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Solid-State Reactions

Multilateral Solid-State Metathesis Reactions for the Preparation of Materials with Heteroanions: The $[Si(CN_2)_4]^{4-}$ Ion**

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The search for nonoxidic inorganic compounds has led beyond simple metal borides, carbides, nitrides, and silicides to the development of interesting materials in whose structures several nonmetallic elements are combined. For example, in the structures of the well-known compounds Ti(C,N)[1] and Mo_2BN,[2] the anions are combined, but are present without bonds between the heteroatoms. An extension to this type of compound comprises metal compounds with element combinations of boron, carbon, nitrogen, and silicon. These elements are bridged to form complex units or ions through heteropolar, covalent bonds.

The systematic development of the nitridoborate,[3] nitridosilicate[4] and carbodiimide[5] compound classes has brought about important advances for materials chemistry. These families can be regarded as metal-salt derivatives of the binary nonmetallic materials BN, Si_3N_4, and C_3N_4. An extension to these compound types in the form of the cyanamidosilicates is reported herein with the example of the first tetracyanamidosilicates, which can be conceived as metal-salt derivatives of $Si(CN_2)_2$.[6]

Compounds with this type of heteroanion possess a number of interesting, often unpredictable properties as high-temperature resistant ceramic materials (Si_3N_4),[7] mechanically resistant materials (BC_2N),[8] luminophores (nitridosilicates),[9] superconductors ($LuNi_2(B_2C)$,[10,11] $La_3Ni_2(BN)_2N$),[12] sensors (Li_2SiN_2),[13] ionic liquids, and conducting salts in batteries ($Li[B(CN)_4]$).[14]

Like binary metal borides, carbides, and nitrides, many of these compounds can be prepared from suitable element combinations (or precursor compounds) by direct solid-state reactions at high reaction temperatures; for example, the carbidonitridosilicates $(RE)_2[Si_4N_6C]$ (RE (rare earth) = Tb, Ho, Er) were prepared at 1600–1700 °C.[15] Solid-state metathesis reactions, which are well established for the synthesis of metal carbides and nitrides, provide an alternative to the use of high temperatures.[16,17] Recently, solid-state metathesis reactions have also been used successfully for the synthesis of nitridoborates of rare-earth elements ($La_3B_3N_6$),[18] carbodiimides of rare-earth[19] ($(RE)_2(CN_2)_3$) and d elements ($MnCN_2$),[20] nitridosilicates (Li_2SiN_2, $MgSiN_2$),[21] tetracyanoborates ($A[B(CN)_4]$; A = alkali metal),[22] and many other compounds. Solid-state metathesis reactions are also of particular importance in the preparation of thermally metastable compounds, including metal carbodiimides of the rare-earth and d elements.

In the development of nitridoborates of the rare-earth elements, metathesis reactions between rare-earth trichlorides ($RECl_3$) and lithium nitridoborate (Li_3BN_2) were carried out and investigated systematically. The ignition and reaction temperature of such a solid-state metathesis reaction is characterized by an exothermic effect, which is usually recognized readily by thermoanalysis (DTA: differential thermal analysis). Solid-state metathesis reactions enable rational planning of a synthesis in which even more than two reaction partners may be combined with one another. Thus, in the preparation of certain nitridoborates, the nitride content can be adjusted in a targeted manner by the addition of Li_3N. In the synthesis of metal-rich nitridoborates, metallothermic reduction was carried out by the addition of a suitable metal (e.g. Li).[3]

An analogous concept to that applied in the synthesis of nitridoborates was used recently for the synthesis of rare-earth carbodiimides, whereby rare-earth trichlorides ($RECl_3$) were treated with lithium carbodiimide (Li_2CN_2) according to Equation (1):[23]

$$2\,RECl_3 + 3\,Li_2CN_2 \rightarrow (RE)_2(CN_2)_3 + 6\,LiCl \qquad (1)$$

In an extension to the concept of such a solid-state metathesis reaction, an alkali-metal hexafluorosilicate (A_2SiF_6) was integrated into the process as a reactive silicon source [Eq. (2)]:

$$RECl_3 + A_2SiF_6 + 4\,Li_2CN_2 \rightarrow A(RE)[Si(CN_2)_4] + 3\,LiCl + 5\,LiF + AF \qquad (2)$$

By this method, air- and water-stable compounds with the novel tetracyanamidosilicate ion $[Si(CN_2)_4]^{4-}$ were formed in transformations that proceeded with almost quantitative conversion. These compounds were prepared with A = K and Rb, as well as with RE = La, Ce, Pr, Nd, Sm, Gd, and characterized by X-ray crystallography.

