Chem. Rev. **1996,** *96,* 2053−2062 **2053**

Group V and VI Alkali Nitridometalates: A Growing Class of Compounds with Structures Related to Silicate Chemistry

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Received January 23, 1996 (Revised Manuscript Received May 6, 1996)

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I. Introduction

The class of compounds of ternary nitrides has been nearly ignored for many years. But recently, it has become a rapidly growing field of interest. This is shown not only by an increasing number of papers especially since 1990, but also by review articles on this topic by Brese and O'Keeffe,[1] DiSalvo,[2] Schnick,[3] and Kniep.[4] The first one is a structural encyclopedia of nitrides, azides, and related compounds containing nitrogen and hydrogen, like amides and imides, known up to 1991. The second provides information on some selected compounds, and the third cited review describes the structures and properties of nonmetal nitrides known up to 1993. The last one gives a survey of actually known alkali and alkaline earth nitridometalates depending on their structural features. Most earlier investigations on ternary nitrides with lithium were done by the group of Juza and collaborators resulting in reviews in the 1950s[5] and in the 1960s.[6] Two additional reviews were made by Lang et al. in 1976[7] and 1979.[8]

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Herbert Jacobs was born in Kiel, Germany, in 1936. He studied chemistry at the Universität Kiel where he received his Dr. degree in 1966 and subsequently habilitate in 1971. From 1973 to 1983 he was Professor at the RWTH Aachen. Since 1983 he has been Professor at the Universität Dortmund. His special field of interest is inorganic chemistry with the emphasis on solid state chemistry.

In comparison to oxides and halides, the number of nitrides known is small. By applying the Born−Haber cycle to these compounds the high dissociation energy of nitrogen, and its unfavorable electron affinity may give arguments for the low thermal stability of nitrides of transition metals in high oxidation states. This is expressed by the compositions of the known binary nitrides of the transition metals of group V and VI. Whereas oxides of these elements in their highest oxidation state are well known, only tantalum forms a tantalum(V) nitride Ta_3N_5. The other five elements do not reach the oxidation state V or VI, respectively, in combination with nitrogen. On the other hand within the group of alkali metals only one binary nitride, Li_3N, is known. Li_3N and a great number of ternary nitrides with lithium are sensitive to water or moist air. In

S0009-2665(94)00515-7 CCC: $25.00

general the reactivity of ternary nitrides of the heavier alkali metals is increased. This causes problems as to the preparation and handling of samples. One aim of this article therefore must be to discuss in some detail the chosen routes for the preparation of ternary and higher nitrides of these metals.

In the present the special properties of the binary nitrides of the transition elements of group V and VI make ternary compounds to a class of substances of major interest. Most times binary nitrides are refractory materials and resistant to aggressive chemical agents. So reduced, ternary nitrides should result in new developments over the next years as, e.g., to their electric, electronic and magnetic properties. The similarity of nitrogen and oxygen in size, electronegativity, and polarizability make ternary nitrides possible candidates for high-temperature superconductors.

Most of the ternary nitrides with transition metals in high oxidation states can be described as nitridometalates in analogy to the corresponding oxo compounds. Transition metals mainly of the right side of the periodic table such as Cu,[9−13] Zn,[14,15] Fe,[16,17] Co,[12,18−20] Ni,[12,20−29] and boron[30−40] have mostly linear coordination by nitrogen. Trigonal planar species are reported for V,[41] Cr,[42] Mn,[43−45] Fe,[17,46−50] Co,[51] and Ga.[48] However Al,[13,52,53] Ti,[54,55] Zr,[56−58] Hf,[58,59] V, Nb, Ta, Cr, Mo, and W prefer higher coordination numbers in nitridometalates with tetrahedral or octahedral coordination environments. In one exception, zirconium, is found in a quadratic pyramidal coordination mode in $Ba[ZrN_2]$.[56] Chromium(I) and manganese(I) are able to form nitrides with chains of corner-sharing squares $^{1}_{\infty}[CrN_2N_{2/2}{}^{8-}]$ in $Ce_2[CrN_3]$,[60] $U_2[MN_3]$,[61] and $Th_2[MN_3]$[61] (M = Cr, Mn). Tetrahedral coordination is also known for the nitrides of silicon,[62−78] germanium,[76,79−88] and phosphorous.[89−103]

The nitridometalates with tetrahedral coordination of the transition metals of group V and VI, discussed in this paper, show especially broad analogies to the structural chemistry of silicates. Therefore, we occasionally use the nomenclature for silicate compounds of Liebau[104] to describe the anionic substructure of the nitridometalates.

II. Preparation

A. Reactions of Elements or Binary Nitrides at High Temperatures

Most ternary nitrides have been prepared by the reaction of the elements or the binary nitrides under flowing ammonia at rather high temperatures above 700 °C. This strategy was very successful for producing transition metal nitrides with lithium[105−120] or alkaline earth metals.[41,42,56,121−127]

Sometimes, reactions with amides instead of nitrides were used to prepare ternary nitrides, e.g. Ca_xMN_2 (M = Nb, Ta; $x = 1, 0.74$)[108,117] from $Ca(NH_2)_2$ or $Li_2Ta_3N_5$ from $LiNH_2$,[118] since at high temperatures the binary amides of lithium and of alkaline earth metals decompose to the corresponding binary nitrides.

The synthesis of nitrides of the heavier alkali metals from sodium to cesium under flowing gas is rather difficult. The corresponding binary alkali metal nitrides are unknown, and the vaporization of the alkali metals at temperatures above 900 °C results in the loss of these metals. Nevertheless in the case of $Na_3[MN_3]$ (M = Mo, W)[128] and $A[MN_2]$ (A = Na, K; M = Nb, Ta)[129] DiSalvo et al. were successful in using reactions with alkali metals and the corresponding binary transition metal nitrides under flowing ammonia at temperatures of 600−700 °C (bp (Na) ≈ 881 °C, bp (K) ≈ 766 °C).

B. Reactions in Salt Melts

Sometimes the complicated crystal structures of ternary nitrides are difficult to solve or to refine from powder data. So, several different attempts to grow single crystals have been undertaken. One interesting way is the reaction in salt melts as a flux. The elements or binary nitrides have been used as starting materials. This method works with calcium, tungsten, and Li_3N in LiCl to get $Li_6Ca_{12}[WN_4]_4O_3$.[130] Niobium metal and Li_3N in a mixture of Zn_3N_2/Ca_3N_2 yields $Li_7[NbN_4]$.[116] Other authors start with ternary nitrides and react them with the salt melt. $LiBa_4[Mo_2N_7]\cdot BaCl_2$[131] results from $Ba_3[MoN_4]$ and LiCl, $Li_{14}[CrN_4]_2O$,[106] from $Li_6[CrN_4]$ and Li_3N in a melt of LiCl/LiF. Melts of lithium halides or lithium nitride are favored in spite of their low melting points.

