

Synthesis and structure determination of $\text{Co}(\text{HNCN})_2$ and $\text{Ni}(\text{HNCN})_2$

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In memoriam DIDO (1961–2006)

Abstract

Well-crystallized cobalt and nickel hydrogencyanamide, $\text{Co}(\text{HNCN})_2$ and $\text{Ni}(\text{HNCN})_2$, were synthesized from the corresponding ammonia complexes $[\text{M}(\text{NH}_3)_6]^{2+}$ under aqueous cyanamide conditions. The X-ray and neutron powder data evidence the orthorhombic system and space group *Pnmm*. The cell parameters for $\text{Co}(\text{HNCN})_2$ are $a = 6.572(1)$, $b = 8.805(2)$, $c = 3.267(1)$ Å, and $Z = 2$; for the isotopic $\text{Ni}(\text{HNCN})_2$, the cell parameters arrive at $a = 6.457(1)$, $b = 8.768(2)$, $c = 3.230(1)$ Å. The octahedral coordinations of the metal ions are marginally squeezed, with interatomic distances of $4 \times \text{Co-N} = 2.134(5)$ Å, $2 \times \text{Co-N} = 2.122(9)$ Å, and $4 \times \text{Ni-N} = 2.133(6)$ Å, $2 \times \text{Ni-N} = 2.035(11)$ Å. The HNCN^- units appear as slightly bent ($177.5(2)^\circ$ for $\text{Co}(\text{HNCN})_2$ and $175.7(2)^\circ$ for $\text{Ni}(\text{HNCN})_2$) and exhibit cyanamide shape character due to triple- and single-bond C–N distances (1.20(2) vs. 1.33(2) Å for $\text{Co}(\text{HNCN})_2$ and 1.15(2) vs. 1.38(2) Å for $\text{Ni}(\text{HNCN})_2$). The infrared vibration data compare well with those of the three existing alkali-metal hydrogencyanamides.

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1. Introduction

Combining paramagnetic (transition-)metal centers with diamagnetic polynuclear bridging ligands is a promising approach to create new and interesting magnetic compounds. Two examples of such ligands are given by the NCN^{2-} and HNCN^- anions, the corresponding bases of the H_2NCN (cyanamide) molecule. While the twofold deprotonated anion (NCN^{2-}) of the H_2NCN molecule has been successfully used to prepare a large number of salts comprising alkali metals [1–3], alkaline-earth metals [4–7], main-group elements [8–11], transition metals [12–20], and also rare-earth metals [21–23], the anion with one remaining proton (HNCN^-) has only been used in combination with alkali metals up to now [24–26].

For example, sodium hydrogencyanamide, NaHNCN , has been synthesized by the deprotonation of cyanamide with sodium ethoxide in ethanol under anhydrous conditions, and it crystallizes in the orthorhombic space group *Pbcm* where the sodium ions are coordinated by four nitrile nitrogens and two amino nitrogens [24]. The synthesis of potassium hydrogencyanamide, KHNCN , on the other hand, is carried out by the reaction of melamine with potassium amide in liquid ammonia [25] while rubidium hydrogencyanamide, RbHNCN , is obtained from a solution of cyanamide and rubidium amide in liquid ammonia [26]. The latter two compounds are chemically isotopic and crystallize in space group *P2₁2₁2₁*, with a sevenfold coordination of the cations, thereby reflecting the larger size of K^+/Rb^+ compared to Na^+ . In all of these phases, the HNCN^- anion appears as slightly bent and exhibits two different C–N bond lengths, characteristic of the cyanamide shape with one single and one triple bond. In this contribution, we present an alternative and rather simple way to synthesize salts containing metals with a

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Table 1
Crystallographic data and structural refinement of Co(HNCN)₂ and Ni(HNCN)₂

