macrocyclic compounds, the conformation of the cyclic oligo esters **2** and **3** is much more restricted because the binaphthyl groups are not allowed to rotate around the 1,1′ axis because of steric repulsion between the 8- and 8′-hydrogen atoms. Thus once the configuration of the biphenyl groups is regulated in **2** and **3**, the conformation of the whole molecule is restricted unequivocally except for the small changes in the torsion angles of the biaryl groups. Accordingly, a double-helical structure similar to that of **2** is suggested for **3**.

Experimental Section

2 and **4a**. A solution of biphenyl-2,2′,6,6′-tetrol (1.10 mmol) in THF[9] was added to a solution of the acid chloride derived from (*S*)-1,1′-binaphthyl-2,2′-dicarboxylic acid[10] (1.00 mmol) in CH_2Cl_2, and the resulting mixture was stirred at 20 °C for 22 h. Aqueous work-up followed by purification by silica-gel column chromatography (CH_2Cl_2/EtOAc, 9/1) gave **4a** (41% yield) and **2** (54% yield) as colorless solids. **4a**: Sublimed above 206.0 °C; ^{1}H NMR ($CDCl_3$): $\delta = 7.95-7.89$ (m, 4H), 7.81 (d, 2H, $J = 8.58$ Hz), 7.52 (t, 2H, $J = 6.93$ Hz), 7.30–7.03 (m, 6H), 6.79 (d, 2H, $J = 8.25$ Hz), 6.60 (d, 2H, $J = 8.25$ Hz); ^{13}C NMR ($CDCl_3$): $\delta = 166.76$, 154.16, 149.27, 136.95, 134.39, 133.01, 129.60, 129.49, 128.57, 128.17, 127.71, 127.53, 127.22, 124.56, 115.44, 113.98, 111.32. **2:** M.p. (CH_2Cl_2/hexane) 274.3–274.9 °C; ^{1}H NMR ($CDCl_3$): $\delta = 7.97-7.91$ (m, 8H), 7.81 (d, 4H, $J = 8.58$ Hz), 7.52 (t, 4H, $J = 6.93$ Hz), 7.31–7.24 (m, 4H), 7.05–6.99 (m, 6H), 6.75 (d, 4H, $J = 7.92$); ^{13}C NMR ($CDCl_3$): $\delta = 166.34$, 149.00, 136.35, 134.29, 132.96, 129.58, 128.57, 128.37, 128.18, 127.63, 127.42, 127.26, 124.56, 119.37, 116.17; HR-MS: *m*/*z* found for $[M+H]^+$: 831.1975; calcd.: 831.2017.

3: Biphenyl-2,2′,6,6′-tetracarboxylic acid[11] (0.21 mmol) was converted into the corresponding acid chloride and condensed with **4a** (0.41 mmol) in the presence of triethylamine (21 mmol). Work-up followed by purification by column chromatography (CH_2Cl_2) gave **3** (48% yield) as fine needles: Sublimed above 470.0 °C. ^{1}H NMR (CD_2Cl_2): $\delta = 8.02-7.78$ (m, 16H), 7.58 (t, 4H, $J = 7.92$ Hz), 7.47 (t, 2H, $J = 8.24$ Hz), 7.32 (t, 4H, $J = 8.24$ Hz), 7.21–7.02 (m, 12H), 6.79 (d, 4H, $J = 8.25$ Hz); ^{13}C NMR (CD_2Cl_2): $\delta =$ 166.54, 165.35, 149.65, 149.14, 137.39, 136.80, 134.77, 133.46, 133.40, 131.75, 129.88, 129.04, 128.77, 128.68, 128.52, 128.21, 127.71, 127.65, 124.63, 120.39, 120.14, 116.33; HR-MS: *m*/*z* found for $[M+H]^+$: 1307.2607; calcd.: 1307.2548.

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From Molecular to One-Dimensional Polychalcogenides: Preparation, Structure, and Reactivity of $NaNbS_6$, the First Ternary Alkali Metal Niobium Polychalcogenide Exhibiting Infinite Anionic Chains**

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The preparation of multinary transition metal chalcogenides in reactive alkali polychalcogenide melts at temperatures between 250 and 500 °C is a fast-growing area of inorganic solid state chemistry.[1,2] Owing to the relatively low reaction temperatures, compounds containing large Q_x^{2-} ions ($x > 1$) are accessible which cannot be obtained with classical high-temperature syntheses.

