rate of 300 K h^{-1} to 1800 K and held there for 10 d, then cooled at 100 K h^{-1} to 1300 K and finally allowed to cool in the furnace to room temperature.

Crystal structure data for $Rb_{10}Mo_{36}S_{38}$: trigonal rhombohedral, space group $R\bar{3}$ (no. 148), $a = 9.0968(7)$, $c = 77.37(1)$ Å, $V = 5544.6(1)$ Å^3, $Z = 3$, $\rho_{calcd} = 4.966$ Mg m^{-3}, $F(000) = 7470$, $\lambda(Mo_{K\alpha}) = 0.71073$ Å, $\mu(Mo_{K\alpha}) = 13.484$ mm^{-1}, $T = 298$ K. Of 6270 reflections collected in the θ range 1–35° using the $\theta-2\theta$ scan mode on a Nonius CAD-4 diffractometer, 5443 were independent ($R_{int} = 0.040$). Lorentzian polarization and empirical absorption corrections using the psi-scan technique[13] ($T_{min} = 0.794$, $T_{max} = 1.00$) were applied. The structure was solved and refined against F^2 using SHELXS[14] and SHELXL97.[15] The positional and anisotropic displacement parameters for all atoms were refined to the values $R_1 = 0.0394$, $wR_2 = 0.0671$ for 128 parameters and 2659 reflections with $I > 2\sigma(I)$, $w = 1/[\sigma^2(F_o^2) + (0.0132\,P)^2 + 235.0669\,P]$ where $P = [\max(F_o^2, 0) + 2F_c^2]/3$; max./min. residual electron density 2.237/–1.976 e Å^{-3}. Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666, on quoting the depository number CSD-410865.

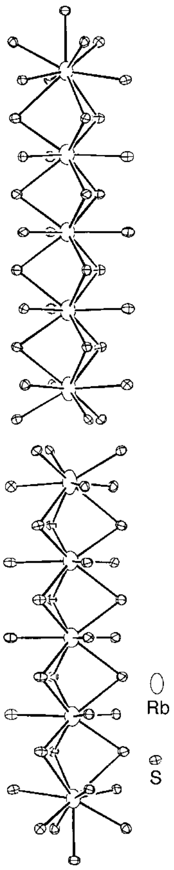

Figure 3. Distribution of the Rb^+ cations within the inter $Mo_{36}S_{44}$ cluster unit cavities.

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Non-Oxide Sol–Gel Chemistry: Preparation from Tris(dialkylamino)silazanes of a Carbon-Free, Porous, Silicon Diimide Gel

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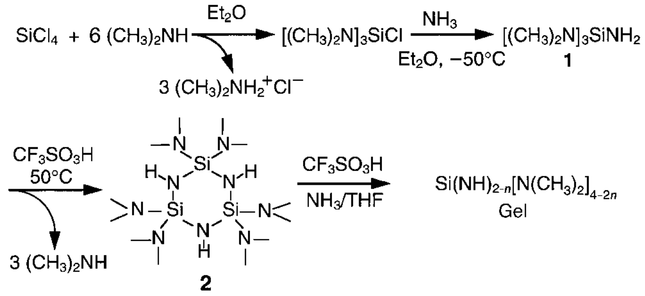
Sol–gel chemistry plays an important role in the preparation and processing of oxide materials, including microporous oxides and dense ceramics.[1, 2] There are few examples of non-oxide sol–gel techniques,[3–5] and the only reported sol–gel preparation in silicon–nitrogen chemistry is the synthesis of a Si/C/N solid by the reaction of methyltrichlorosilane with bistrimethylsilylcarbodiimide to form a nonporous gel in which the structural framework contains only SiNCNSi units.[6, 7] We are attempting to apply the chemistry of silicon amide compounds to the development of a "chimie douce" methodology for carbon-free $SiM(NH)_x$ gels (M = Si or metal), to give a sol–gel route to non-oxide ceramics and provide an alternative, mild synthetic route to nitridosilicates.[8–10] Such gels would be the azo analogues of silica-based amorphous oxide gels, and the nitridosilicate analogue to silica gel would be a gel of silicon diimide ($Si(NH)_2$). A putative imide/nitride pathway can be envisioned in which dialkylamido compounds of silicon are subjected to ammonolysis and condensation to an imide.

The reactions of $Si(NR_2)_4$ compounds, and of bimetallic analogues, with ammonia have been reported to give amorphous powders[11–16] and, in OMCVD experiments, silicon nitride films.[17] However, silicon diimide gels have not been reported from these or any other starting materials. We report here the preparation of a silicon imide gel by acid-catalyzed ammonolysis of the hitherto unreported tris(dimethylamino)silylamine $[(CH_3)_2N]_3SiNH_2$, **1**, which we have prepared from silicon tetrachloride in high yield and purity. The probable first step in this process is the acid-catalyzed self-condensation of **1** to the cyclic trimer $[\{(CH_3)_2N\}_2SiNH]_3$ (**2**), for which we report the X-ray crystal structure. The acid-catalyzed ammonolysis of **2**, or the equivalent sequential self-condensation and ammonolysis of **1**, under mild conditions, yields a semirigid translucent gel. On drying under mild conditions in an ammonia atmosphere this non-oxide gel yields a high surface area silicon diimide xerogel, the first example of a porous non-oxide silicate gel.

Compound **1** was prepared in high yield from silicon tetrachloride (Scheme 1) as a colorless liquid, and characterized by elemental analysis, IR and ^1H, ^{13}C, and ^{29}Si NMR spectroscopies, and mass spectrometry. It can be distilled under atmospheric pressure without detectable decomposition. Compound **1** is the simplest member of the series $(R_2N)_nSi(NH_2)_{(4-n)}$ (R = Me, $n = 3$), and is one of very few examples of a tris(amido)silylamine yet reported.[18] We have also prepared tris(morpholino)silylamine as a crystalline solid analogue to **1**. Details of the synthesis and structure of this compound will be published separately.



Scheme 1. Synthesis of **1** and **2** as well as the translucent gel of the composition $Si(NH)_{2-n}[N(CH_3)_2]_n$.

When **1** is heated in the presence of excess ammonia under autogenous pressure (100 bar) at 110 °C, a white powder is obtained, which is shown by IR spectroscopy to be $Si(NH)_2$.[19] The material is of low surface area ($< 50\,m^2g^{-1}$), and is presumably identical to the powder prepared by Union Carbide workers by the acid-catalyzed ammonolysis of $(Me_2N)_4Si$.[11] However, when **1**, either neat or in THF, is treated at 50 °C with a catalytic amount of trifluoromethanesulfonic acid, self-transamination occurs with loss of dimethylamine to give predominantly the cyclic trimer **2** (80 % according to MS, 61 % after recrystallization; Scheme 1). Compound **2** has been previously described as a product of the reaction of $(Cl_2SiNH)_3$ (a by-product (3 % yield) of the

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