Formula; molar mass	Co(HNCN) ₂ ; 141.00 g/mol	Ni(HNCN) ₂ ; 140.76 g/mol
Crystal color and form	Auburn powder	Light-green powder
Lattice parameters	$a = 6.572(1) \text{ \AA}$ $b = 8.805(2) \text{ \AA}$ $c = 3.267(1) \text{ \AA}$	$a = 6.457(2) \text{ \AA}$ $b = 8.768(3) \text{ \AA}$ $c = 3.230(1) \text{ \AA}$
Cell volume	189.04(2) Å ³	182.89(4) Å ³
Space group; formula units	<i>Pnmm</i> (no. 58); 2	<i>Pnmm</i> (no. 58); 2
Number of reflections	109 ($2\theta = 4\text{--}95^\circ$)	178 ($2\theta = 4\text{--}120^\circ$, X-ray); 165 ($2\theta = 9\text{--}76^\circ$, neutrons)
R_p , R_{wp} , R_{Bragg} (X-ray)	0.012, 0.015, 0.116	0.042, 0.061, 0.060
R_p , R_{wp} , R_{Bragg} (neutrons)		0.025, 0.030, 0.185

Table 2
Positional and isotropic displacement parameters for Co(HNCN)₂ and Ni(HNCN)₂ with standard deviations in parentheses

Atom	Wyckoff site	<i>x</i>	<i>y</i>	<i>z</i>	B_{iso} (Å ²)
Co	2 <i>a</i>	0	0	0	1.9 (1)
N1	4 <i>g</i>	0.294 (3)	0.525 (5)	0	2.5 (4)
N2	4 <i>g</i>	0.091 (4)	0.769 (4)	0	0.4 (4)
C	4 <i>g</i>	0.816 (5)	0.349 (4)	0	1.9 (2)
Ni	2 <i>a</i>	0	0	0	0.9 (1)
N1	4 <i>g</i>	0.288 (4)	0.530 (5)	0	1.2 (3)
N2	4 <i>g</i>	0.083 (5)	0.776 (4)	0	1.2 (4)
C	4 <i>g</i>	0.830 (7)	0.339 (5)	0	1.0 (4)
H	4 <i>g</i>	0.777 (19)	0.550 (15)	0	2.2 (9)

All parameters were extracted from either pure X-ray (Co(HNCN)₂) or combined X-ray/neutron data (Ni(HNCN)₂).

*non-d*¹⁰ electron configuration and HNCN[−] as a small nitrogen-containing ligand.

The main problem in generating M(HNCN)₂ compounds (M = 3*d*⁴–3*d*⁹ atoms) in aqueous solutions is given by their tendency to form complexes such as [M(NCNH₂)₄]²⁺ ions, in particular with M=Co, Ni, and Cu [27,28], and it has proven difficult to further remove the hydrogen atoms from the complex ions. To avoid this problem, a large excess of ammonia in a concentrated aqueous solution of H₂NCN and MCl₂ (M=Co, Ni) has been used because, in such a case, ammonia acts both as a base and as an alternative ligand to avoid the formation of the aforementioned complexes. The interim ammonia complexes may then be slowly destroyed by reducing the ammonia concentration (realized with a slight argon stream which is blown over the solution), thereby removing excess ammonia gas and protecting air-unstable species such as Co(II). Eventually, well-crystallized powders are gained within a few hours. The synthesized Co(HNCN)₂ and Ni(HNCN)₂ have been characterized by X-ray and neutron powder diffraction and turn out as chemically isotypic.

2. Experimental section

A dark-green aqueous solution (10 mL) of NiCl₂·6H₂O (2.38 g, 10 mmol) and H₂NCN (2.10 g, 50 mmol) was

Table 3
Selected bond lengths (Å) and angles (°) in Co(HNCN)₂ and Ni(HNCN)₂ with standard deviations in parentheses; compare with Fig. 3

	Co(HNCN) ₂	Ni(HNCN) ₂
M–N1	2.134 (5)	2.133 (6)
M–N2	2.122 (9)	2.035 (11)
C–N1	1.33 (2)	1.38 (2)
C–N2	1.20 (2)	1.15 (2)
H–N1		0.81 (4)
N1–M–N1	80.1 (5)	81.6 (5)
N1–M–N1	99.9 (3)	98.4 (2)
N1–M–N2	94.7 (5)	93.0 (6)
N1–M–N2	85.3 (6)	87.0 (6)
N2–M–N2	180.0 (4)	180.0 (9)
N1–C–N2	177.5 (2)	175.7 (2)
C–N1–H		116 (5)
Ni–N1–H		103 (4)

prepared in a beaker, and 30 mL of a half-concentrated ammonia solution (12.5 wt%) were added with stirring; the solution became dark blue with a pH around 10. The beaker was then covered with a watchglass, and only the muzzle remained as a small opening. Upon stirring overnight, a light-green crystalline solid was yielded. It was separated by filtration, washed with water, and dried in vacuo. Yield: 1.10 g (78% with respect to NiCl₂·6H₂O). Analytical data for Ni(HNCN)₂ (140.76): calcd. Ni 41.76; C 17.07; N 39.81; H 1.43. Found Ni 41.37; C 15.71; N 39.61; H 2.15. IR (KBr, cm^{−1}): ν(NH) = 3300 (s); ν_{as}(NCN) = 2215 (s); δ(CNH) = 1210 (m); ν_s(NCN) = 1160 (m); δ(NCN) = 635 (m) and γ(NCN) = 570 (m).