C. Preparation from Other Ternary Nitrides

As mentioned in the preceding section (II.B) some nitrides were synthesized by reactions of ternary nitrides with salt melts of Li_3N or lithium halides. Often lithium or halide ions were included in the compounds obtained by this route, or oxygen from impurities was added. In one special case a cation exchange of sodium by copper(I) was successful:[9]

$$Na[TaN_2] + CuI \rightarrow Cu[TaN_2] + NaI$$

This reaction most probably is driven by the lattice energy of the alkali metal halide. But the alkali metal atoms in other ternary nitrides could be easily exchanged, too. This was shown for the reaction of $Na_3[WN_3]$ with excess potassium to form microcrystalline $Na_2K[WN_3]$.[132,133]

It is also possible to prepare ternary nitrides with new compositions from e.g. the tantalum-rich lithium nitride $Li_2Ta_3N_5$[118] by thermal decomposition. Depending on the reaction temperature, the formation of $Li_{2-x}Ta_{2+x}N_4$ ($x = 0.2-1.0$) or $LiTa_3N_4$[117,119] occurs.

D. Preparation from Oxides or Organic Precursors by Ammonolysis

Several attempts to prepare ternary nitrides from ternary oxide precursors were made. Recently, the reaction of $Li_2[MO_4]$ (M = Mo, W) with flowing ammonia was reported. $LiMN_2$, Li_2O, and water were the products at temperatures slightly above 700 °C,[134,135] where the ternary oxide is molten. On the other hand $LiMoN_2$ was prepared from the organic precursor $Li_2Mo(N^tBu)_4$ by ammonolysis at 650 °C.[134] Further reduced transition metal(V) nitrides $M'WN_2$ (M′ = Fe, Mn, Co, Ni)[136−138] and $(Fe_{0.8}Mo_{0.2})MoN_2$[139]

were prepared by ammonolysis of the corresponding ternary oxides M′MO$_4$.

Ammonolysis of sodium oxometalates like Na$_2$[MO$_4$] (M = Mo, W) leads to the oxonitridometalates(VI) Na$_3$[MNO$_3$].[140] The formation of oxonitridometalates instead of nitrides under these conditions was approximately calculated by thermodynamical considerations from the known data of binary oxides and nitrides.[141]

E. Reactions in Autoclaves

As described before (section II.A) some nitridometalates of the heavier alkali metals from sodium to cesium were prepared in streaming ammonia. But the best results in preparing ternary nitrides of the heavier alkali metals Na−Cs were achieved with reactions in autoclaves. The niobium compounds A[NbN$_2$] (A = Na, Cs) are preferably prepared from NbN (there is no Nb$_3$N$_5$ known) and the corresponding alkali metal amides.[142,143] In order to obtain the tantalum compounds A[TaN$_2$] (A = Na, K, Rb, Cs)[144] one may start with Ta$_3$N$_5$, TaCl$_5$, or NH$_4$[TaF$_6$] and the alkali metal amides at temperatures between 400 and 800 °C. It is even possible to synthesize these ternary nitrides by the reaction of Ta$_2$O$_5$ with the alkali metal amides.

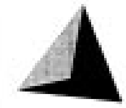
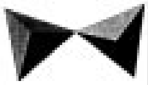
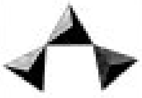
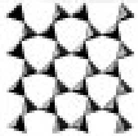
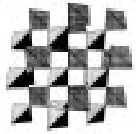
In contrast to the reactions of compounds of niobium and tantalum, oxonitridometalates(VI) result exclusively if binary oxides of molybdenum or tungsten are reacted with alkali metal amides. In closed systems of autoclaves the oxygen content of the products can be controlled by the composition of the starting mixture as for example M/MO$_3$ (M = Mo, W). Normally, the total amount of oxygen is found in the oxonitridometalates(VI) after the reaction is carried out, whereas excess nitrogen forms N$_2$. Thereby the compounds Na$_4$[WN$_2$O$_2$],[145] A$_6$[M$_2$N$_4$O$_3$] (A = Na, K, Rb, Cs; M = Mo, W),[146,147] and NaA$_4$[(WN$_{2.5}$O$_{0.5}$)$_2$] (A = Rb, Cs)[148] were prepared as single crystals. Reactions of sodium amide with pure WO$_3$ produce Na$_5$[WNO$_4$][149] as well as Na$_4$[WN$_2$O$_2$].

Alkali metal nitridometalates(VI) of molybdenum and tungsten containing no oxygen were prepared by the reactions of the transition metal powders with an excess of the alkali metal amides at temperatures above 600 °C. At these temperatures the amides decompose to nitrogen, hydrogen, and the corresponding alkali metal. The hydrogen leaves the autoclave through a nickel membrane. The partial pressure of nitrogen obtained by the decomposition reaction is high (up to 2 kbar). This favors the formation of alkali metal nitridometalates(VI). They crystallize in a matrix of the corresponding alkali metal. Surprisingly hitherto only nitrides with transition metals in their highest oxidation states were obtained under these usually strongly reducing conditions. By this procedure the compounds Na$_3$[MN$_3$] (M = Mo, W),[150,151] Na$_2$K[WN$_3$],[132] Na$_{11}$Rb[(WN$_3$)$_4$],[132] Na$_5$A[(WN$_3$)$_2$] (A = Rb, Cs),[152] Na$_2$K$_{13}$[W$_7$N$_{19}$],[153] K$_{14}$[W$_6$N$_{16}$NH],[154] and Cs$_5$[Na{W$_4$N$_{10}$}][155] were prepared.

III. Structures and Properties

Table 1 gives examples of silicates and nitridometalates arranged with increasing degree of connectivity of ligand tetrahedra around silicon and some transition metals in comparison. The following chapters are organized with respect to these structural features.

