



New nitridocobaltates(I): Crystal structures and physical properties

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ABSTRACT

The members $\text{Ca}_5[\text{CoN}_2]_2$, $\text{Sr}_5[\text{CoN}_2]_2$ and $\text{BaCa}_4[\text{CoN}_2]_2$ of the novel isotypic nitridocobaltate series $\text{AE}_5[\text{CoN}_2]_2$ ($P4/ncc$) containing linear $[\text{Co}^{\text{I}}\text{N}_2]^{5-}$ complexes were synthesized via high-temperature route. On addition of carbon to the reaction mixtures the nitridocobaltate(I) carbodiimides $(\text{Sr}_6\text{N})[\text{Co}^{\text{I}}\text{N}_2][\text{CN}_2]_2$ ($P2_12_12$), and $\text{Sr}_2[\text{Co}^{\text{I}}\text{N}_2]_{1-x}[\text{CN}_2]_x$ ($x = 0.27$) $\approx \text{Sr}_6[\text{Co}^{\text{I}}\text{N}_2]_2[\text{CN}_2]$ ($I4/mmm$) are formed. The low-valence states of Co are investigated in detail. X-ray absorption spectroscopy (XAS) data confirm the assigned low oxidation states for Co in all the compounds under consideration. At high temperatures the nitridocobaltates reveal Curie–Weiss paramagnetic behaviour consistent with Co^{I} and d^8 configuration ($S = 1$). Electronic structure calculations and magnetic susceptibility data indicate antiferromagnetic interactions in $\text{Ca}_5[\text{CoN}_2]_2$ and $\text{BaCa}_4[\text{CoN}_2]_2$.

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1. Introduction

Nitridometalates of the transition elements reveal a wide spectrum of novel crystal structures [1], which are often controlled by the size of the alkaline-earth metals incorporated in these compounds. They display interesting physical properties due to the high polarizability of the nitride ion and the low oxidation states of the transition metals. Nitridocobaltates exclusively show low-valence states ($\sim \text{Co}^{\text{I}+}$) and linear coordination of Co by nitrogen. Two different motifs of the complex nitridocobaltate anions can be distinguished: isolated $[\text{Co}^{\text{I}}\text{N}_2]^{5-}$ units (e.g. $\text{Ca}_5[\text{CoN}_2]_2$ [2], $\text{BaCa}_4[\text{CoN}_2]_2$ [3], $\text{Sr}_5[\text{CoN}_2]_2$ [4], $(\text{Sr}_6\text{N})[\text{CoN}_2][\text{CN}_2]_2$ [5], $\text{Sr}_2[\text{Co}^{\text{I}}\text{N}_2]_{1-x}[\text{CN}_2]_x \approx \text{Sr}_6[\text{Co}^{\text{I}}\text{N}_2]_2[\text{CN}_2]$ [6]) and 1D infinite chains $_{\infty}[\text{Co}^{\text{I}}\text{N}_2/2]$ (e.g. $\text{Ba}[\text{CoN}]$ [7]).

Here, we report on the crystal structure of $\text{Sr}_6[\text{Co}^{\text{I}}\text{N}_2]_2[\text{CN}_2]$ and physical properties of five alkaline-earth nitridocobaltates(I) of which two also contain carbodiimide anions.

2. Experimental

Due to the sensitivity of all compounds against air and moisture all manipulations were performed in an argon-filled glove box. $\text{Ca}_5[\text{CoN}_2]_2$ [2], $\text{BaCa}_4[\text{CoN}_2]_2$ [3], $\text{Sr}_5[\text{CoN}_2]_2$ [4], $(\text{Sr}_6\text{N})[\text{Co}^{\text{I}}\text{N}_2][\text{CN}_2]_2$ [5], and $\text{Sr}_6[\text{Co}^{\text{I}}\text{N}_2]_2[\text{CN}_2]$ [6] were prepared from mixtures of the respective binary alkaline-earth nitrides together with Co and

C (if needed). Nitrogen gas or NaN_3 were used as the nitrogen source. Reactions were run in the temperature range 900–1150 °C as described [2–6].

