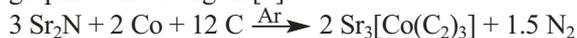
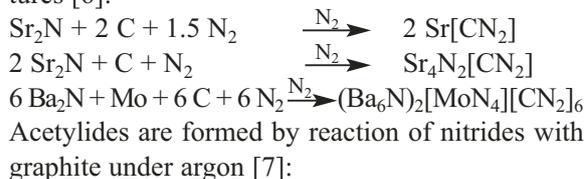


## Sr<sub>2</sub>[Ni(CN)N]: The Role of Carbon During Nitride Formation

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The chemistry of ternary and higher nitridometalates is a rapidly growing field of inorganic solid state chemistry [1-3]. In the case of nickel, an abundance of compounds with nickel in low oxidation states  $\leq +1$  was reported. Crystal structures and physical properties of the ternary alkaline earth metal nitridonickelates Ca[Ni<sup>+1</sup>N], Sr[Ni<sup>+1</sup>N], Ba[Ni<sup>+1</sup>N], Ba<sub>8</sub>N[Ni<sup>+5/6</sup>N]<sub>6</sub>, and Ba<sub>2</sub>[Ni<sup>+2/3</sup>N<sub>2</sub>] [4] were investigated in detail. The existence of a nitridonickelate(II), “Sr<sub>2</sub>[Ni<sup>+2</sup>N<sub>2</sub>]” [5], has been reported. However, its existence is doubtful, not only because of the relatively high oxidation state of Ni but also due to disorder phenomena and split atom positions which both hampered a satisfactory crystal structure refinement.

Our attempts to synthesize this Ni(II)-compound according to literature data were unsuccessful. On the other hand, our investigations in nitride-cyanamides [6] indicated that carbon as an impurity in the starting materials could be necessary in the synthesis of the purported “Sr<sub>2</sub>[NiN<sub>2</sub>]”. Subsequent investigations on the effect of carbon added to the educt mixtures provided several new compounds depending on the amount of N<sub>2</sub> available in the system. Excess N<sub>2</sub> in the carbon containing systems results in the formation of cyanamides or cyanamide-nitrides depending on the composition of the starting materials and the reaction temperatures [6]:



The title compound was obtained by the reaction of appropriate mixtures of fine powders of Sr<sub>2</sub>N, Ni, and carbon (<sup>12</sup>C as well as <sup>13</sup>C) with the addition of NaN<sub>3</sub> as an in-situ nitrogen source. Pressed pellets of the mixture were sealed in Ni tubes and annealed at 1203 K for up to 100 hours. The crystal structure and the composition of the title compound have been unambiguously determined by X-ray crystal structure analyses of black tabular specimens and Rietveld profile refinements of neutron

diffraction powder data for distinguishing C and N positions. Chemical analyses confirmed the composition, however, the content of Na is below the limit of detection. In the Raman spectra of the <sup>12</sup>C and <sup>13</sup>C compounds (Fig. 1) modes are visible at 1794 cm<sup>-1</sup> and 1753 cm<sup>-1</sup>, respectively. The ratio of the <sup>12</sup>C and <sup>13</sup>C frequencies (1.023) corresponds well with the calculated ratio of 1.021 for the frequencies of the <sup>12</sup>C≡N and the <sup>13</sup>C≡N groups [8], thus the presence of cyanide groups in Sr<sub>2</sub>[Ni(CN)N] is proven. Magnetisation data obtained from preliminary measurements of samples containing traces of metallic nickel indicate a diamagnetic behaviour of Sr<sub>2</sub>[Ni(CN)N].