Recently we investigated new polychalcogenide compounds of niobium. There are only a few examples of such compounds prepared by the reactive flux method.[3] Systematic variation of the preparation conditions yielded several novel niobium chalcogenides, all containing molecular $[Nb_2Q_{11}]^{4-}$ subunits (Figure 1).[4–7] These units occur as isolated anions, as in $K_4Nb_2S_{11}$,[4] or are connected through terminal sulfur ligands, as in $Rb_6Nb_4S_{22}$ or $Cs_6Nb_4S_{22}$.[5] Incorporation of additional S_3^{2-} fragments, which are present under the preparation conditions, can lead to an expansion of the $[Nb_2Q_{11}]^{4-}$ subunits. In $K_4Nb_2S_{14}$[6] the S_3^{2-} ion acts as a terminal ligand, and in $K_6Nb_4S_{25}$[7] it connects two units to form the novel complex $[Nb_4S_{25}]^{6-}$ ion.

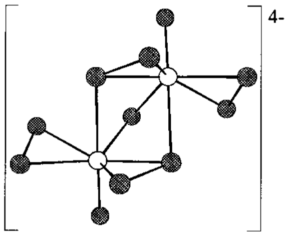

Figure 1. View of the $[Nb_2Q_{11}]^{4-}$ unit (Nb = ○, Q = ⊗).

By extending the synthetic conditions used for preparing the novel niobium compounds to sodium polysulfide melts, we succeeded in synthesizing transparent, orange-red needles.[8] All crystals investigated were grown together, and a twin refinement had to be performed.[9] Here we report on the synthesis, crystal structure, optical behavior, and reactivity of $NaNbS_6$, the first ternary niobium chalcogenide containing one-dimensional anionic polymeric chains.

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The results of the structure determination revealed that a polymeric structure was formed, which is surprisingly not based on the above-mentioned $[Nb_2Q_{11}]^{4-}$ subunits. The structure of $NaNbS_6$ consists of $^1_\infty[NbS_6]^-$ chains running parallel to [001] (Figure 2a and b). These chains are separated by the Na^+ ions. The shortest interchain S–S contacts of 3.396(3) Å are only slightly shorter than the sum of the van der Waals radii (3.6 Å). Within the chains the Nb centers are ninefold coordinated by S atoms. The environment is best described as a pentagonal plane that contains one S_2 unit and three S atoms. Two S_2 units above and below this plane are twisted by about 90° to provide a $Nb(S_2)_3(S)_3$ polyhedron (Figure 2c). These polyhedra are condensed through three S atoms to one-dimensional chains. Every S_2^{2-} unit is coordinated to two Nb centers in a $\mu\eta^1\eta^2$ mode. The description of the title compound as $NaNb(S_2)_3$ leads to an assignment of the formal valences as Na^+, Nb^{5+}, and $(S_2)^{2-}$.