A bright-red aqueous solution was prepared by dissolving CoCl₂·6H₂O (0.71 g, 3 mmol) and H₂NCN (0.63 g, 15 mmol) in a Schlenk flask with 5 mL of a concentrated ammonia solution (25 wt%). To get rid of the excess ammonia, an argon stream was led over the solution; the argon gas also prevents the oxidation of Co(II). Upon stirring for several hours, an auburn-colored crystalline solid was yielded. It was separated by filtration, dried, washed with water, and also dried in vacuo. Yield: 0.30 g (72% with respect to CoCl₂·6H₂O). Analytical data for Co(HNCN)₂ (141.00): calcd. Co 41.79; C 17.04; N 39.74; H 1.43. Found Co 40.49; C 16.62; N 38.76; H 2.26. IR (KBr, cm^{−1}): ν(NH) = 3295 (s); ν_{as}(NCN) = 2210 (s);

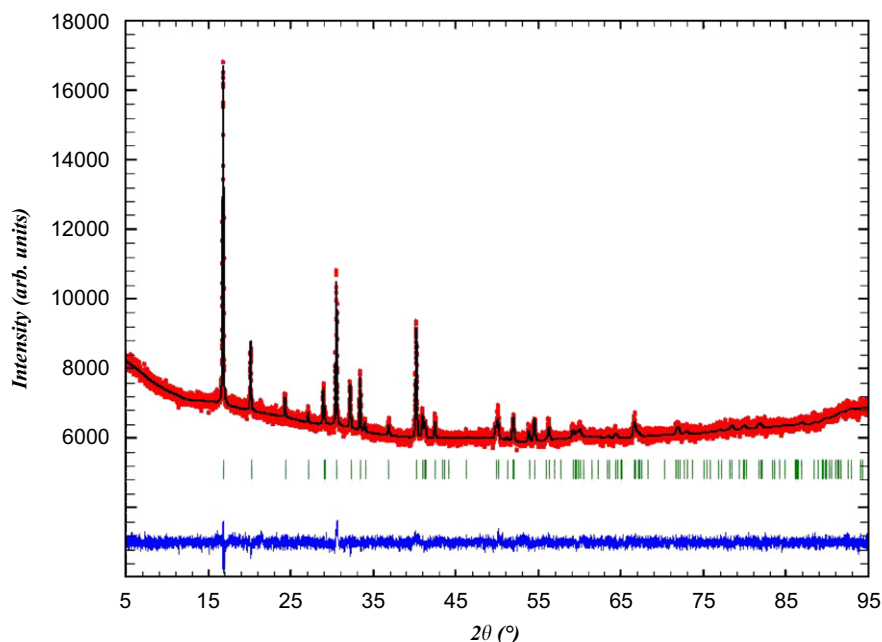


Fig. 1. Observed, calculated, and difference intensities for the X-ray Rietveld refinement of $\text{Co}(\text{HNCN})_2$. The vertical markers show the positions of the Bragg reflections.

$\delta(\text{CNH}) = 1200$ (m); $\nu_s(\text{NCN}) = 1165$ (m); $\delta(\text{NCN}) = 625$ (m) and $\gamma(\text{NCN}) = 560$ (m).