The investigation of the physical properties was performed using bulk samples (finely ground powders cleaned from adhering ferromagnetic impurities using a permanent magnet). Samples for X-ray absorption spectra at the Co *K*-edge were mixed with B_4C in a volume ratio of 1:3 and loaded into steel holders with Be-windows. The data were collected at HASYLAB at DESY in Hamburg between 7620 eV and 7900 eV and normalized. Data analyses and theoretical calculations of the XAS spectra were done following standard procedures by using XAS analysis software (IFEFFIT program package [8]). FT-IR spectra were collected with a Bruker IFS 66 v/S spectrometer in the range between 400 cm^{-1} and 4000 cm^{-1} . For each of these measurements 1 mg of the finely powdered compounds was mixed with 150 mg dried potassium bromide (Merck 99.99%) and pressed into a pellet. The magnetization $M(T,H)$ of the powdered compounds encapsulated in pre-calibrated quartz tubes under He gas was measured by the use of a SQUID magnetometer (MPMS-XL7, Quantum Design) with fields up to $\mu_0 H = 7$ T between 1.8 K and 400 K. In some cases corrections for ferromagnetically ordered impurities with high Curie temperature were applied (Honda-Owen method). The electrical resistivity $\rho(T)$ was measured in a van der Pauw contact arrangement on cold pressed powders in a sapphire die cell (4–320 K).

First-principles electronic structure calculations were performed using the full-potential all-electron code FPLO [9]. Both, the local spin density approximation (LSDA) and the LSDA + *U* [9] scheme were used to account for exchange and correlation effects.

3. Discussion

The predominant structural feature of $\text{Ca}_5[\text{CoN}_2]_2$, $\text{Sr}_5[\text{CoN}_2]_2$, $\text{BaCa}_4[\text{CoN}_2]_2$, $(\text{Sr}_6\text{N})[\text{Co}^{\text{I}}\text{N}_2][\text{CN}_2]_2$, and $\text{Sr}_6[\text{Co}^{\text{I}}\text{N}_2]_2[\text{CN}_2]$ is given by the presence of linear $[\text{Co}^{\text{I}}\text{N}_2]^{5-}$ units ($\text{Ca}_5[\text{CoN}_2]_2$:

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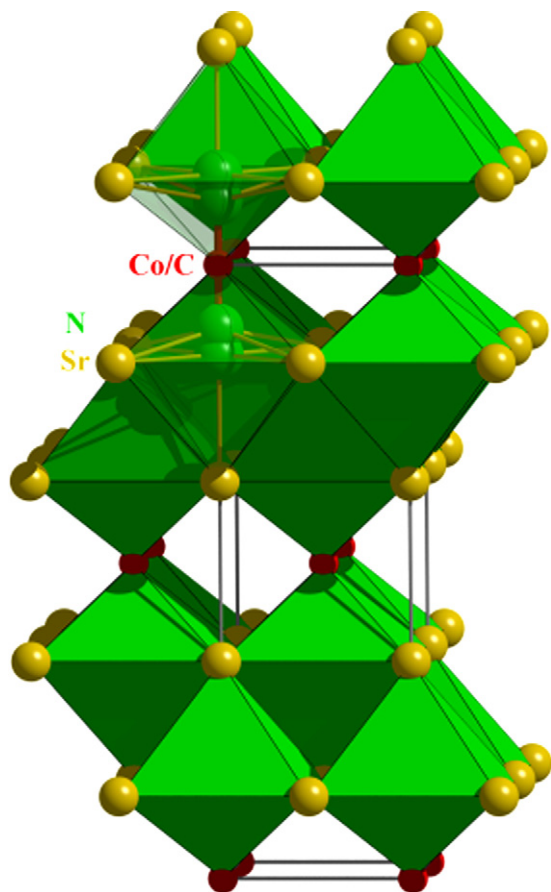


Fig. 1. The crystal structure of $\text{Sr}_6[\text{Co}^{\text{I}}\text{N}_2]_2[\text{CN}_2]$; the $[(\text{Co}/\text{C})\text{N}_2]$ ions are emphasised.