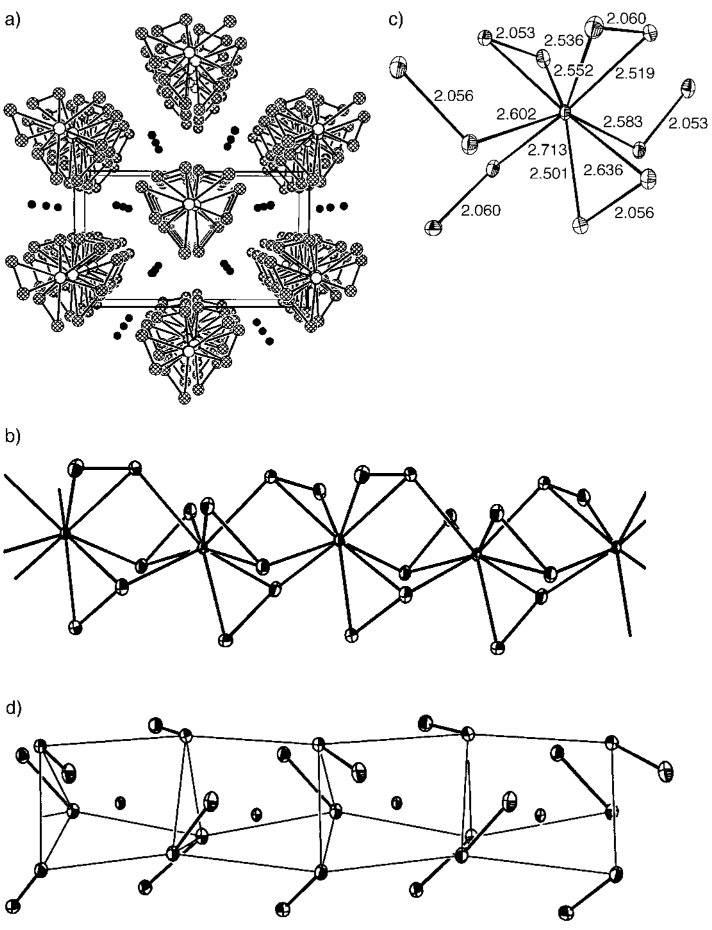

Figure 2. Crystal structure of $NaNbS_6$: a) view along the *c* axis (S = ⊗, Nb = ○, Na = ●); b) connection of the $NaNbS_6$ polyhedra; c) coordination sphere of the Nb centers with selected bond lengths [Å]; d) the NbS_6 trigonal prisms joined through common trigonal faces (thermal ellipsoids are drawn at the 50 % probability level).

Alternatively, the environment at the Nb centers can be described as distorted trigonal prisms in which the basal planes are formed by the condensation of three S atoms. These prisms are joined through the trigonal faces to give rise to infinite columns parallel to [001]. Every corner of the prisms is occupied by a S atom of a S_2^{2-} ion. The environment of the Nb centers is completed by three S atoms of the S_2 dumbells, which are in turn directed towards the rectangular faces of the distorted prisms (Figure 2d). The Nb–S distances range from 2.501(2) to 2.713(2) Å (av 2.573(2) Å).

Bond-valence calculations according to Equation (1) developed by Pauling give Nb–S bond valences between 0.65 and 0.36, which are smaller than for a Nb–S single bond.

$$S_{ij} = \exp((r_0 - D_{ij})/b) \qquad (1)$$

The chains are not strictly linear but slightly bent, as evidenced by the angle between three successive Nb atoms of 169.9°, and are better described as zigzag chains. The distance of 3.589(4) Å between adjacent Nb centers is about 0.7 Å larger than in metallic niobium and too long for Nb–Nb interactions. The S–S distances of 2.056(2) Å within the S_2^{2-} units are in the usual range. The Na centers are ninefold coordinated by S atoms with a mean Na–S distance of 3.090(4) Å. These values correspond to the sum of the ionic radii for Na^+ (1.24 Å) and S^{2-} ions (1.84 Å).[10]

The optical properties of $NaNbS_6$ were investigated with UV/Vis diffuse reflectance measurements.[11,12] The spectra showed a steep absorption edge, from which an optical band gap of about 2.3 eV is estimated (Figure 3). The orange-red color of the material as well as the value for the band gap corroborate the semiconducting nature. These findings are also in agreement with the oxidation states mentioned above.

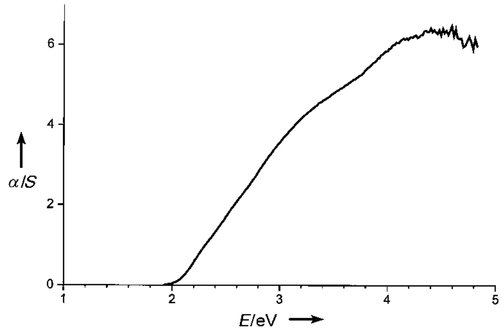

Figure 3. UV/Vis reflectance spectra of $NaNbS_6$ showing an optical band gap of 2.3 eV; α is the absorption coefficient, and S the scattering coefficient.