The X-ray diffraction data of $\text{M}(\text{HNCN})_2$ were recorded at room temperature by means of a calibrated STOE STADI-P powder diffractometer with strictly monochromatized $\text{CuK}\alpha_1$ radiation and a linear position-sensitive detector (PSD) with a flat-sample holder; the range of measurement was $4\text{--}95^\circ$ for $\text{Co}(\text{HNCN})_2$ and $4\text{--}120^\circ$ for $\text{Ni}(\text{HNCN})_2$ in 2θ with individual steps of 0.01° . The X-ray powder diagram was indexed using the WinXPOW program package [29] and an orthorhombic cell; the extinction rules were compatible with space group $Pnmm$. The backgrounds of the data sets were manually subtracted by linear interpolation, and the FULLPROF program package [30] was used for the Rietveld refinement employing a pseudo-Voigt profile function; pattern matching was used to extract the integrated intensities. Within space group $Pnmm$, Wyckoff position $2a$ was occupied with the metal atoms, and subsequent calculations with difference Fourier syntheses led to the light atom positions of nitrogen and carbon.

To determine the hydrogen position, neutron diffraction data were collected at room temperature with the Powder and Texture Diffractometer (SV7) at the DIDO neutron reactor of Forschungszentrum Jülich [31] using a neutron wavelength of $\lambda = 1.0952(4)$ Å and a linear JULIOS detector with a vanadium cylinder (10 mm diameter, 30 mm height) as a sample holder. The range of measurement was $4\text{--}89^\circ$ in 2θ with individual steps of 0.10° . For the data refinement, the FULLPROF program package was also used, but now by simultaneously refining both X-ray and neutron data; equal weights were given to the two data sets during the combined refinement. The fact

that we did not prepare a deuterated sample results in a rather poor powder diagram with a high background but the data quality was nonetheless sufficient to extract good intensity data for the combined refinement, see Table 1. The extracted intensities immediately gave the position of the hydrogen atom from a difference Fourier map, and the final combined refinement of both powder patterns led to the positional parameters given in Table 2.

More details of the crystal-structure refinements are given in Table 1 while the positional and isotropic displacement parameters are presented in Table 2. A list of selected bond lengths and angles is given in Table 3. An overview of the Rietveld refinement is shown in Fig. 1 for $\text{Co}(\text{HNCN})_2$ and in Fig. 2 for $\text{Ni}(\text{HNCN})_2$.

IR spectra of both compounds were recorded using a Nicolet Avatar 360 FT-IR E.S.P. spectrophotometer measuring a range from 400 to 4000 cm^{-1} with KBr windows (500 mg KBr/0.5 mg sample).

3. Results and discussion

Both $\text{M}(\text{HNCN})_2$ phases have been prepared as phase-pure and well-crystalline materials from aqueous solutions. Light-green ($\text{M}=\text{Ni}$) or auburn ($\text{M}=\text{Co}$) powders were obtained in 78% and 72% yield, respectively, and their chemically isotopic structures were determined by Rietveld refinements of powder X-ray and neutron diffraction data.

The crystal structure of $\text{M}(\text{HNCN})_2$ is presented in Fig. 3, and it is characterized by a primitive orthorhombic unit cell ($Pnmm$) where the metal atoms alone adopt a body-centred Bravais lattice. Each M^{2+} ion is coordinated by six nitrogen atoms (four amino nitrogens and two nitrile nitrogens, see Fig. 3, left, and Table 3 for further