A series of NMR-spectra were recorded for a <sup>13</sup>C enriched sample. Magic angle spinning (MAS) with various rotation frequencies was used to enhance the resolution of the signals. The speed of rotation was reduced from  $\nu_{\text{rot}} = 15$  kHz to  $\nu_{\text{rot}} = 2.5$  kHz in steps of  $\Delta\nu = 2.5$  kHz. The SIMPSON package [9] was used to analyse the signals by least square fitting. Two signals for rotation frequencies

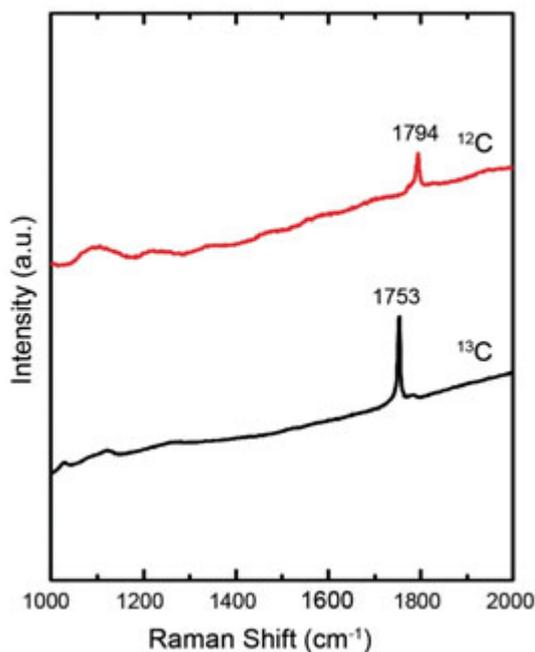


Fig. 1: Raman spectra of Sr<sub>2</sub>[Ni(CN)N] with isotopes <sup>12</sup>C and <sup>13</sup>C. For further details see text.

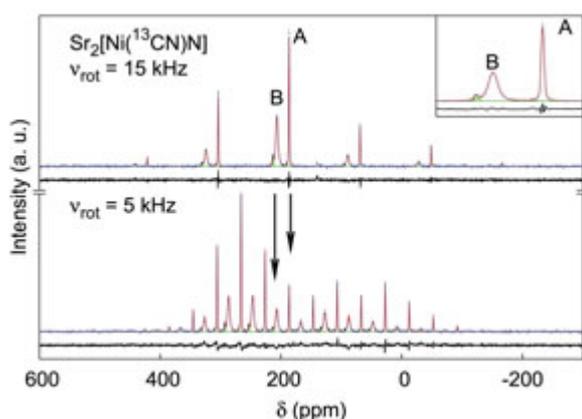


Fig. 2:  $^{13}\text{C}$  NMR spectra of  $\text{Sr}_2[\text{Ni}(\text{CN})\text{N}]$ . The spectra were recorded using rotating samples at the magic angle (MAS) with rotation frequencies of  $\nu_{\text{rot}} = 15$  Hz (top) and  $\nu_{\text{rot}} = 5$  kHz (bottom). The arrows mark the isotropic shift of the main signal contributions measured using  $\nu_{\text{rot}} = 5$  kHz. The blue lines represent the measured signals, the red lines the sum of the individual signal contributions of the fits and the green lines the individual contributions. The black lines represent the difference between calculated and observed signals. The inset shows the individual contributions for the isotropic lines  $\nu_{\text{rot}} = 15$  kHz).

of  $\nu_{\text{rot}} = 15$  kHz and  $\nu_{\text{rot}} = 5$  kHz are shown together with their fitted curves in Fig. 2. Three contributions describing the chemical shift anisotropy of the single signals were fitted to the line shape (see inset Fig. 2). The two main contributions to the signal are of equal intensity whereas the minor signal has an intensity of about 2%. Both main signals are due to an anisotropic chemical shielding of  $\eta = 0.18(2)$  and  $\eta = 0.34(3)$  for signal A and B, respectively. Signal A is characterized by an isotropic shift of  $\delta_{\text{iso}} = 187(1)$  ppm and an anisotropy parameter of  $\Delta = -253(3)$  ppm. Signal B is described by an isotropic shift of  $\delta_{\text{iso}} = 207(1)$  ppm and an anisotropy parameter of  $\Delta = -202(5)$  ppm. Assuming single phase materials, the results are in contradiction to those of X-ray and neutron diffraction showing only one position for the C atoms. Therefore, the NMR experiments indicate a multiphase sample. The broadening of the signal contribution B at  $\delta_{\text{iso}} = 207$  ppm is obvious. This might indicate structural disorder or an amorphous compound. On the other hand, both samples used for neutron scattering and NMR experiments did not show any crystalline minority phases. Following these observations it seems to be reasonable to assign signal A to  $\text{Sr}_2[\text{Ni}(\text{CN})\text{N}]$ . Due to the expected chemical bonding of carbon and nickel a