The structure of the $[Si(CN_2)_4]^{4-}$ ion can be derived from that of an orthosilicate ion by considering that the oxide ions have been replaced by approximately linear cyanamide ligands ($\sphericalangle_{N'\text{-}C\text{-}N}$: 177–180°), which are linked by covalent Si–N′ ($\bar{d}_{Si\text{–}N'} = 1.716(5)$ Å) and N′–C–N bonds ($\bar{d}_{N'\text{–}CN} = 1.276(8)$ Å, $\bar{d}_{N'C\text{–}N} = 1.168(8)$ Å; Figure 1). The mean SiN′–C–N distances are similar to the corresponding distances in

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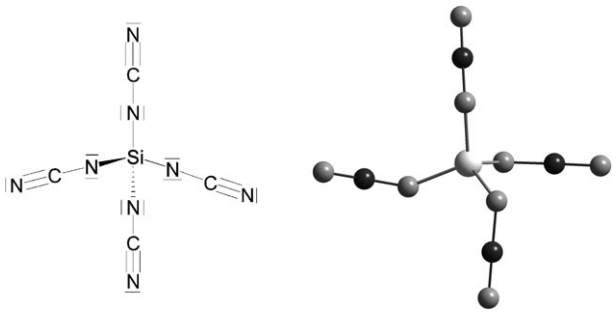

Figure 1. Lewis formula and structure of the tetracyanamidosilicate ion.

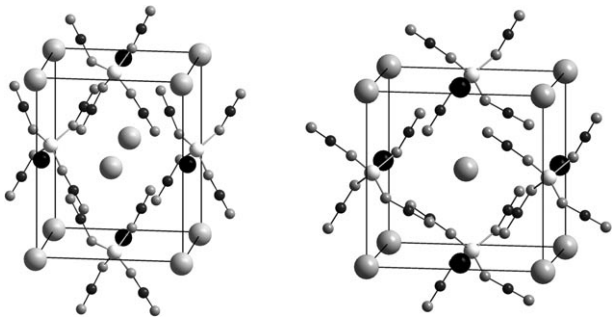

Figure 2. Projections of the crystal structures of orthorhombic KLa[$Si(CN_2)_4$] (left) and tetragonal RbLa[$Si(CN_2)_4$] (right). La black (large spheres), Si light gray, C black (small spheres), N medium gray (small spheres), alkali metal medium gray (large spheres).

the crystal structure of cyanamide,[24] $H_2N'-CN$ ($d_{N'-CN}$ = 1.315(1) Å, $d_{N'C-N}$ = 1.152(1) Å).

An analogous but bridged $[Si(CN_2)_{4/2}]_n$ structural motif was described for the silicon dicarbodiimide $Si(CN_2)_2$, the structure of which was determined by X-ray powder diffraction. In the cubic structure, linear carbodiimide ions with unusually short C–N distances (d_{N-C-N} = 1.104 Å) bridge the Si ions in a tetrahedral formation (d_{Si-N} = 1.576 Å). In this way, two interpenetrating, three-dimensional networks of $[Si(CN_2)_{4/2}]_n$ tetrahedra are formed, the arrangement of which corresponds to the motif in the anticuprite structure (anti-Cu_2O). The crystal structures refined from single crystals of ALa[$Si(CN_2)_4$][25] (A = K, Rb) contain $[Si(CN_2)_4]^{4-}$ ions with approximately linear cyanamide units. However, the variability of the Si-N-C angle in the $Si(N-C{\equiv}N)_4$ units introduces an astonishing flexibility of the $[Si(CN_2)_4]^{4-}$ ions in the formation of network structures.