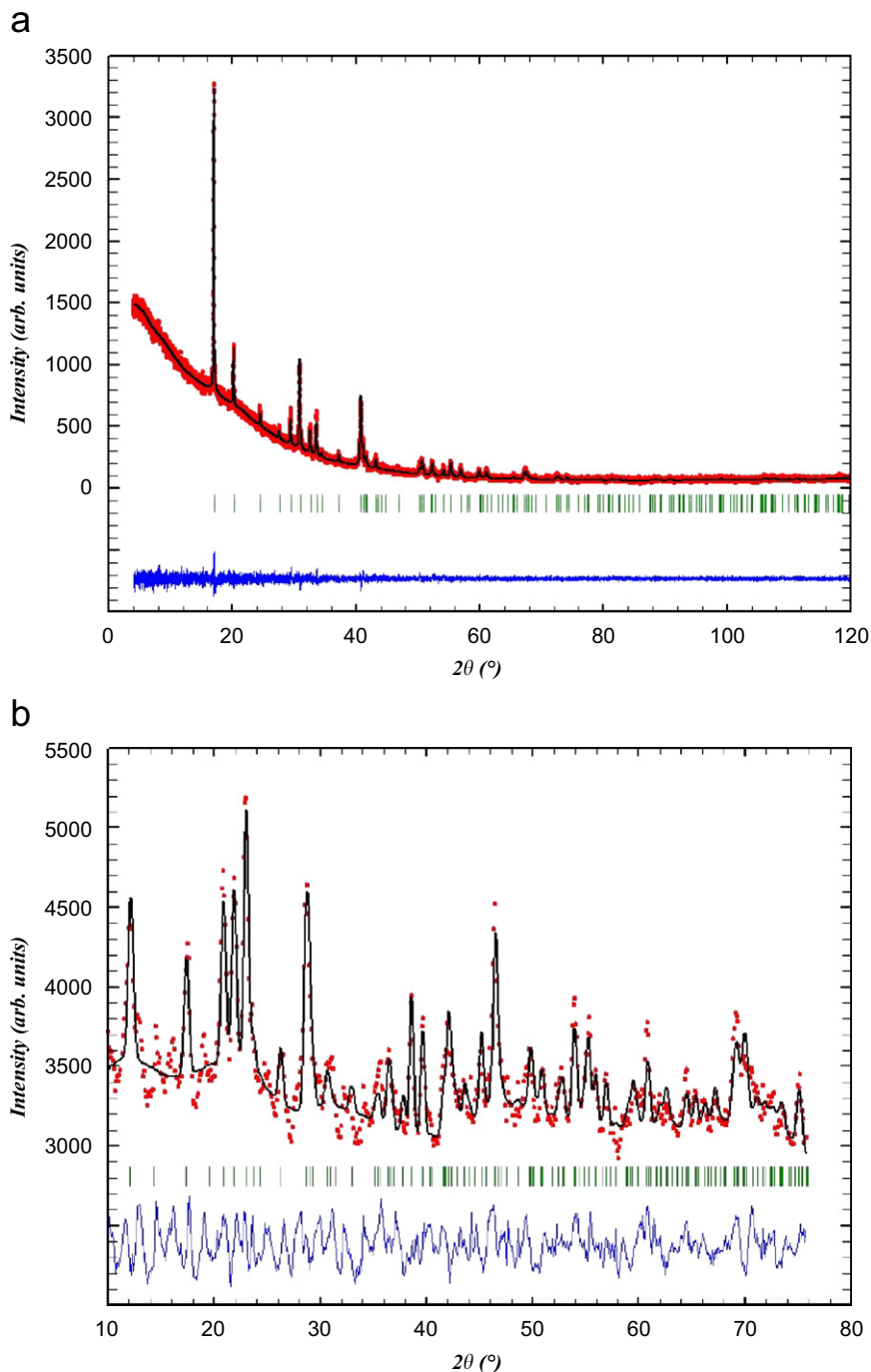


Fig. 2. Observed, calculated, and difference intensities for the X-ray (top) and neutron (bottom) Rietveld refinement of $\text{Ni}(\text{HNCN})_2$. The vertical markers show the positions of the Bragg reflections.

information), and the experimental M–N distances arrive at $4 \times 2.134(5) \text{ \AA}$ and $2 \times 2.122(9) \text{ \AA}$ for the Co phase whereas those of the Ni phase are $4 \times 2.133(6) \text{ \AA}$ and $2 \times 2.035(11) \text{ \AA}$. Thus, the experimental M–N bond lengths are shorter by only 0.08 \AA (Co phase) and 0.05 \AA (Ni phase) than those that would have been predicted on the basis of effective (high-spin for Co^{2+}) ionic radii [32]. Alternatively, the absence of any significant variations in the bond lengths in terms of Jahn–Teller distortions immediately confirms a high-spin configuration for Co^{2+}

(d^7). On the other hand, it is surprising to note that standard parameters for empirical bond-valence summations [33] might require modification because they clearly overestimate the atomic valences as $+2.74$ (Co phase) and $+2.35$ (Ni phase). In fact, a newer set of parameters [34] arrives at much better values, namely $+1.61$ for the Co and $+1.77$ for the Ni phase.

