

## Synthesis, Crystal-Structure Determination and Magnetic Properties of Two New Transition-Metal Carbodiimides: CoNCN and NiNCN

Manuel Krott, Xiaohui Liu, Boniface P. T. Fokwa, Manfred Speldrich, Heiko Lueken, and Richard Dronskowski\*

Institute of Inorganic Chemistry, RWTH Aachen University, D-52056 Aachen, Germany

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Synthesis, structure determination, and magnetic properties are reported for the metastable and crystal-chemically isotypic phases cobalt carbodiimide, CoNCN, and nickel carbodiimide, NiNCN, adopting the hexagonal system and space group  $P6_3/mmc$  (NiAs type) with interatomic distances of Co–N = 2.17 Å and Ni–N = 2.12 Å and an octahedral coordination of the transition-metal ions; the  $\text{NCN}^{2-}$  units reveal the carbodiimide shape with two C=N double bonds. The low-susceptibility data go back to strong antiferromagnetic spin–spin coupling, similar to the behavior of the electronically related oxides CoO and NiO.

### Introduction

The design and successful synthesis of new magnetic materials by coupling various magnetic centers with the help of diamagnetic polynuclear bidentate ligands in the form of extended coordination complexes is an interesting and ongoing challenge within inorganic solid-state chemistry. One of these ligands is the  $\text{NCN}^{2-}$  anion, the corresponding base of the cyanamide molecule. Despite the existence of a number of  $\text{M}(\text{NCN})$  cyanamide or carbodiimide salts of the main-group and nonmagnetic transition metals, the formation of such phases for non- $d^{10}$  metal cations has been achieved in only two cases so far: Manganese carbodiimide, MnNCN, is gained by a delicate metathesis reaction around 600 °C,<sup>1</sup> and the much more temperature-sensitive copper phase CuNCN crystallizes from an aqueous solution at 20 °C by the oxidation of the copper(I) cyanamide complex  $\text{Cu}_4(\text{NCN})_2\text{-NH}_3$ , thus by a two-step synthesis.<sup>2</sup>

The experimental difficulties in synthesizing such nitrogen-based transition-metal salts are easily explainable. A little earlier, quantum-chemical total-energy calculations for the crystalline phases had predicted the complete set of  $\text{M}(\text{NCN})$  ( $\text{M} = \text{Mn, Fe, Co, Ni, Cu}$ ) phases to be *unstable* in terms of both formation enthalpy  $\Delta H_f$  and Gibbs formation energy  $\Delta G_f$ .<sup>3</sup> Thus, it is clear why the successful metathesis route

for the least unstable phase MnNCN fails for the corresponding Fe, Co, Ni, and Cu compounds: At temperatures higher than 400 °C—necessary for the metathesis reaction—such sensitive compounds immediately decompose, which results in the bare metals or metal nitrides; CuNCN, for example, decays at 250 °C already. A synthesis following the CuNCN route, on the other hand, is impossible for CoNCN and NiNCN because precursors similar to  $\text{Cu}_4(\text{NCN})_2\text{-NH}_3$  containing a monovalent  $\text{Co}^+$  or  $\text{Ni}^+$  do not exist. In this contribution we present a novel and completely different two-step way to the carbodiimide compounds CoNCN and NiNCN which adopt a new crystal structure. As a prerequisite for the synthesis of CoNCN and NiNCN, their corresponding hydrogencyanamide precursors,  $\text{M}(\text{HNCN})_2$ , had to be prepared first. These precursors were heated up to 400 °C, thereby producing the carbodiimides as phase-pure substances and melamine as a stable byproduct which was removed during the reaction.