$d(\text{Co}-\text{N}) = 1.821(4)$ Å, $\angle(\text{N}-\text{Co}-\text{N}) = 178.1(2)^\circ$; $\text{BaCa}_4[\text{CoN}_2]_2$: $d(\text{Co}-\text{N}) = 1.805(3)$ Å, $\angle(\text{N}-\text{Co}-\text{N}) = 177.02(16)^\circ$; $(\text{Sr}_6\text{N})[\text{CoN}_2]_2[\text{CN}_2]_2$: $d(\text{Co}-\text{N}) = 1.832(4)$ Å, $\angle(\text{N}-\text{Co}-\text{N}) = 178.6^\circ$; $\text{Sr}_6[\text{Co}^{\text{I}}\text{N}_2]_2[\text{CN}_2]_2$: $d(\text{Co}-\text{N}) = 1.819(3)$ Å, $\angle(\text{N}-\text{C}/\text{Co}-\text{N}) = 180^\circ$. The crystal structure of $\text{Sr}_6[\text{Co}^{\text{I}}\text{N}_2]_2[\text{CN}_2]$ represents the first example with a nitridometalate $[\text{M}^{\text{I}}\text{N}_2]^{5-}$ complex ($d(\text{Co}-\text{N}) = 1.819(3)$ Å) partially substituted by a carbodiimide unit $[\text{N}=\text{C}=\text{N}]^{2-}$ ($d(\text{C}-\text{N}) = 1.281(9)$ Å). This compound has a homogeneity range indicated by variations of lattice parameters and significant differences in XRD peak intensities, an observation which is still under investigation [6].

The alkaline-earth–nitrogen sublattices in all the compounds under consideration can be derived from the rocksalt structure type. In the series $\text{AE}_5[\text{Co}^{\text{I}}\text{N}_2]_2$, the structures can be described in terms of alkaline-earth–nitrogen double layers running parallel to the (001) plane with the Co species interconnecting the layers. The atomic ratio $\text{AE}:\text{N} = 5:4$ leads to voids in the N partial structures formed by edge-sharing NCA_5 , NSr_5 , or NBaCa_4 units, respectively. In the crystal structure of $(\text{Sr}_6\text{N})[\text{Co}^{\text{I}}\text{N}_2]_2[\text{CN}_2]_2$ Sr–N rocksalt-like 3×5 columns running along [001] build up a 3D array by sharing common corners thereby forming channels in which the Co and C atoms are located. In case of $\text{Sr}_6[\text{Co}^{\text{I}}\text{N}_2]_2[\text{CN}_2]$ (Fig. 1) the Sr–N rocksalt-like motif is based on double layers of NSr_5 units which are separated by Co and C species (occupying identical crystallographic positions in a disordered fashion) to form the 3D-framework.

Up to now only a few nitridocobaltates are known and the oxidation state of Co has never been found to exceed the Co^{I} state. The assignment of the oxidation states of Co in the compounds was accomplished by simple valence rules as well as on the basis of X-ray absorption spectroscopy (XAS) and evaluation of X-ray absorption near edge structures (XANES) which also provide infor-

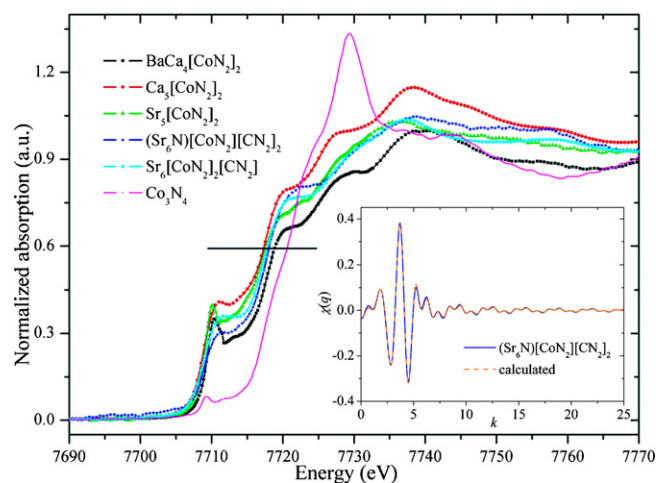


Fig. 2. Co K -edge X-ray absorption spectra of $(\text{Sr}_6\text{N})[\text{CoN}_2][\text{CN}_2]_2$, $\text{Ca}_5[\text{CoN}_2]_2$, $\text{BaCa}_4[\text{CoN}_2]_2$, $\text{Sr}_5[\text{CoN}_2]_2$, and $\text{Sr}_6[\text{Co}^{\text{I}}\text{N}_2]_2[\text{CN}_2]$. Co_3O_4 was used as a reference material. The chemical shift of energy at 0.6 of the normalized absorption is clearly visible. The inset (k [\AA^{-1}], χ [\AA^{-2}]) shows the experimental (blue line) and the calculated (orange broken line) XAFS spectra for $(\text{Sr}_6\text{N})[\text{CoN}_2][\text{CN}_2]_2$.