Table 1. Comparison of Structure Elements of Some Selected Silicates and Nitridometalates

Dimensionality	Unit	Examples	
0 Monometalates		Li$_4$[SiO$_4$][186]	Li$_7$[TaN$_4$][156]
0 Dimetalates		Li$_6$[Si$_2$O$_7$][187]	LiBa$_4$[W$_2$N$_7$][159]
1 Monopolymetalates		Na$_2$[SiO$_3$][188]	Na$_3$[WN$_3$][151]
2 Phyllometalates		Ba[Si$_2$O$_5$][189]	Na$_2$K$_{13}$[W$_7$N$_{19}$][153]
3 Tectometalates		K$_2$Ce[Si$_6$O$_{15}$][177]	Cs[TaN$_2$][144]

A. Compounds with Isolated Tetrahedra

The first detailed information about alkali metal nitrides of the group V transition metals was reported for Li$_7$[MN$_4$] (M = V, Nb, Ta).[110−112] All three compounds were reported to crystallize in CaF$_2$-type superlattices. The niobium and tantalum compounds are isotypic, but Li$_7$[VN$_4$] has a different structure. Recently, the structures of Li$_7$[NbN$_4$][116] and Li$_7$[TaN$_4$][156] were solved from single-crystal data (see Figure 1). Furthermore, the formation of intergrowing compounds of these nitrides with Li$_2$O giving new CaF$_2$-type superlattice compounds[111,157] was reported. Later on this observation was confirmed

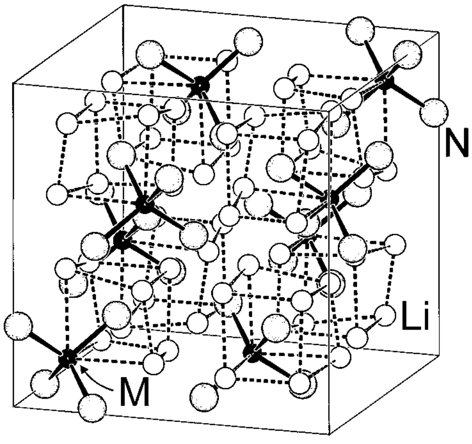


Figure 1. Unit cell of the CaF$_2$-type compounds Li$_7$[MN$_4$] (M = Nb, Ta).

with the preparation and structure determinations of $Li_{16}[NbN_4]_2O$[108] and $Li_{16}[TaN_4]_2O$.[115]

The transition metals of group VI form the compounds $Li_6[MN_4]$ (M = Cr, Mo, W)[106] and $Li_{15}[CrN_4]_2N$,[106] as well as the reduced nitrides $LiMN_2$ (M = Mo, W),[134,135] which are discussed later in section III.F. Earlier reports on Li_9MN_5 (M = Cr, Mo, W)[105] could not be verified. But the formation of intergrowing compounds with Li_2O was again confirmed with the structural determination of $Li_{14}[CrN_4]_2O$.[106] Systems analogous with Li_2O/Li_5SiN_3[157] and some compounds of the higher homologues of nitrogen Li_3P/Li_7VP_4[158] and Li_3As/Li_7VAs_4[158] are known. In the latter two systems no superstructures were observed, but increasing densities were noted. This suggests the presence of interstitial excess lithium.

With the exception of $LiMN_2$ (M = Mo, W)[134,135] all these compounds are colored and sensitive to moist air, giving oxometalates. They crystallize in CaF_2-type superstructures in which nitrogen atoms occupy the positions of the calcium atoms. Lithium and the transition metal atoms occupy the position of fluorine in an ordered way: Resulting $[MN_4]$ tetrahedra are only surrounded by lithium atoms and not connected with other $[MN_4]$ tetrahedra. In the compounds of the fifth group transition metals one lithium position is unoccupied in an ordered way giving $Li_6\square[MN_4]$ (M = Cr, Mo, W). In the case of oxygen-containing compounds the transition metals are only surrounded by nitrogen atoms. The oxygen is exclusively in the coordination sphere of the lithium atoms, giving again CaF_2-type superstructures with larger unit cells. Figure 1 shows the unit cell of $Li_7[MN_4]$ (M = Nb, Ta).[116,156]

In compounds with some larger cations like the alkaline earth metals the CaF_2-type structure is not attainable for geometric reasons. In $Li_2Sr_5[MN_4]_2$ (M = Mo, W)[107] and $Li_3Ba_2[MN_4]$ (M = Nb, Ta)[113,114] tetrahedral coordination of the transition metal atoms is conserved, but the packing of the tetrahedra $[MN_4]$ and the electropositive metal cations is rather different. This is also known from some nitridometalates of the transition metals of the fifth and the sixth group containing alkaline earth metals.[107,122,123,127] The same findings are observed in the structures of the nitridometalates oxides $Li_6Ca_{12}[MN_4]_4O_3$ (M = Mo, W),[130] where the tetrahedral coordination of the transition metal atoms is only formed by nitrogen ligands. The oxygen atoms are surrounded only by lithium and alkaline earth metal atoms, as described previously for CaF_2-type lithium nitridometalate oxides. An example of a comparable structural motif involving chloride is the known compound $Ba_4[WN_4]Cl_2$,[108] which is best described as a nitridotungstate chloride.

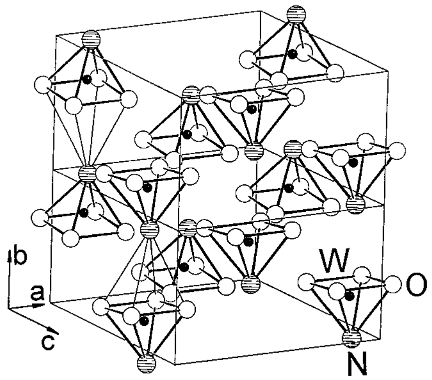


Figure 2. Part of the structure of $Na_5[WNO_4]$.

In contrast to the lithium nitridometalates, in all known oxide nitride compounds of the heavier alkali metals, the oxygen is located in the first coordination sphere of the transition metals. In the compounds containing sodium $Na_4[MN_2O_2]$[145] and $Na_3[MNO_3]$[140] (M = Mo, W) the ligands form tetrahedra around the transition metal atoms. In the structures of these compounds it was not possible to distinguish between oxygen or nitrogen as ligands either with X-ray or with neutron diffraction techniques. The latter investigations showed best results by assuming a statistical distribution of oxygen and nitrogen on the sites of the ligands. The only known oxonitridometalate of this type with ordered oxygen and nitrogen partial structures is $Na_5[WNO_4]$.[149] In this compound the ordered structure is forced by the formation of a tetragonal pyramid of oxygen and nitrogen around tungsten with the oxygen atoms in the base and the nitrogen atom in a distinguished position at the apex. This special anionic partial structure in this particular compound with high oxygen content can be understood as a transition to octahedral coordination, which is largely known from the chemistry of the oxotungstates. The nearly octahedral coordination of tungsten in $Na_5[WNO_4]$ is approached by the orientation of the tetragonal pyramids as seen in Figure 2. The top of the pyramids point directly to the middle of the base of the next pyramid but the resulting distance between the tungsten and this nitrogen atom is much longer than the distances within the pyramid. Analogous tetragonal pyramidal anions with molybdenum in the centers are known for example from $[Ph_4As][MoNCl_4]$ and $[Ph_4As][MoOCl_4]$[159] with nitrogen or oxygen in the apex of the pyramid.