### Experimental Section

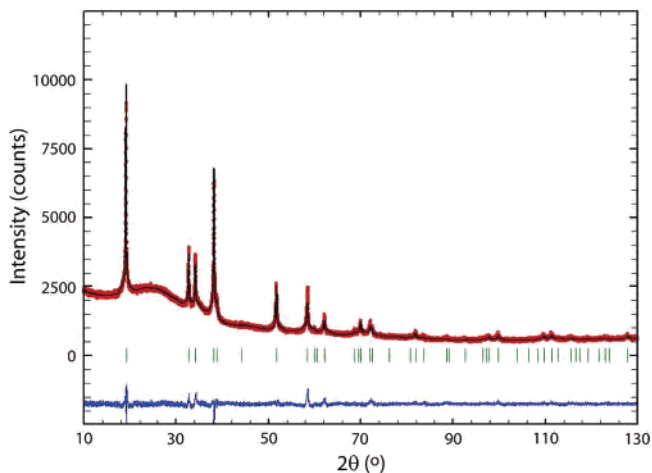
**Synthesis.** Auburn-colored cobalt hydrogencyanamide,  $\text{Co}(\text{HNCN})_2$ , and light-green nickel hydrogencyanamide,  $\text{Ni}(\text{HNCN})_2$ , were synthesized as phase-pure products from the metal chlorides and molecular cyanamide in aqueous ammonia solutions. To achieve good crystalline qualities, the interim ammonia complexes  $[\text{M}(\text{NH}_3)_6]^{2+}$  were slowly destroyed by reducing the ammonia concentration.<sup>4</sup> For the subsequent preparation of the hydrogen-free  $\text{M}(\text{NCN})$  phases, the precursors  $\text{Co}(\text{HNCN})_2$  and  $\text{Ni}(\text{HNCN})_2$  were mingled with a mixture of LiCl/KCl (46:54, mp = 352 °C)

\* To whom correspondence should be addressed. Fax: +49-241-80 92642. Tel: +49-241-80 93642. E-mail: drons@HAL9000.ac.rwth-aachen.de.

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**Figure 1.** Rietveld refinement of the X-ray powder pattern of NiNCN showing measured and fitted intensities (top), the position of the Bragg peaks (middle), and the difference intensity curve (bottom).

as a flux and heated up to 400 °C under a protective argon atmosphere in a closed ampule, thereby expelling melamine to the cold side of the glass container (held at room temperature, sticking out of the tube furnace). Thus, this reaction is not a metathesis and differs from the syntheses of MnNCN or of the carbodiimides of the trivalent rare earths.<sup>1,5</sup> After the ampule was cooled down to room temperature, the orange-brown CoNCN and light-brown NiNCN phases were washed with water and dried in vacuo. Very fortunately, both substances were received as phase-pure products, as evidenced by X-ray powder diffraction (for example, see Figure 1) and elemental analysis based on atomic-absorption spectroscopy, the latter yielding metal contents of 99.92% (CoNCN) and 99.70% (NiNCN) compared to the ideal stoichiometric values. Following the above procedure, even single crystals may be obtained.

**X-ray Diffraction Studies.** The X-ray diffraction data of CoNCN and NiNCN were first recorded at room temperature by means of a calibrated STOE STADI2/PL powder diffractometer (Cu K $\alpha_1$  radiation, linear position-sensitive detector, range of measurement: 8–110° in  $2\theta$  with individual steps of 0.01°) with a flat-sample (CoNCN) and a glass-capillary (0.3 mm diameter) holder (NiNCN). The X-ray powder diagrams were indexed using primitive hexagonal unit cells, and the primary structural models were deduced by a comparison with the crystal structure of CuNCN and earlier quantum-chemical predictions.<sup>2,3</sup> The backgrounds of the data set were manually subtracted by linear interpolation, and the FULLPROF program package<sup>6</sup> was used for the Rietveld refinements using a pseudo-Voigt profile function, revealing both substances as pure phases. The isotypism of the crystal structures of CoNCN and NiNCN was immediately obvious, but the crystal-structure details presented here stem from better resolved single-crystal data. Both phases crystallize in the same structure of the hexagonal system and space group  $P6_3/mmc$ . For the cobalt phase, the powder cell parameters were determined as  $a = 3.211(2)$  Å,  $c = 9.381(3)$  Å, and  $Z = 2$ . For the nickel phase, the powder cell parameters are  $a = 3.153(1)$  Å and  $c = 9.255(2)$  Å.

X-ray single-crystal measurements of CoNCN and NiNCN were performed at 293(2) K using a Bruker SMART APEX CCD diffractometer (Mo K $\alpha$ ). The single-crystal lattice parameters are  $a = 3.2129(4)$  Å,  $c = 9.390(2)$  Å for CoNCN and  $a = 3.1533(8)$

