Phase Transition of a Dicyanamide with Rutile-like Structure: Syntheses and Crystal Structures of α- and β-$Cd[N(CN)_2]_2$

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Abstract. Cadmium dicyanamide $Cd[N(CN)_2]_2$ was synthesized through aqueous ion exchange at room temperature. A reversible phase transition was detected by in situ X-ray powder diffractometry above 55 °C. The crystal structures of both phases were determined by X-ray powder diffraction (β-$Cd[N(CN)_2]_2$: T = 22 °C, a = 621.60(3), b = 748.76(4), c = 770.21(5) pm, β = 91.784(3)°, $P2_1/n$ (no. 14), Z = 2, wR_p = 0.063, R_p = 0.050, R_F = 0.059; α-$Cd[N(CN)_2]_2$: T = 150 °C, a = 624.62(5), b = 752.92(6), c = 768.30(7) pm, *Pnnm* (no. 58), Z = 2, wR_p = 0.083, R_p = 0.064, R_F = 0.087). Both polymorphs consist of Cd^{2+} and bent planar $[N(CN)_2]^-$ ions. α-$Cd[N(CN)_2]_2$ crystallizes analogously to rutile and is isotypic with $M^{II}[N(CN)_2]_2$ (M = Mg, Cr, Mn, Co, Ni, Cu). The monoclinic low-temperature polymorph β-$Cd[N(CN)_2]_2$ is closely related to that of the orthorhombic high-temperature polymorph α-$Cd[N(CN)_2]_2$ by a translationengleiche transition of index 2.

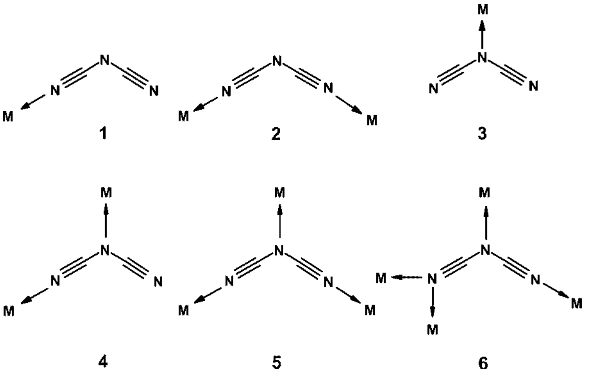
Keywords: Cadmium; Dicyanamide; Phase transition; Rutile structure type

Phasenumwandlung eines Dicyanamides mit Rutil-artiger Struktur: Synthese und Kristallstrukturen von α- und β-$Cd[N(CN)_2]_2$

Inhaltsübersicht. Cadmiumdicyanamid $Cd[N(CN)_2]_2$ wurde durch wässerigen Ionenaustausch bei Raumtemperatur erhalten. Eine reversible Phasenumwandlung wurde mittels *in-situ*-Röntgen-Pulverdiffraktometrie oberhalb von 55 °C nachgewiesen. Die Kristallstrukturen beider Phasen wurden mittels Pulver-Röntgenbeugung bestimmt (β-$Cd[N(CN)_2]_2$: T = 22 °C, a = 621,60(3), b = 748,76(4), c = 770,21(5) pm, β = 91,784(3)°, $P2_1/n$ (Nr. 14), Z = 2, wR_p = 0,063, R_p = 0,050, R_F = 0,059; α-$Cd[N(CN)_2]_2$: T = 150 °C, a = 624,62(5), b = 752,92(6), c = 768,30(7) pm, *Pnnm* (Nr. 58), Z = 2, wR_p = 0,083, R_p = 0,064, R_F = 0,087). Beide Polymorphe enthalten Cd^{2+} und gewinkelte $[N(CN)_2]^-$-Ionen. α-$Cd[N(CN)_2]_2$ kristallisiert analog Rutil und ist isotyp mit $M^{II}[N(CN)_2]_2$ (M = Mg, Cr, Mn, Co, Ni bzw. Cu). Die orthorhombische Hochtemperaturform α-$Cd[N(CN)_2]_2$ leitet sich strukturell von der monoklinen Tieftemperaturform β-$Cd[N(CN)_2]_2$ durch einen translationengleichen Übergang vom Index 2 ab.