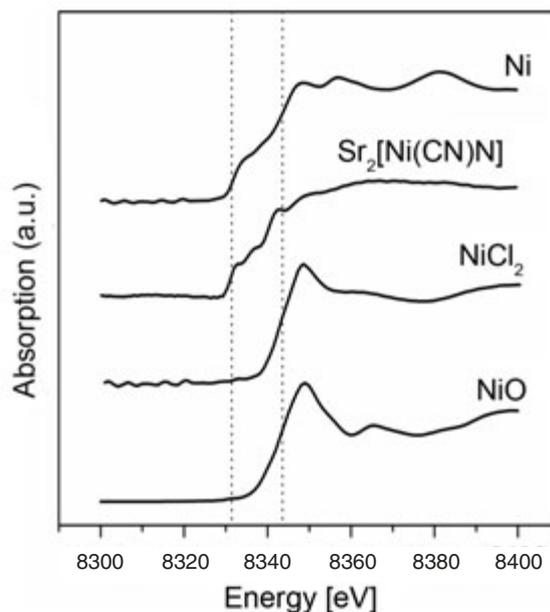


Fig. 3: XAS spectrum at the Ni K-edge of  $\text{Sr}_2[\text{Ni}(\text{CN})\text{N}]$ . Reference compounds are added for comparison.

comparison of the chemical shielding with other compounds containing CN groups would be speculative. More advanced NMR experiments like REDOR have to be performed in the future to give valuable proof for the existence of the CN group by NMR experiments. Currently we are optimizing the synthesis in order to prepare new single phase samples enriched with  $^{15}\text{N}$  and  $^{13}\text{C}$ .

The XAS spectra of  $\text{Sr}_2[\text{Ni}(\text{CN})\text{N}]$  and different reference compounds are shown in Fig. 3. The data are consistent with nickel in a low oxidation state  $\leq 1$  (far away from  $+2$ ). Due to the complex non-centrosymmetrical local site symmetry of Ni in this crystal structure, the spectra show several transitions very close together.

The predominant feature of the crystal structure of  $\text{Sr}_2[\text{Ni}(\text{CN})\text{N}]$  (Fig. 4) are isolated units  $[\text{N}-\text{Ni}(\text{C}\equiv\text{N})]$  which have to be regarded as cyanonitridonickelate(0) anions (Fig. 5). The discrete unit  $[\text{NNi}(\text{C}\equiv\text{N})]$  is the first cyanonitridonickelate anion reported up to now. The crystal structure is built up by slabs of edge sharing octahedra  $\text{NSr}_5\text{Ni}$  and  $(\text{CN})\text{Sr}_5\text{Ni}$ , which in turn are connected by common Ni corners resulting in a close relationship to the  $\text{Na}_2[\text{HgO}_2]$  structure type (inset of Fig. 4).