**Table 1.** Crystallographic Data and Structural Refinement of CoNCN and NiNCN

formula; molar mass	CoNCN; 98.96 g/mol	NiNCN; 98.72 g/mol
cryst color	orange-brown	light-brown
lattice parameters	$a = 3.2129(4)$ Å $c = 9.3902(2)$ Å	$a = 3.1533(8)$ Å $c = 9.272(3)$ Å
cell volume	83.95(2) Å <sup>3</sup>	79.85(4) Å <sup>3</sup>
space group;	$P6_3/mmc$ (No. 194); 2	$P6_3/mmc$ (No. 194); 2
formula units		
R1, wR2 (all data)	0.0158, 0.0389	0.1045, 0.1638

Å,  $c = 9.272(3)$  Å for NiNCN. The collected data were empirically corrected with respect to absorption:  $\mu(\text{Mo K}\alpha) = 9.67$  (CoNCN) and  $11.57 \text{ mm}^{-1}$  (NiNCN).<sup>7</sup> The crystal structures were refined by means of anisotropic displacement parameters for all atoms (Co phase) and anisotropic ones for the metal atom (Ni phase); M on  $2a$ , C on  $2c$ , N on  $4f$  with  $z = 0.3805(3)$  for CoNCN and  $0.383(2)$  for NiNCN. 1742/1689 reflections (CoNCN/NiNCN) measured, max  $2\theta = 71.64^\circ/71.97^\circ$ , 99/94 unique intensities ( $R_{\text{int}} = 0.0290/0.2101$ ) which were all used in the 8/6-parameter refinement;<sup>7</sup> see also Table 1.

The larger size and excellent quality of the single crystal of CoNCN allowed for an anisotropic refinement of the light atoms N and C, whereas, for NiNCN, these two atoms could only be refined isotropically. Nonetheless, the final  $z$  parameters of the nitrogen atom (Wyckoff position  $4f$  in space group  $P6_3/mmc$ ) arrived at a very similar  $0.3805(3)$  for CoNCN and  $0.383(2)$  for NiNCN, thereby yielding the identical crystal-chemical motif of a carbodiimide unit with two C=N double bonds (see below).

**Infrared Spectroscopy.** The infrared spectra were recorded using a Nicolet Avatar 360 FT-IR E.S.P. spectrophotometer in a range from 400 to 4000  $\text{cm}^{-1}$  with KBr windows (500 mg KBr/0.5 mg sample).

**Magnetic Measurements.** The magnetic susceptibilities of the two solid-state carbodiimides were determined by SQUID magnetometry (MPMS-5S, Quantum Design) in the temperature range 2–400 K at an applied field  $B_0 = 0.5$  T. The data were corrected for diamagnetic contributions of  $\text{Co}^{2+}/\text{Ni}^{2+}$  and  $\text{NCN}^{2-}$  (approximately  $-41 \times 10^{-11} \text{ m}^3 \text{ mol}^{-1}$ ).

## Results and Discussion

Both M(NCN) compounds were synthesized following the procedure shown in eq 1. Orange-brown CoNCN and light-brown NiNCN powders were received as phase-pure materials and structurally characterized by X-ray diffraction (powder Rietveld and single-crystal refinement). Melamine is received as a byproduct, also in good crystalline quality.



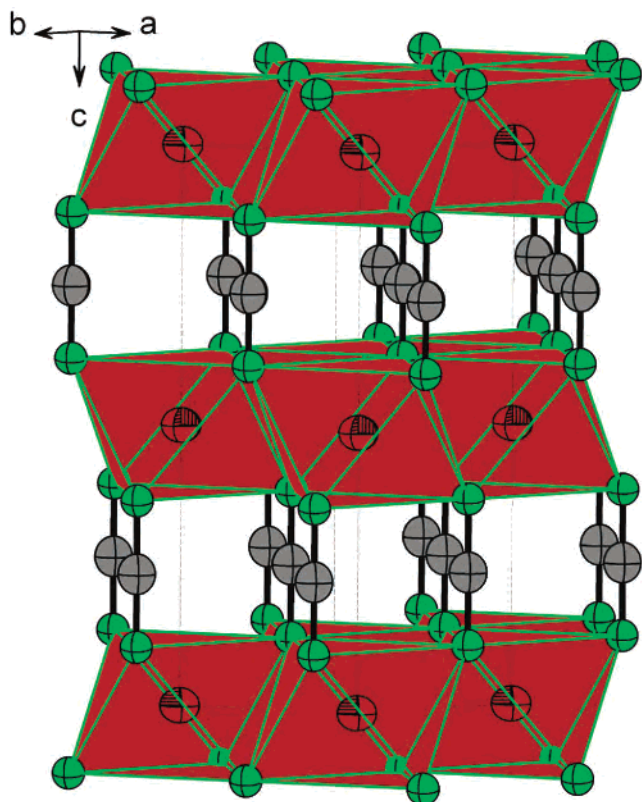
The crystal structure of CoNCN and NiNCN may formally be considered a layered structure in which each layer consists of alternating  $\text{M}^{2+}$  and  $\text{NCN}^{2-}$  ions (see Figure 2), somewhat similar to the situation in MnNCN; nonetheless, the metal arrangement is *not* the same, as evident from the different space group ( $R\bar{3}m$  for MnNCN).<sup>1</sup> In fact, the crystal structure found for CoNCN and NiNCN resembles the NiAs type with octahedral coordination for the metal cations and a trigonal-prismatic one for the linear  $\text{NCN}^{2-}$  units, the C atom having replaced the As atom inside NiAs. Because the elongated