The marginally squeezed octahedra around M (see Table 3) are linked with each other using shared edges along the short c -axis, while they are isolated in the two

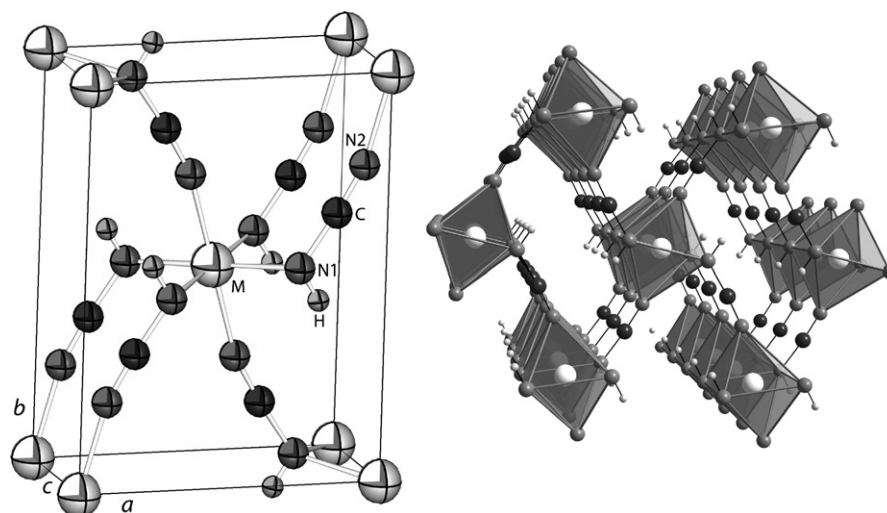


Fig. 3. Crystal structure (left) of $M(\text{HNCN})_2$ with M ($= \text{Co}, \text{Ni}$) atoms as white, N as grey, C as dark-grey, and H as light-grey balls; the position of the H atom has been determined on the basis of the neutron-diffraction data of the Ni phase; packing diagram (right) of the two isotopic phases.

Table 4

Infrared frequencies (cm^{-1}) of $\text{Co}(\text{HNCN})_2$ and $\text{Ni}(\text{HNCN})_2$ compared to the frequencies found for NaHNCN , KHNCN and RbHNCN

	NaHNCN [24]	KHNCN [25]	RbHNCN [26]	$\text{Co}(\text{HNCN})_2$	$\text{Ni}(\text{HNCN})_2$
$\nu(\text{NH})$	3295	3235	3248	3295	3300
$\nu_{\text{as}}(\text{NCN})$	2160	2085	2081	2210	2215
$\delta(\text{CNH})$	1258	1190	1185	1200	1210
$\nu_{\text{s}}(\text{NCN})$	1155	1092	1090	1165	1160
$\delta(\text{NCN})$	620	570	569	625	635
$\gamma(\text{NCN})$	585	538	523	560	570

other directions, depicted in Fig. 3, right. The NCN core of the HNCN^- unit is slightly bent ($177.5(2)^\circ$ for $\text{Co}(\text{HNCN})_2$ and $175.7(2)^\circ$ for $\text{Ni}(\text{HNCN})_2$), and the hydrogencyanamide anions are arranged in a zig-zag manner along the y direction. Each amino nitrogen atom (N1) bonds to two metal ions and one hydrogen atom, and each nitrile nitrogen (N2) bonds to only one metal ion, a rather typical bonding pattern for the cyanamide anion. The single hydrogen atom is bonded to the amino N1 atom and points into an empty void of the crystal structure. The resolution of the powder-based crystal-structure refinement is limited but sufficient to clearly confirm different C–N bond lengths, indicative of the cyanamide character of the complex anion, and this is in coincidence with the data of the infrared spectra which exclude a carbodiimide structure by showing strong symmetrical bands $\nu_{\text{s}}(\text{NCN}) = 1160 \text{ cm}^{-1}$ ($\text{Ni}(\text{HNCN})_2$) and 1165 cm^{-1} ($\text{Co}(\text{HNCN})_2$) which would not be allowed for an $[\text{N}=\text{C}=\text{N}]^{2-}$ carbodiimide unit with two double bonds. The closest N–H \cdots N distance is beyond 3.6 \AA which excludes significant hydrogen bonding, and this is also reflected by a sharp (instead of broad) infrared signal around 3300 cm^{-1} (Table 4).

The other IR data (see Table 4) further evidence that cobalt and nickel hydrogencyanamide mostly resemble the

corresponding sodium phase, not the potassium or rubidium compounds. This is anything but surprising because it reflects that these two transition-metal hydrogencyanamides incorporate a large amount of covalent M–N bonding, and within the alkali-metal series Na/K/Rb it is the relatively small and electronegative Na atom which comes closest to Co and Ni.