The thermal behavior was studied by differential thermal analysis/thermogravimetry (DTA/TG) measurements.[13] The title compound is stable up to 400 °C. At 407 °C the onset of an endothermic peak together with a weight loss of 41 % indicates decomposition of the material. The weight loss can be attributed to the loss of four equivalents of sulfur.[14] The X-ray powder pattern of a decomposed sample obtained at 600 °C under vacuum could be indexed on the basis of a hexagonal cell of the intercalation compound Na_xNbS_2.[15] This result is also consistent with the atomic absorption spectrometry (AAS) analysis, which yields a composition of $NaNbS_2$ for the decomposed material. We note that the Nb centers in $NaNbS_2$ are in a trigonal-prismatic coordination of six S atoms. However, within the NbS_2 layers these prisms are joined by common edges. Hence, there is no simple relationship between the structures of the title compound and $NaNbS_2$.

The results presented clearly demonstrate the enormous synthetic potential of the reactive flux method. The mild reaction temperatures, at which the polychalcogenide building blocks are retained, together with a large pool of preparative data should enable the inorganic chemist to synthesize new compounds more predictably. This seems to be possible at least for the niobium compounds. In agreement with these assumptions we isolated the first chainlike niobium polyselenide using similar reaction conditions as for the sulfur compounds.[16] Again, its structure is based on $[Nb_2Q_{11}]^{4-}$ units connected through Se_2^{2-} and Se_3^{2-} ligands. It can be expected that many more new and interesting niobium compounds will be accessible by a systematic variation of the reaction conditions.

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[9] Crystal structure determination of $NaNbS_6$ ($M_r = 308.26$), orange-red needles, crystal size: $0.05 \times 0.05 \times 1$ mm^3, $a = 7.451(2)$, $b = 12.743(2)$, $c = 7.151(2)$ Å, $\beta = 96.81(1)^\circ$, $V = 674.18$ Å^3 (RT), $\rho_{calcd} = 3.037$ g cm^{-3}, monoclinic, space group *Cc* (no. 15), $Z = 4$, STOE-AED-II four-circle diffractometer, $Mo_{K\alpha}$ radiation, $\mu = 3.58$ mm^{-1}, 1311 measured reflections in the range $3^\circ < 2\theta < 60^\circ$, 1249 independent reflections used for refinement, structure solution with direct methods (SHELXS-86), structure refinement against F^2 (SHELXL-93), 74 parameters, $w = 1/[\sigma^2(F_o^2) + (0.0235 \cdot P)^2 + 2.88P]$, R for 1224 $F_o > 4\sigma(F_o) = 0.0191$, $wR2$ for all 1249 data = 0.0547, GOF = 1.579, residual electron density: $0.56/-0.48$ e Å^{-3}. Flack parameter: 0.08(7). All crystals investigated were grown together. For one crystal all 86 reflections found by searching the reciprocal space could be separated into two groups. The reflections in each of these two groups were successfully indexed on the basis of the same monoclinic *C*-centered cell. From the transformation matrix between both individuals, it was shown that all reflections *hk*0 as well as *hk*11 were overlapping. Therefore, a twin refinement with SHELXL-93 was performed. This led to a significantly improved model compared to those obtained only with the raw data (R for all reflections with $F_o > 4\sigma(F_o) = 0.0939$; $wR2 = 0.2887$; residual electron density: $11.60/-1.72$ e Å^{-3}). Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-407708.

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Spin Polarization and Ferromagnetism in Two-Dimensional Sheetlike Cobalt(II) Polymers: $[Co(L)_2(NCS)_2]$ (L = Pyrimidine or Pyrazine)**

Francesc Lloret,* Giovanni De Munno,* Miguel Julve, Juan Cano, Rafael Ruiz, and Andrea Caneschi

The spin-polarization mechanism[1] describes how an unpaired electron on one atom polarizes the electron cloud on the adjacent atom in the opposite sense. This would result in an alternation of the spin density at atoms in a bridging unit, and consequently the sign of the magnetic exchange parameter *J* should alternate at each atom in the bridging unit. In this way, oligocarbenes or radicals linked through *m*-phenyl-

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