mation about local structural details. The following compounds were investigated: $(\text{Sr}_6\text{N})[\text{CoN}_2][\text{CN}_2]_2$, $\text{Ca}_5[\text{CoN}_2]_2$, $\text{BaCa}_4[\text{CoN}_2]_2$, $\text{Sr}_5[\text{CoN}_2]_2$, $\text{Sr}_6[\text{Co}^{\text{I}}\text{N}_2]_2[\text{CN}_2]$. Co_3O_4 was used as a reference material (see Fig. 2).

According to literature data [10] the energy at the main edge at about 0.6 of the normalized absorption as well as the pre-edge peak positions are usually considered for oxidation state assignments of the transition metals. Some weak pre-edge features ($1s \rightarrow 3d$ transition [10,11]) appearing as a shoulder of the main edge for all the nitridocobaltates at ~ 7713 eV, are also observed. As expected, the Co K -edges of nitridocobaltates(I) are located at lower energy (shift ≈ 4 eV) in comparison with Co_3O_4 which contains $\text{Co}^{\text{III/IV}}$. Since all nitridocobaltates contain $[\text{Co}^{\text{I}}\text{N}_2]^{5-}$ units their XANES spectra show similar shapes of the K -edges and their main features reveal striking similarities.

$(\text{Sr}_6\text{N})[\text{CoN}_2][\text{CN}_2]_2$ was chosen to check the compatibility of experiment and theory by calculating the X-ray absorption fine structure (XAFS) spectrum using the IFEFFIT program package [8]. For the calculation Co was set as central atom. For general information all Co neighbours up to a distance of 6 Å were included. The inset in Fig. 2 shows a perfect agreement between the calculated and experimental XAFS spectra of $(\text{Sr}_6\text{N})[\text{CoN}_2][\text{CN}_2]_2$ in the whole range.

To investigate the vibrational behaviour of the carbodiimide ($[\text{N}=\text{C}=\text{N}]^{2-}$) group, infrared and Raman spectra of $\text{Sr}_6[\text{Co}^{\text{I}}\text{N}_2]_2[\text{CN}_2]$ and $(\text{Sr}_6\text{N})[\text{CoN}_2][\text{CN}_2]_2$ were recorded. $\text{Sr}_6[\text{Co}^{\text{I}}\text{N}_2]_2[\text{CN}_2]$ ($D_{\infty h}$ symmetry) shows three bands observed at ≈ 1990 cm^{-1} (ν_{as} , antisymmetric stretching), 1264 cm^{-1} (ν_{s} , symmetric stretching) and at ≈ 640 cm^{-1} (δ , deformation vibration). In case of $(\text{Sr}_6\text{N})[\text{CoN}_2][\text{CN}_2]_2$ (C_{2v} symmetry) ν_{as} , ν_{s} and δ modes were registered at 1950 cm^{-1} and 1978 cm^{-1} , 1240 cm^{-1} , and 663 cm^{-1} and 676 cm^{-1} , respectively. No indications for significant differences in chemical bonding are observed for the $[\text{CN}_2]^{2-}$ units in both compounds. Together with data from the literature [12] we conclude that the $[\text{CN}_2]^{2-}$ units have to be considered as symmetric carbodiimide and not cyanamide species. A detailed discussion of the IR and Raman spectra of these and other related compounds is in preparation [10].