Similar network structures are found with polycyano anions, such as dicyanamide $[N(CN)_2]^-$ and tricyanomethanide $[C(CN)_3]^-$, which are known for their versatility in the bridging of metal centers. Such structures produce magnetic ordered states of extended range if their conjugated π systems enable coupling pathways for magnetic interactions between paramagnetic metal centers,[26,27] as, for example, in compounds of the type $M[N(CN)_2]_2$ with divalent metal ions (M = Cr, Mn, Co, Ni, Cu).[28–30] Similar properties are known for tricyanomethanides $M[C(CN)_3]_2$ (M = V, Cr, Mn, Fe, Co, Ni, Cu),[31–34] whose interpenetrating network structures show antiferromagnetic couplings attributable to spin frustration. Compounds with polycyano anions are products of reactions in solution, as is the rare-earth compound $KLa[C(CN)_3]_4{\cdot}H_2O$.[35]

The lanthanum and silicon atoms are arranged in the three-dimensional network structures of ALa[$Si(CN_2)_4$] (A = K, Rb) as two interpenetrating face-centered sublattices. This arrangement is identical in principle to that of the ions in the NaCl structure. Half of the tetrahedral gaps in this arrangement are occupied by A ions (Figure 2).

The bridging function of the $[Si(CN_2)_4]^{4-}$ ions, which cross-link the lanthanum ions in a quasioctahedral arrangement, is remarkable. This bonding pattern, unexpected for an ion with an approximately tetrahedral structure, involves four terminal N atoms of $[Si(N'CN)_4]$, each of which is bonded to one lanthanum atom, and four internal N′ atoms, which bond in pairs to two further lanthanum centers (Figure 3). The lanthanum centers have a total of eight N neighbors in their coordination sphere as a result of this scissorlike coordination of two pairs of N′ atoms.

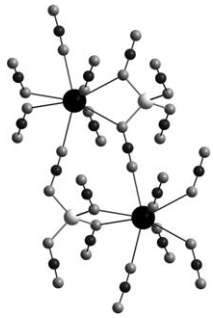

Figure 3. Section of the three-dimensional network structure of RbLa[$Si(CN_2)_4$]. La black (large spheres), Si light gray, C black (small spheres), N medium gray (small spheres). A quasioctahedral bridging of Si-centered tetrahedra through two opposing edges and four points forms the basis of the face-centered arrangement of the lanthanum and silicon atoms in the structure.

The environment of the rare-earth ions in the A(RE)[$Si(CN_2)_4$] structures is remarkable, because, like the rare-earth ions in the garnet structure ($(RE)_3Al_5O_{12}$), they are surrounded by eight nitrogen atoms, according to the motif of a (trigonal) dodecahedron (Figure 4). The individual symmetries and distances in the structures are somewhat different. The rare-earth ions of the orthorhombic structure have the point symmetry 2, and those of the tetragonal structure have the point symmetry $\bar{4}$, whereas the rare-earth ions in the garnet structure of $Y_3Al_5O_{12}$ have the point symmetry 222. As a result of the symmetries of the structures, four different La–N distances occur in KLa[$Si(CN_2)_4$] (2 × (2.549(6), 2.574(6), 2.621(5), 2.690(5) Å)), two different La–N distances occur in Rb(RE)[$Si(CN_2)_4$] (4 × (2.555(7), 2.659(5) Å)), and two different Y–O distances occur in $Y_3Al_5O_{12}$ (4 × (2.306, 2.439 Å)).

The differences in the radii of the alkali-metal ions K and Rb lead to differences in the structures of ALa[$Si(CN_2)_4$]; thus, the structures occur in the orthorhombic (A = K) and in the tetragonal (A = Rb) crystal system (Figure 2). In the structure of ALa[$Si(CN_2)_4$], the K ions are surrounded by six N atoms (at a distance of 2.937(7)–3.081(5) Å), and the Rb ions by twelve N atoms (at a distance of 3.42(1)–3.70(1) Å); in both cases, short alkali-metal–C distances are also observed.