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References

- [1] M.G. Down, M.J. Haley, P. Hubberstey, R.J. Pulham, A.E. Thunder, *J. Chem. Soc. Dalton Trans.* 1407 (1978).
- [2] A. Harper, P. Hubberstey, *J. Chem. Res. (S)* 7 (1989) 194.
- [3] M. Becker, J. Nuss, M. Jansen, *Z. Anorg. Allg. Chem.* 626 (2000) 2505.
- [4] N.G. Vannerberg, *Acta Chem. Scand.* 16 (1962) 2263.
- [5] U. Berger, W. Schnick, *J. Alloy Compd.* 206 (1994) 179.
- [6] O. Reckeweg, F.J. DiSalvo, *Angew. Chem. Int. Ed.* 39 (2000) 412.
- [7] W. Liao, R. Dronskowski, *Acta Crystallogr. E* 60 (2004) 124.

- [8] R. Dronskowski, *Z. Naturforsch.* 50b (1995) 1245.
- [9] R. Riedel, A. Greiner, G. Miehe, W. Dreßler, H. Fueß, J. Bill, F. Aldinger, *Angew. Chem. Int. Ed. Engl.* 36 (1997) 603.
- [10] M.J. Cooper, *Acta Crystallogr.* 17 (1964) 1452.
- [11] X. Liu, A. Decker, D. Schmitz, R. Dronskowski, *Z. Anorg. Allg. Chem.* 626 (2000) 103.
- [12] F.P. Bowden, H.M. Montagu-Pollock, *Nature* 191 (1961) 556.
- [13] M. Becker, J. Nuss, M. Jansen, *Z. Naturforsch.* 55b (2000) 383.
- [14] M. Becker, M. Jansen, *Acta Crystallogr. C* 57 (2001) 347.
- [15] G. Baldinozzi, B. Malinowska, M. Rakib, G. Durand, *J. Mater. Chem.* 12 (2002) 268.
- [16] M. Becker, M. Jansen, *Z. Anorg. Allg. Chem.* 626 (2000) 1639.
- [17] X. Liu, P. Müller, P. Kroll, R. Dronskowski, *Inorg. Chem.* 41 (2002) 4259.
- [18] X. Liu, P. Müller, R. Dronskowski, *Z. Anorg. Allg. Chem.* 631 (2005) 1071.
- [19] X. Liu, M. Krott, P. Müller, C. Hu, H. Lueken, R. Dronskowski, *Inorg. Chem.* 44 (2005) 3001.
- [20] X. Liu, M.A. Wankeu, H. Lueken, R. Dronskowski, *Z. Naturforsch.* 60b (2005) 593.
- [21] O. Reckeweg, F.J. DiSalvo, *Z. Anorg. Allg. Chem.* 629 (2003) 177.
- [22] R. Srinivasan, M. Ströbele, H.-J. Meyer, *Inorg. Chem.* 42 (2003) 3406.
- [23] W. Liao, C. Hu, R.K. Kremer, R. Dronskowski, *Inorg. Chem.* 43 (2004) 5884.
- [24] M.G. Barker, A. Harper, P. Hubberstey, *J. Chem. Res. (S)* 432 (1978).
- [25] W. Schnick, H. Huppertz, *Z. Anorg. Allg. Chem.* 621 (1995) 1703.
- [26] M. Becker, M. Jansen, *Z. Naturforsch.* 54b (1999) 1375.
- [27] X. Liu, P. Kroll, R. Dronskowski, *Z. Anorg. Allg. Chem.* 627 (2001) 1682.
- [28] X. Liu, R. Dronskowski, *Z. Kristallogr. NCS* 217 (2002) 118.
- [29] WinXPOW, Version 1.06, STOE & CIE GmbH, 1999.
- [30] J. Rodriguez-Carvajal, *Physica B* 192 (1993) 55.
- [31] This was one of the last neutron data sets collected with the most powerful and reliable German neutron research reactor which was shut down on May 2, 2006, after more than four decades of continuous use and constant modernization, at its peak neutron production as a consequence of the preceding political decision by the federal government.
- [32] R.D. Shannon, *Acta Crystallogr. A* 32 (1976) 751.
- [33] N.E. Brese, M. O'Keeffe, *Acta Crystallogr. B* 47 (1991) 192.
- [34] I.D. Brown, *J. Appl. Cryst.* 29 (1996) 479 (including December 2005 update).