At high temperatures the magnetic susceptibilities $\chi(T)$ of the compounds $\text{AE}_5[\text{CoN}_2]_2$ can be described by a Curie–Weiss law. For $\text{Ca}_5[\text{CoN}_2]_2$ ($\text{BaCa}_4[\text{CoN}_2]_2$) an effective magnetic moment of

3.22 μ_B per Co-atom (3.10 μ_B per Co-atom) is obtained. These values indicate an $S = 1$ state (spin-only value: 2.83 μ_B ; values for Ni^{2+} ($3d^8$): 2.80–3.50 μ_B [13]) of the $3d^8$ configuration which is in agreement with the assignment of a Co^I oxidation state by XAS. At low temperatures and high fields a rounded maximum in $\chi(T)$ is visible, followed by a sharp decrease (at 44 K and 42 K for $Ca_5[CoN_2]_2$ and $BaCa_4[CoN_2]_2$, respectively) indicating low-dimensional antiferromagnetic interactions at high temperatures and long-range antiferromagnetic ordering below 50 K.

$[Sr_6N][CoN_2][CN_2]_2$ represents a Curie–Weiss paramagnet with an effective moment of 3.26 μ_B (consistent with Co^{1+}) and weak ferromagnetic interactions ($\theta_{CW} = +7.4$ K). No magnetic ordering was detected at low temperatures. $Sr_6[Co^I N_2]_2[CN_2]$ also follows a Curie–Weiss law at high temperatures (3.22 μ_B /Co-atom, i.e. Co^{1+} with $S = 1$) but with a large Weiss parameter $\theta_{CW} = -82$ K indicating strong low-dimensional antiferromagnetic exchange interactions. At low temperatures (below 10 K) the susceptibility shows a different behaviour for zero-field cooled and field-cooling curves. The magnetic ground state of this compound is not yet clarified.

Due to the interesting magnetic susceptibility data electronic structure calculations were performed for $Ca_5[CoN_2]_2$ and $BaCa_4[CoN_2]_2$. By this, we found that various antiferromagnetic (AFM) arrangements had lower total energies than ferromagnetic (FM) or nonmagnetic cases. In the LSDA calculations band gaps of about 0.4–0.5 eV are observed, while the nonmagnetic calculations result in a metallic character of the DOS. In LSDA + U [9] calculations ($U = 6$ eV) the band gaps increase to ~ 0.68 eV. The total energy differences between various AFM and FM configurations are mapped to a Heisenberg Hamiltonian. For $BaCa_4[CoN_2]_2$ we found that all exchange integrals calculated up to the fifth neighbours had AFM

signs with a strong interlayer Co–Co coupling. Further investigations on this topic will be published elsewhere [4].

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References

- [1] R. Kniep, *Pure Appl. Chem.* 89 (1997) 185–191.
- [2] J.K. Bendyna, P. Höhn, R. Kniep, *Z. Kristallogr. NCS* 222 (2007) 165–166.
- [3] J.K. Bendyna, P. Höhn, R. Kniep, *Z. Kristallogr. NCS* 222 (2007) 167–168.
- [4] J.K. Bendyna, P. Höhn, A. Ormeci, W. Schnelle, R. Kniep, in preparation.
- [5] J.K. Bendyna, P. Höhn, W. Schnelle, R. Kniep, *Sci. Technol. Adv. Mater.* 8 (2007) 393–398.
- [6] J.K. Bendyna, P. Höhn, W. Schnelle, Yu. Prots, H. Borrmann, R. Kniep, in preparation.
- [7] P. Höhn, R. Kniep, *Z. Naturforsch.* 47b (1992) 434–436.
- [8] M. Newville, *J. Synchrotron Radiat.* 8 (2001) 322–324; B. Ravel, M. Newville, *J. Synchrotron Radiat.* 12 (4) (2005) 537–541; B. Ravel, *J. Synchrotron Radiat.* 8 (2001) 314–316.
- [9] K. Koepf, H. Eschrig, *Phys. Rev. B* 59 (1999) 1743.
- [10] R. Niewa, Z. Hu, R. Kniep, *Eur. J. Inorg. Chem.* 8 (2003) 1632–1634.
- [11] Z. Hu, G. Kaindl, G.A. Hayer, D. Reinen, *Z. Anorg. Allg. Chem.* 627 (2001) 2647–2653.
- [12] G. Baldinozzi, B. Malinowska, M. Rakib, G. Durand, *J. Mater. Chem.* 12 (2002) 268–272.
- [13] A. Weiss, H. Witte, *Magnetochemie*, Verlag Chemie, Weinheim, 1973, p. 136.