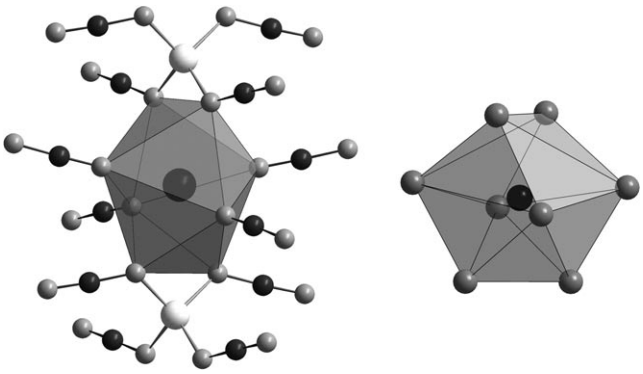

Figure 4. Trigonal-dodecahedral environment of the rare-earth ions in the structures of $A(RE)[Si(CN_2)_4]$ (left) and $(RE)_3Al_5O_{12}$ (right).

Experimental section

All manipulations of the starting materials were carried out in a glove box under an Ar atmosphere. Rare-earth trichlorides ($RECl_3$, ABCR, 99.9%), A_2SiF_6 (Chempur, 99%), and Li_2CN_2 (for the preparation of which, see Ref. [19]) were mixed thoroughly in a mortar according to their molar fractions in the formula $A(RE)[Si(CN_2)_4]$ [see Eq. (2); total amount: ca. 200 mg). The mixture was placed in a dry quartz-glass ampoule. The ampoule was closed with a quickfit stopper and sealed by melting under vacuum. The reaction mixture was then heated to 550°C (within 5 h) in a tubular furnace, held at this temperature for 3 days, and then cooled to room temperature by switching off the oven. The glass ampoule with the reaction product was opened in air. The product was then washed with water, rinsed with acetone, and dried at 100°C in air. Single crystals of $ALa[Si(CN_2)_4]$ with A = K, Rb were selected under a microscope for X-ray crystal-structure investigations.

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[25] a) Crystal-structure data for $KLa[Si(CN_2)_4]$: $M_r = 732.44$, orthorhombic, space group $P2_122_1$, $a = 7.601(1)$, $b = 6.854$ (1), $c = 9.486(2)$ Å, $Z = 2$, $F(000) = 340$, $\rho_{calcd} = 2.46\ g\,cm^{-3}$, $\mu = 4.84\ mm^{-1}$, crystal dimensions: $0.17 \times 0.04 \times 0.04\ mm^3$, $\theta = 3.43$–$25.89°$, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $T = 293$ K, 3740 reflections were collected (STOE-IPDS diffractometer), of which 908 were independent ($R_{int} = 0.048$). Data were corrected for Lorentz, polarization, and absorption effects (software: STOE IPDS I). The structure was solved by direct methods (SHELXS) and refined by the method of full matrix least squares against F^2, data/parameter ratio 12.97, final R values: $R1 = 0.0287$, $wR2 = 0.0612$ for all data, GOF = 1.030. b) Crystal-structure data for $RbLa[Si(CN_2)_4]$: $M_r = 825.18$, tetragonal, space group $I\bar{4}$, $a = 8.556(1)$, $c = 6.852(1)$ Å, $Z = 2$, $F(000) = 376$, $\rho_{calcd} = 2.73\ g\,cm^{-3}$, $\mu = 9.18\ mm^{-1}$, crystal dimensions: $0.22 \times 0.02 \times 0.02\ mm^3$, $\theta = 3.81$–$30.35°$, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $T = 293$ K, 3740 reflections were collected (STOE-IPDS diffractometer), of which 749 were independent ($R_{int} = 0.048$). Data were corrected for Lorentz, polarization, and absorption effects (software: STOE IPDS I). The structure was solved by direct methods (SHELXS) and refined by the method of full matrix least squares against F^2, data/parameter ratio 21.4, final R values:

$R1 = 0.0276$, $wR2 = 0.0602$ for all data, GOF = 1.048. Further details on the crystal-structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de) on quoting the depository numbers CSD-419336 ($KLa[Si(CN_2)_4]$) and CSD-419337 ($RbLa[Si(CN_2)_4]$).

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