All these nitrido- and oxonitridometalates, with the transition metal in its highest oxidation state, are yellow to red compounds which are highly sensitive to moist air.

B. Compounds with Dimetalate Units of Corner-Sharing Tetrahedra

The connection of two tetrahedra by corner sharing results in dimetalate units $[M_2N_7]^{9-}$ in $LiBa_4[M_2N_7]$ (M = Mo, W).[109] The same kind of attachment results in the structures of the oxonitrido compounds $A_6[M_2N_4O_3]$ (A = K, Rb, Cs; M = Mo, W).[146,147] The dimers are in staggered conformation. In the oxonitridodimetalate(VI) ions $[M_2X_7]^{6-}$ it was again not possible to distinguish between oxygen and nitrogen. One example of a dimetalate ion is shown in Figure 3.

In the lithium-containing dimetalates the anions are connected by layers containing lithium. The oxonitridodimetalates can be described as a distorted cubic body-centered packing of the anions, connected by the alkali metal atoms.

The compound $LiBa_4[Mo_2N_7]\cdot BaCl_2$ of a comparable composition contains again dimetalate units $[Mo_2N_7]^{9-}$ but surprisingly in an eclipsed conformation.[131]

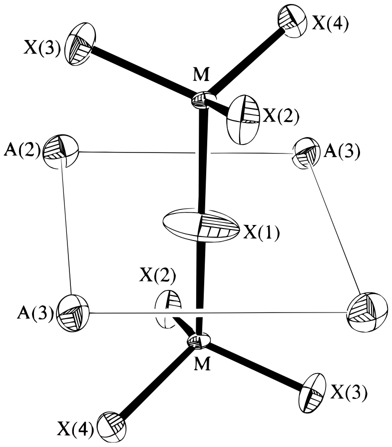


Figure 3. $[M_2X_7]^{6-}$ unit in the structures of the compounds $A_6[M_2N_4O_4]$ (A = K, Rb, Cs; M = Mo, W).

In the chemistry of nitridometalates of the transition metals of group V no structural analogs to these colored and water-sensitive compounds of Mo and W are known. But in the silicate chemistry, the unit $[Si_2O_7]^{6-}$ is common, especially for the high number of thortveitite class compounds (thortveitite: $Sc_2[Si_2O_7]$).[160,161]

C. Compounds with Infinite Chains of Corner-Sharing Tetrahedra

The exchange of lithium in nitridometalates by the larger alkali metal cations results in further condensation of the nitridometalate tetrahedra. In compounds with a high sodium content $Na_3[MN_3]$ (M = Mo, W),[128,150,151] $Na_2K[WN_3]$,[132] $Na_{11}Rb[(WN_3)_4]$,[132] and $Na_5A[(WN_3)_2]$ (A = Rb, Cs)[152] infinite chains $^{1}_{\infty}[MN_2N_{2/2}{}^{3-}]$ with different conformations are found. The compounds $Na_3[MN_3]$ (M = Mo, W) containing only sodium are built of nearly "zweier" single chains[104] as shown in Figure 4. Only a slight distortion results in "vierer" single chains, i.e. four tetrahedra in the repeat unit. The chains are stacked together in the motif of a hexagonal rod packing connected by sodium atoms.

The structures of the compounds $Na_2K[WN_3]$ and $Na_{11}Rb[(WN_3)_4]$ are closely related to one another.

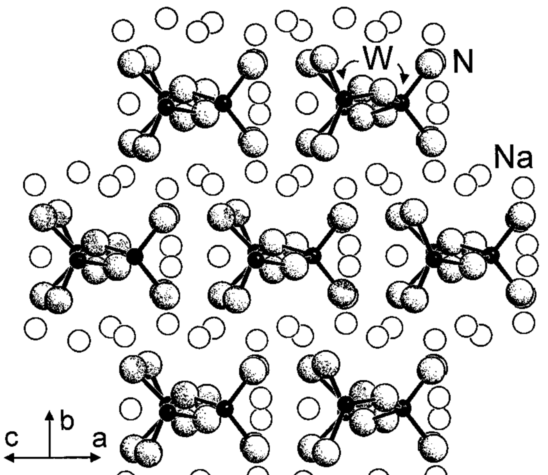


Figure 4. Projection of the hexagonal rod packing of the infinite chains $^{1}_{\infty}[MN_2N_{2/2}{}^{3-}]$ in the structures of the compounds $Na_3[MN_3]$ (M = Mo, W).

The chains $^{1}_{\infty}[WN_2N_{2/2}{}^{3-}]$ show alternating orientation of tetrahedra at the sides and in the center (Figure 5), giving again "vierer" single chains. This type of conformation was also found in the silicate mineral krauskopfite $Ba[(SiO_2OH)_2]\cdot 2H_2O$.[162] The chains in this compound are much broader. So, in contrast to the slim chains in $Na_3[MN_3]$ (M = Mo, W) they are stacked together in a motif of a tetragonal rod packing.

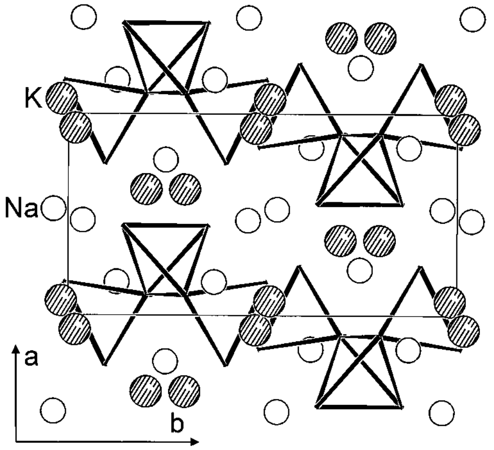


Figure 5. Projection of the unit cell of $Na_2K[WN_3]$ along the direction of infinite chains $^{1}_{\infty}[WN_2N_{2/2}{}^{3-}]$.