Taking into account all investigations of the present work and the information reported for

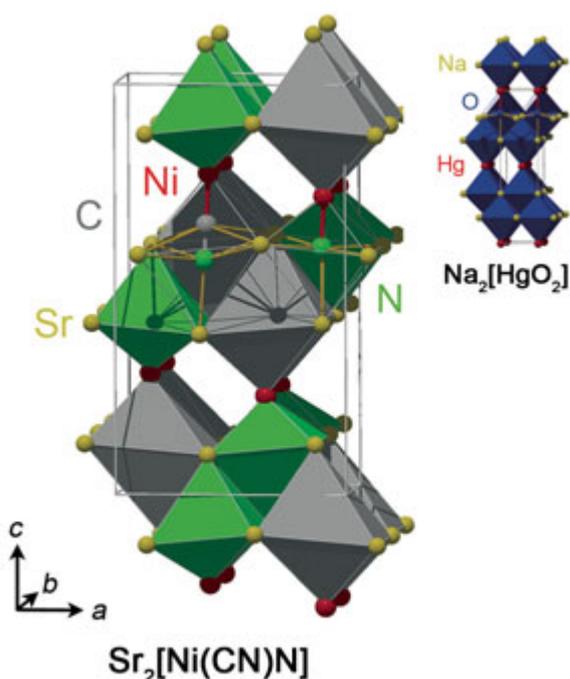


Fig. 4: Crystal structure of Sr<sub>2</sub>[Ni(CN)N]. Octahedra NSr<sub>3</sub>Ni (green) and (CN)Sr<sub>5</sub>Ni (grey) are emphasized. Inset: the Na<sub>2</sub>[HgO<sub>2</sub>] type structure, octahedra ONa<sub>3</sub>Hg (blue) emphasized.

“Sr<sub>2</sub>[NiN<sub>2</sub>]”, one has to assume that composition and crystal structure have been insufficiently interpreted. The crystal structure refinement of “Sr<sub>2</sub>[NiN<sub>2</sub>]” was strongly hampered by symmetry and twinning problems (substructure: *I4/mmm*,  $a = 388.74(3)$  pm,  $c = 1399.2(2)$  pm; superstructure: *P2<sub>1</sub>/c*,  $a = 778.99(5)$  pm,  $b = 1401.51(9)$  pm,  $c = 781.20(6)$  pm,  $b = 90.043(23)^\circ$  [10]). However, there is a close relationship between the unit cell reported for “Sr<sub>2</sub>[NiN<sub>2</sub>]” and that of the title compound Sr<sub>2</sub>[Ni(CN)N] (*Pnma*,  $a = 781.5(5)$  pm,  $b = 389.4(3)$  pm,  $c = 1399.8(2)$  pm):  $a_{\text{title}} = 2 a_{\text{sub}} = c_{\text{super}}$ ,  $b_{\text{title}} = a_{\text{sub}} = 0.5 a_{\text{super}}$ ,  $c_{\text{title}} = c_{\text{sub}} = b_{\text{super}}$ . Reaction conditions as well as heavy atom positions of “Sr<sub>2</sub>[NiN<sub>2</sub>]” and Sr<sub>2</sub>[Ni(CN)N] correspond very well. Therefore, our final conclusion is that “Sr<sub>2</sub>[Ni<sup>+</sup><sub>2</sub>N<sub>2</sub>]” is in fact Sr<sub>2</sub>[Ni<sup>0</sup>(CN)N].

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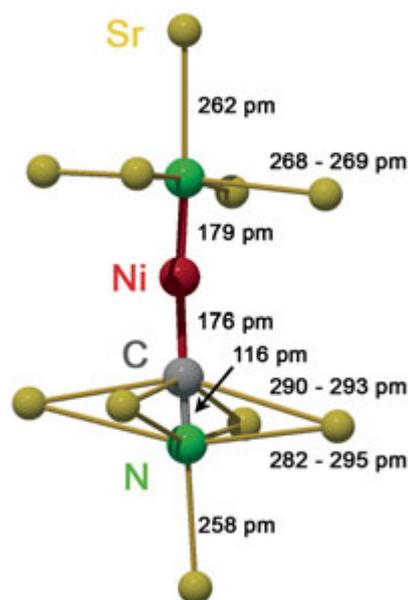


Fig. 5: The complex anion [NNi(CN)]<sup>4-</sup> and neighboring Sr atoms. Selected distances for interatomic bonds are given.

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