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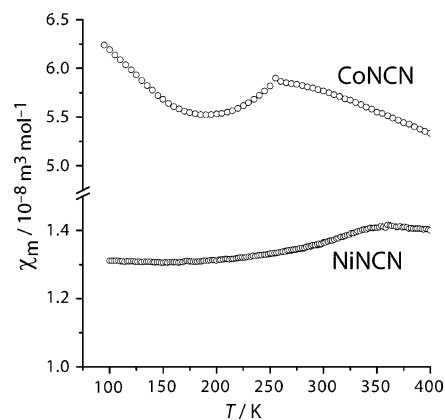
**Figure 2.** Crystal structure of CoNCN and NiNCN, with octahedral nitrogen (in green) coordination around Co/Ni (in red) and linearly coordinated carbon atoms (in gray); the thermal ellipsoids correspond to 99% probability using the anisotropically refined CoNCN structure.

NCN<sup>2-</sup> unit runs parallel with the *c* axis, the latter is also elongated. In an alternative description, the M<sup>2+</sup> ions on Wyckoff position 2*a* form cationic sheets parallel to the *ab* face with a Co–Co distance of 3.2129(4) Å; for the nickel phase, the corresponding Ni–Ni distance is 3.1533(8) Å. Each M<sup>2+</sup> ion is coordinated by six nitrogen atoms on 4*f* leading to a slightly flattened octahedral coordination with Co–N = 2.168(1) Å and Ni–N = 2.119(8) Å, a bit shorter (0.03 Å) than the sum of the effective ionic radii (2.21 and 2.15 Å)<sup>8</sup> but still about 0.07 Å longer than within the cyanamide complexes Co(NCNH<sub>2</sub>)<sub>4</sub>Cl<sub>2</sub> and Ni(NCNH<sub>2</sub>)<sub>4</sub>Cl<sub>2</sub>.<sup>9</sup> In these compounds, however, only four nitrogen atoms bond to the central Co/Ni ion, and the coordination of the metal cation is augmented by two additional chlorine atoms.

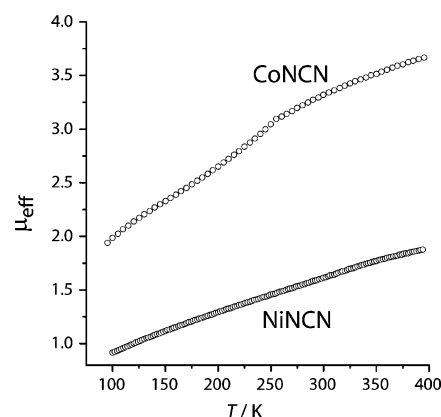
The NCN<sup>2-</sup> units experience trigonal-prismatic metal coordinations along *c*, and the complex anion is strictly linear (N–C–N = 180°) by reasons of space-group symmetry. The C=N double-bond lengths arrive at the expected 1.226(2) Å for CoNCN and 1.233(16) Å for NiNCN, and the central C atom on 2*c* coincides with the inversion-symmetry element such that the two nitrogen atoms are generated by only one crystallographic N site (4*f*); the anionic shape conforms to *D*<sub>∞h</sub> (carbodiimide) symmetry. For comparison, the C=N double-bond length in MnNCN, also based on single-crystal data, arrived at 1.227(4) Å.<sup>1</sup> In accord with the crystal-