The isotypic compounds $Na_5Rb[(WN_3)_2]$ and $Na_5Cs[(WN_3)_2]$ contain chains $^{1}_{\infty}[WN_2N_{2/2}{}^{3-}]$ in a conformation that is very common in the silicate chemistry. They form "vierer" single chains with tungsten and the bridging nitrogen atoms nearly in one plane (Figure 6). This is known for example from batisite $Na_2BaTi_2[(SiO_3)_4]O_2$,[163] but also from other silicates and oxometalates with very different compositions.[164−168] In the nitrides the chains are connected by rubidium or cesium atoms, respectively, to form layers. The sodium atoms are mainly located between these layers.

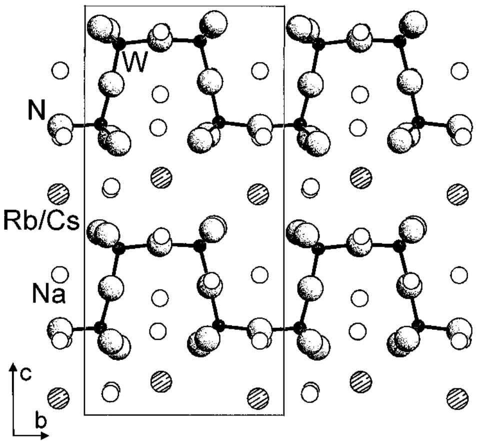


Figure 6. Projection of the unit cell of the compounds $Na_5A[(WN_3)_2]$ (A = Rb, Cs).

Related compounds are known for the oxonitridotungstate(VI) chemistry with $NaA_4[(WN_{2.5}O_{0.5})_2]$ (A = Rb, Cs).[148] The structures of these compounds show "zweier" single chains $^{1}_{\infty}[MX_2X_{2/2}{}^{2.5-}]$ (X = N, O) like that which has been found in the structures of CrO_3[169] and the germanates $Na_2[GeO_3]$[170] and $Na_2K[GeO_3]$.[171] In the oxonitrido compounds these chains are connected by sodium atoms to double-chain units $^{1}_{\infty}[\{WX_2X_{2/2}\}_2Na^{4-}]$, which form the motif of a hexagonal rod packing (Figure 7).

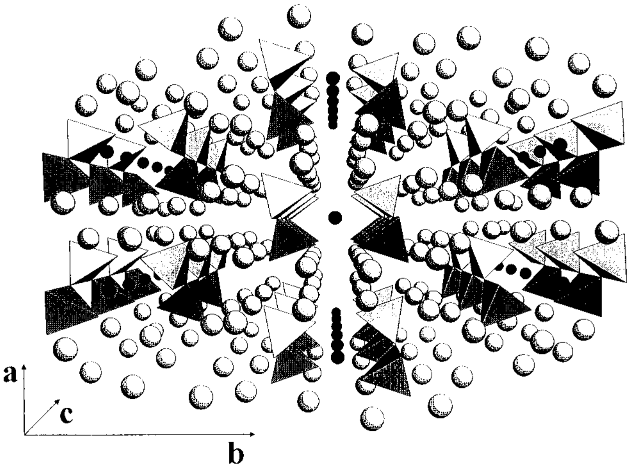


Figure 7. View into the structure of the compounds $NaA_4[(WN_{2.5}O_{0.5})_2]$ (A = Rb, Cs) showing the hexagonal rod packing of the double chain units $^{1}_{\infty}[\{WX_2X_{2/2}\}_2Na^{4-}]$. The larger balls represent rubidium or cesium, respectively, the smaller sodium ions.

All these compounds are also colored yellow, orange, or red and are highly sensitive to moisture. For the most part single crystals grow in the shape of long needles. These can be easily split into thinner needles along the needle axis which is the direction of the chains.

In the chemistry of alkali metal nitridometalates of the group V transition metals there are no compounds with infinite chains known presently. But alkaline earth compounds with the representative composition $Ea_2[MN_3]$ (Ea = Sr, Ba; M = V, Nb, Ta)[56,125,126] contain infinite "zweier" single chains $^{1}_{\infty}[MN_2N_{2/2}{}^{4-}]$.

D. Compounds with Loop-Branched Units

A higher degree of condensation than that in the above discussed chains sometimes results in very complicated anionic partial structures. In the structure of the dark red $K_{14}[W_6N_{16}NH]$[154] there are rings of six corner-connected tetrahedra giving $[W_6N_{16}(NH)_{2/2}{}^{14-}]$. These are linked by corner sharing of two tetrahedra in para positions of the rings. The connections between the rings occur via NH groups. The boat configuration of the individual rings causes peculiar waved ropes which run one dimensionally infinitely through the structure. This rope is shown in Figure 8. The ropes run parallel and interlace resulting in macroscopic mechanically stable layers. In the silicate chemistry, pellyite $CaBa_2(Fe,Mg)_2[Si_6O_{17}]$,[172] is an example of a structural correspondence.

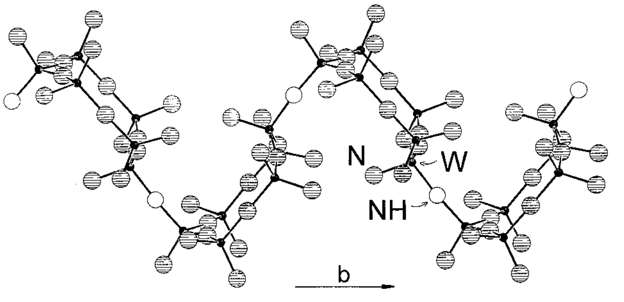


Figure 8. Fragment of an infinite rod $^{1}_{\infty}[W_6N_{16}(NH)_{2/2}{}^{14-}]$ in the structure of $K_{14}[W_6N_{16}NH]$.

In the very complex structure of the red $Na_2K_{13}[W_7N_{19}]$[153] ropes like discussed before are part of the anionic partial structure. In this compound the ropes are stretched and connected by an extra tetrahedron to form layers $^{2}_{\infty}[(WN_2N_{2/2})_3(WNN_{3/2})_4{}^{15-}]$ (Figure 9). This structural feature can be inferred by the mechanical properties. The crystals have the shape of platelets which can easily be cleaved between the layers.

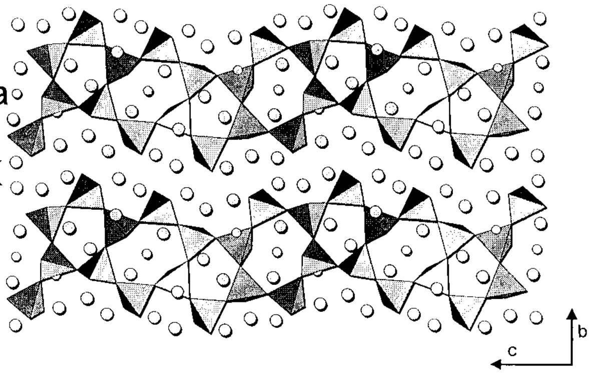


Figure 9. Projection of the structure of $Na_2K_{13}[W_7N_{19}]$, showing the layers $^{2}_{\infty}[(WN_2N_{2/2})_3(WNN_{3/2})_4{}^{15-}]$.

An additional nitridometalate with layers of connected tetrahedra is known, γ-$Ca_3[Al_2N_4]$.[13] In this compound the layers are formed by corner and edge sharing of the tetrahedra $^{2}_{\infty}[AlN_{2/2}N_{2/2}{}^{3-}]$.

Compounds with isolated rings of corner-sharing tetrahedra as seen in a number of silicates[173−176] and the ternary nitride $Ba_{10}[Ti_4N_{12}]$[54] are hitherto unknown in the chemistry of alkali metal nitridometalates.

E. Compounds with Three-Dimensional Frameworks

Partial exchange by cesium of the alkali metals in the chain compounds discussed before (section III.C) results in a higher degree of connectivity of corner-sharing tetrahedra as in $Cs_5[Na\{W_4N_{10}\}]$.[155] The nitridotungstate partial structure consists of $[WN_4]$ tetrahedra, sharing three nitrogen ligands with other tetrahedra. This causes a three-dimensional network $^{3}_{\infty}[WNN_{3/2}{}^{1.5-}]$ which is also known from the synthetic silicate $K_2Ce[Si_6O_{15}]$.[177] In the nitride the sodium atoms with a slightly larger ionic radius than tungsten(VI) complete a distorted β-crystobalite type structure $^{3}_{\infty}[Na\{W_4N_{10}\}^{5-}]$. The distortion is mainly caused by the different sizes of the tungsten and sodium atoms.[178,179] In this structure the cesium atoms fill the large holes, Friauf polyhedra (Figure 10).

An undistorted filled β-crystobalite-type structure is realized in the compounds of $Cs[MN_2]$ (M = Nb, Ta).[142,144] The $^{3}_{\infty}[MN_{4/2}{}^{1-}]$ framework is filled by cesium atoms (Figure 11). Like in the structure of β-crystobalite itself, the nitrogen atoms are distributed around the ideal position between the transition metals. In the related compounds $K[MN_2]$ (M = Nb, Ta) and $Rb[TaN_2]$[144] the $^{3}_{\infty}[MN_{4/2}{}^{1-}]$ network is dis-

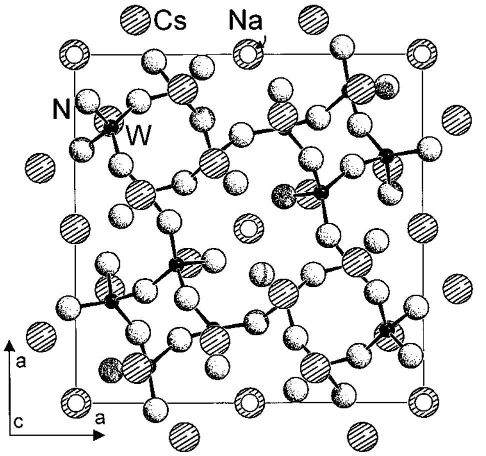


Figure 10. Projection of the structure of $Cs_5[Na\{W_4N_{10}\}]$.

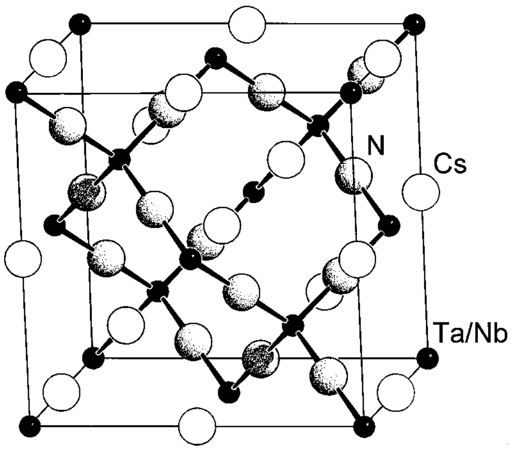


Figure 11. Unit cell of the filled β-cristobalite-type compounds $Cs[MN_2]$ (M = Nb, Ta).

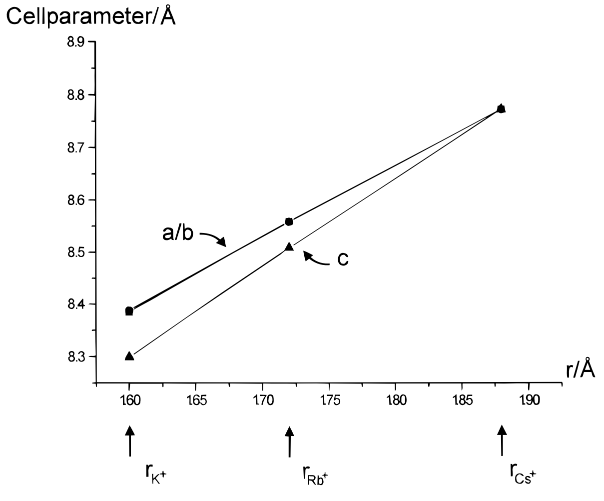


Figure 12. Diagram showing the pseudocubic unit cell parameters of the compounds $A[TaN_2]$ (A = K, Rb, Cs) as function of the ionic radii of the alkali metals.[178,179]

torted. The smaller ionic radii of potassium and rubidium in contrast to the cesium ions cause this distortion, as indicated by the comparison of the cell parameters (Figure 12). Both compounds are realized as a variant of the $K[GaO_2]$-type structure.[180]