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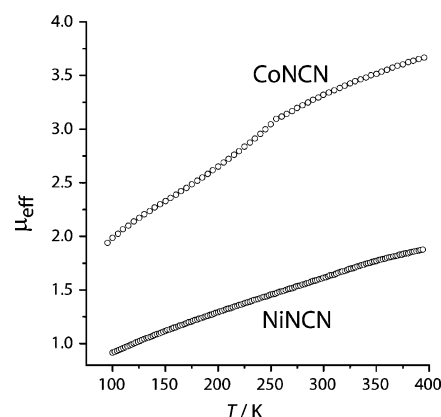
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**Figure 3.** Variation of the molar magnetic susceptibility (SI units) of CoNCN (top) and NiNCN (bottom) as a function of the temperature at an applied field of  $B_0 = 0.5$  T.



**Figure 4.** Same as Figure 3 but showing the course of the effective moments as a function of the temperature.



structure analysis, the infrared spectra of both M(NCN) phases exhibit only strong carbodiimide-type asymmetrical vibrations,  $\nu_{as}(\text{NCN}) = 2090$  for CoNCN and  $2040 \text{ cm}^{-1}$  for NiNCN, plus a strong deformation vibration,  $\delta(\text{NCN}) = 650$  for CoNCN and  $660 \text{ cm}^{-1}$  for NiNCN. In contrast, no symmetrical  $\nu_s$  band (around  $1200 \text{ cm}^{-1}$ ) is observed because such a breathing mode is IR-forbidden for the  $[\text{N}=\text{C}=\text{N}]^{2-}$  carbodiimide unit, although it would be allowed for the less-symmetrical cyanamide  $[\text{N}-\text{C}\equiv\text{N}]^{2-}$  anion.

Figures 3 and 4 show the results of the magnetic measurements in the significant temperature range 100–400 K by means of molar susceptibility (SI units) and  $\mu_{\text{eff}}$  (with  $\mu_{\text{eff}} = 797.74 [\chi_m T]^{1/2}$ ) vs temperature plots; the presentation of the magnetic data follows the recommendation of Hatscher et al.<sup>10</sup> As compared with octahedral mononuclear complexes, the magnetic susceptibility data are considerably reduced on account of antiferromagnetic exchange interactions. While, as a result of spin and first-order orbital contributions, magnetically dilute Co(II) high-spin ( $S = 3/2$ ) systems exhibit  $\mu_{\text{eff}}$  values in the range 4–5,<sup>11</sup> lower values are observed for the magnetically condensed compound CoNCN, for example  $\mu_{\text{eff}} = 3.7$  at 400 K. For dilute Ni(II) ( $S = 1$ ) systems

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$\mu_{\text{eff}} \approx 3$  is expected, whereas for NiNCN merely  $\mu_{\text{eff}} = 1.9$  has been measured at 400 K. Moreover, the strong antiferromagnetic spin–spin coupling is supported by susceptibility maxima at the relatively high temperatures  $T(\chi_{\text{m}}^{\text{max}}) = 255$  and 360 K for CoNCN and NiNCN, respectively, where  $\chi_{\text{m}}^{\text{max}}$  corresponds to  $\mu_{\text{eff}} = 3.1$  and 1.8, respectively. To more closely investigate the types of magnetic ordering, field-dependent susceptibility measurements around  $T(\chi_{\text{m}}^{\text{max}})$  are under way. Nonetheless, CoNCN and NiNCN can already be qualitatively classified to resemble their electronically related oxide counterparts CoO and NiO in terms of both structure and magnetism. The magnetic data  $T(\chi_{\text{m}}^{\text{max}})$  and  $\mu_{\text{eff}}$  at  $T(\chi_{\text{m}}^{\text{max}})$  amount to 293 K and 3.6, respectively, for CoO, as well as 620 K and 2.0, respectively, for NiO.<sup>12</sup>

In summary, we have presented the synthesis and structural characterization of two new M(NCN) transition-metal cyanamide phases which turned out as carbodiimides by

structure. Both compounds were originally predicted as thermodynamically unstable phases but are accessible by using moderate temperatures, appropriate precursors and by creating the stable side-product melamine; because the activation barrier for the decay into the elements must be rather large, we may consider the compounds as kinetically stable or metastable. Magnetic measurements exhibit relatively small atomic moments due to strong antiferromagnetic spin–spin coupling. We are confident that this method might serve as the key to synthesize other transition-metal cyanamide/carbodiimide phases, yet to be made.

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**Supporting Information Available:** Crystallographic data in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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