F. Compounds with Layers of Connected Octahedra

Whereas all alkali metal nitridometalates(VI) of molybdenum and tungsten and the alkali metal nitridometalates(V) of niobium and tantalum with potassium, rubidium and cesium result in tetrahedral coordination of the transition metal atoms, in the sodium compounds $Na[MN_2]$ (M = Nb, Ta)[129,143,144] the transition metals occupy the centers of distorted octahedra formed by nitrogen. These octahedra are connected by edge sharing to form layers ${}^{2}_{\infty}[MN_{6/3}{}^{1-}]$. Between these layers the sodium atoms fill distorted octahedral sites. This structure is called α-$NaFeO_2$ type[181] (Figure 13). Both compounds $Na[MN_2]$ are colored yellow (Ta) and red (Nb) and are resistant in reaction with air and water. Nevertheless depending on the particle size they can burn in air, forming oxides. Ionic conductivity measurements and impedance spectroscopy on $Na[TaN_2]$ result in a remarkable ionic conductivity for sodium.[182] But elastic and quasielastic neutron diffraction investigations could not solve the problem of the mechanism.[183]

A feature related to the ionic conductivity of $Na[TaN_2]$ is the easy exchange of the sodium atoms by other metals. This is known from the formation of $Cu[TaN_2]$[9] from mixtures of $Na[TaN_2]$ with copper(I) iodide (see section II.C). The structure of $Na[TaN_2]$ in this reaction changes to the dellafosite-type structure α-$CuFeO_2$. The nitridotantalate layers are not varied but only shifted relative to each other, resulting in linear coordination of the copper atoms (see Figure 13). The greyish-green color of the obtained $Cu[TaN_2]$ powder suggests that tantalum is in the V oxidation state and copper in I.

Surprisingly the alkaline earth metal compounds $Ca[MN_2]$ and $Ca_{0.74}[MN_2]$ (M = Nb, Ta)[108,117] realize the same structure type as $Na[MN_2]$ with less occupancy of the calcium site in the second case. These compounds are black powders. The color indicates the reduced oxidation state of the transition metal. The tantalum compounds show superconductivity below 9 K[84] and the corresponding niobium compounds below 14 K.[184]

Closely related structures were found in $Li[MN_2]$ (M = Mo, W)[134,135] but with the transition metal atoms in trigonal prisms formed by nitrogen. These polyhedra are arranged in layers ${}^{2}_{\infty}[MN_{6/3}{}^{1-}]$ which are connected by lithium atoms in octahedral coordination. In these compounds, the shortest known distances between nitride ions are reported, located within the N−M−N double layers. These reduced compounds and the related $M'WN_2$ (M' = Mn, Fe, Co, Ni)[136−138] and $(Fe_{0.8}Mo_{0.2})MoN_2$[139] have stimulated a great deal of interest recently.[141,185]

There are two tantalum-rich lithium nitrides known with NaCl-type structures. The reduced, black $Li_2Ta_3N_5$[118] realizes an ordered NaCl-type superstructure with short tantalum−tantalum distances, indicating metal−metal bonds. For $Li_{2-x}Ta_{2+x}N_4$ ($0.2 < x < 1$)[119] with the ideal composition $LiTaN_2$ ($x = 0$) a NaCl-type lattice with statistical distribution of the cations was found. In contrast $LiTa_3N_4$[119] crystallizes in a filled 2H-MoS_2-type structure with a hexagonal sequence of the nitrogen layers. Two of three tantalum atoms occupy trigonal prisms between similarly arranged nitrogen layers. The remaining tantalum and the lithium atoms fill up octahedral coordinated positions between these layers in a statistically distributed way giving α Ta α Ta/Li β

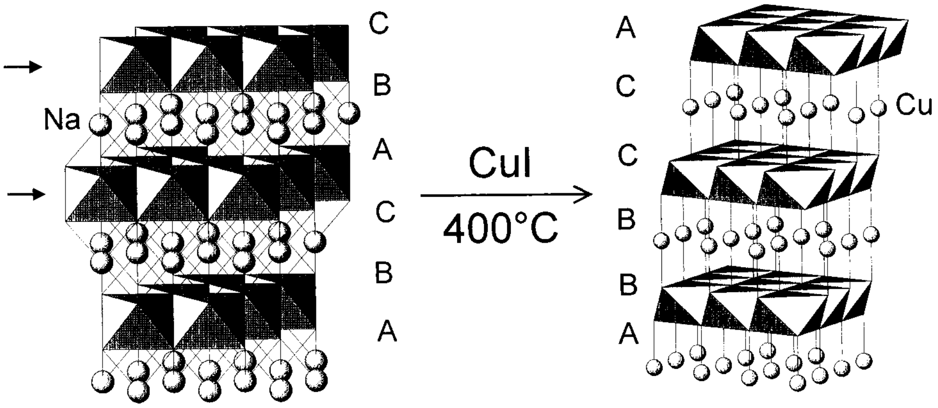


Figure 13. Comparison of the stuctures of the compounds $Na[TaN_2]$ and $Cu[TaN_2]$.

Ta β. The remaining structure is closely related to that of $Li[MoN_2]$[134] discussed previously. The distribution of lithium and a transition metal on one crystallographical site is known from the corresponding nitridoniccolates(I),[21,22] and nitridocuprates(I)[10] and from $Li[MoN_2]$.[134]

IV. Discussion of Bond Lengths

A special feature of the nitridometalates with tetrahedral coordination of the transition metals is the variation of the bond lengths d(M−N) (M = Nb, Ta, Mo, W). Tables 2 and 3 contain bond length data for all known alkali and alkaline earth nitridometalates and some related oxygen and chlorine compounds with tetrahedral coordination of these transition metals. Table 2 sums up the tungsten and molybdenum; Table 3 the niobium and tantalum, compounds. There is no need to differ between the respectively homologous metals because of their nearly identical ionic radii.[178,179] The column $\bar{d}$(M−N) gives the average distances for all bond lengths in the compounds. The following two columns differentiate between terminal and bridging nitrogen ligands.

The data $\bar{d}$(M−N) show that the mean distance for group VI and group V compounds is nearly constant at 1.87 and 1.95 Å, respectively. The mean distances of the oxonitridometalates(VI) are slightly shorter depending on the oxygen content. This results from the shorter bond length d(M−O) compared to d(M−N).

The data for the compound $Cs[NbN_2]$ were excluded from these calculations of mean bond lengths. The distance d(Nb−N) has only been calculated with straight M−N−M bonds, not with the distorted model (see section III.E). So these data for $Cs[NbN_2]$ and $Cs[TaN_2]$ are given in brackets.

The distances of the transition metal atoms to the terminal ligands differ from the distances to the bridging ligands by about 0.1 Å. But a detailed inspection reveals that this bond length decreases with increasing connectivity of tetrahedra. Whereas the nitrogen ligands in the isolated tetrahedra have an average distance to the transition metal atom, the terminal nitrogen ligands in the other compounds form bonds with increasing amounts of π interactions. With increasing connectivity the number of terminal ligands per tetrahedra decreases, and the bridging ligands participate on more of π interactions.

This point of view is supported by the structure data of the compounds $K_{14}[W_6N_{16}NH]$ and $Na_2K_{13}[W_7N_{19}]$. In these structures there are bridg-

Table 2. Mean Distances between Transition Metals and Their Ligands in Alkali and Alkaline Earth Metal Nitridometalates(VI) of Molybdenum and Tungsten

compound	$\bar{d}$(M-N)	$\bar{d}$(M−N$_{terminal}$)	$\bar{d}$(M−N$_{bridging}$)	compound	$\bar{d}$(M-N)	$\bar{d}$(M−N$_{terminal}$)	$\bar{d}$(M−N$_{bridging}$)
$Li_6[MoN_4]$[106]	1.879	1.879		$Ba_4[WN_4]Cl_2$[108]	1.87	1.87	
$Li_6[WN_4]$[106]	1.91	1.91		$LiBa_4[Mo_2N_7]$[109]	1.86	1.83	1.95
$Li_2Sr_5[MoN_4]_2$[107]	1.88	1.88		$LiBa_4[W_2N_7]$[109]	1.86	1.83	1.94
$Li_2Sr_5[WN_4]_2$[107]	1.87	1.87		$LiBa_4[Mo_2N_7]\cdot 2BaCl_2$[131]	1.857	1.837	1.915
$Li_6Ca_{12}[MoN_4]_4O_3$[130]	1.88	1.88		$Na_3[MoN_3]$[150]	1.86	1.79	1.93
$Li_6Ca_{12}[WN_4]_4O_3$[130]	1.876	1.876		$Na_3[WN_3]$[151]	1.88	1.84	1.93
$Sr_3[MoN_4]$[107]	1.87	1.87		$Na_2K[WN_3]$[132]	1.86	1.81	1.92
TT-$Ba_3[MoN_4]$[122]	1.87	1.87		$Na_{11}Rb[(WN_3)_4]$[132]	1.87	1.82	1.93
TT-$Ba_3[WN_4]$[122]	1.90	1.90		$Na_5Rb[(WN_3)_2]$[152]	1.87	1.82	1.92
HT-$Ba_3[MoN_4]$[107]	1.86	1.86		$Na_5Cs[(WN_3)_2]$[152]	1.87	1.83	1.92
HT-$Ba_3[WN_4]$[107]	1.86	1.86		$K_{14}[W_6N_{16}NH]$[154]	1.87	1.80	1.91
$Ca_2Sr[WN_4]$[123]	1.87	1.87		$Na_2K_{13}[W_7N_{19}]$[153]	1.87	1.79	1.91
$Sr_{25.5}[WN_4]_6N_5$[107]	1.88	1.88		$Cs_5[Na\{W_4N_{10}\}]$[155]	1.87	1.82	1.89
$Sr_4[MoN_4]O$[107]	1.87	1.87					

compound	$\bar{d}$(M−X)	$\bar{d}$(M−X$_{terminal}$)	$\bar{d}$(M−X$_{bridging}$)	compound	$\bar{d}$(M−X)	$\bar{d}$(M−X$_{terminal}$)	$\bar{d}$(M−X$_{bridging}$)
$Na_3[WNO_3]$[140]	1.800	1.800		$Rb_6[W_2N_4O_3]$[147]	1.83	1.80	1.897
$Na_4[MoN_2O_2]$[145]	1.840	1.840		$Cs_6[Mo_2N_4O_3]$[147]	1.83	1.81	1.911
$Na_4[WN_2O_2]$[145]	1.844	1.844		$Cs_6[W_2N_4O_3]$[147]	1.82	1.80	1.888
$K_6[Mo_2N_4O_3]$[146,147]	1.837	1.814	1.903	$NaRb_4[(WN_{2.5}O_{0.5})_2]$[148]	1.856	1.804	1.908
$K_6[W_2N_4O_3]$[147]	1.830	1.810	1.891	$NaCs_4[(WN_{2.5}O_{0.5})_2]$[148]	1.854	1.796	1.911
$Rb_6[Mo_2N_4O_3]$[147]	1.83	1.81	1.906				

Table 3. Mean Distances between Transition Metals and Their Ligands in Alkali and Alkaline Earth Metal Nitridometalates(V) of Niobium and Tantalum

compound	$\bar{d}$(M−N)	$\bar{d}$(M−N$_{\text{terminal}}$)	$\bar{d}$(M−N$_{\text{bridging}}$)
$Li_7[NbN_4]$[116]	1.95	1.95	
$Li_7[TaN_4]$[156]	1.974	1.974	
$Li_3Ba_2[NbN_4]$[113]	1.95	1.95	
$Li_3Ba_2[TaN_4]$[114]	1.952	1.952	
$Li_{16}[NbN_4]_2O$[108]	1.954	1.954	
$Li_{16}[TaN_4]_2O$[115]	1.94	1.94	
$Ba_9[TaN_4]_2[N_3]N$[127]	1.96	1.96	
$Ba_2[NbN_3]$[56]	1.94	1.90	1.99
$Ba_2[TaN_3]$[126]	1.96	1.94	1.98
$Cs[NbN_2]$[142]	(1.892)		(1.892)
$Cs[TaN_2]$[144]	1.931		1.931(1.899)
	(1.899)		(1.899)

ing ligands between tertiary and secondary tetrahedra. The ligands are shifted to the tertiary tetrahedra, whereas the other bridging ligands between two secondary or tertiary tetrahedra are located nearly exactly in the middle between the transition metal atoms.

The comparison of the respective distances in silicate structures reveals a mean difference between silicon to bridging and terminal oxygen ligands of about 0.025 Å.[104] This is due to the silicon atom's ability to form four covalent σ bonds. The slightly longer distance is only established by the Coulomb repulsion of the positive polarized silicon atoms.

V. Conclusion

Most alkali and alkaline earth metal nitrides of the transition metals of group V and VI show tetrahedral coordination environments of the transition metals by nitrogen. The structural chemistry of the resulting nitridometalates is closely related to that widely known from oxosilicates or phosphates.

Acknowledgments

This work was supported by grants of the "Deutsche Forschungsgemeinschaft", the "Bundesministerium für Bildung, Wissenschaft, Forschung und Technologie", and the "Fonds der Chemischen Industrie".

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CR9405157