Introduction

In the last few years the coordination chemistry of the bent dicyanamide $[N(CN)_2]^-$ ion has been studied intensively [1−3]. Many complexes with the common formula $\{M^{II}[N(CN)_2]_2(solvent)_x\}$ have been characterized and classified by their coordination modes (scheme 1). Coordination through both the terminal N atoms (modes 1 and 2) as well as the bridging N atom (mode 3) is possible. Additionally, both types of N atoms can coordinate the metal ions simultaneously (modes 4−6).



Scheme 1

For M = Cd only a few coordination compounds were synthesized as yet, i. e. $\{Cd[N(CN)_2]_2(phen)\}$ with phen = phenanthroline, $\{Cd[N(CN)_2]_2(2,2'\text{-bipy})\}$ with bipy = bipyridine) [4], $\{Cd[N(CN)_2]_2(HL)_2 \cdot 2\ H_2O\}$ with HL =

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4-aminobenzoic acid) [5], $\{Cd(dadpm)[N(CN)_2]_2\}_n$ with dadpm = 4,4′-diaminodiphenylmethane, and $\{Cd(dadpm)_2[N(CN)_2]X\}_n$ with X = Cl, Br [6].

Besides solvent containing complexes, the chemistry of solvent-free ternary dicyanamides was studied as well: The salts $M^{II}[N(CN)_2]_2$ (M = Mg, Cr, Mn, Co, Ni, Cu) were found to crystallize in a rutile-analogous structure type [7−10]. The structure of $M^{II}[N(CN)_2]_2$ (M = Ba, Pb) [10−12] derives from the cotunnite structure type ($PbCl_2$), whereas $M^{II}[N(CN)_2]_2$ (M = Ca, Sr) form a new structure type [10].

Surprisingly, during the detailed investigations of the divalent dicyanamides a phase transition only was observed for $Zn[N(CN)_2]_2$ [13,14]: Orthorhombic β-$Zn[N(CN)_2]_2$ (space group: *Pnma*) reversibly transforms into the high-temperature polymorph α-$Zn[N(CN)_2]_2$ (space group: *Cmcm*) at about 215 K. Contrarily, none of the intensively studied dicyanamides $M^{II}[N(CN)_2]_2$ (M = Mg, Cr, Mn, Co, Ni, Cu), which crystallize analogously to rutile, seems to show any phase transition. *Köhler* [15], *Jensen* [14], and *Miller* [2] et al. reported about α- and β-$Co[N(CN)_2]_2$, however these two compounds have been synthesized by quite different syntheses, and they do not exhibit a reversible transition induced by temperature or pressure.

Herein we report about the crystal structures of α- and β-$Cd[N(CN)_2]_2$ and their temperature-dependent phase transition.

Experimental

Syntheses

β-$Cd[N(CN)_2]_2$ was synthesized by aqueous ion exchange: A column with an ion exchange resin (Merck, Ionenaustauscher I, Art. 4765) was completely filled with a solution of 3 $CdSO_4 \cdot 8\ H_2O$ (Merck, puriss.). An excess of the sulfate was removed by washing with water. Subsequently, a solution of $Na[N(CN)_2]$ (Fluka, ≥ 96 %) was poured onto the column and the eluate was collected and dried in different experiments at room temperature and at 10 °C leading to a colorless microcrystalline product of phase pure β-$Cd[N(CN)_2]_2$.

The formation of α-$Cd[N(CN)_2]_2$ only has been observed in situ during heating β-$Cd[N(CN)_2]_2$ above 55 °C utilizing a STOE Stadi P powder diffractometer equipped with a computer controlled STOE furnace.

X-Ray Structure Determination.

It was impossible to isolate single crystals suitable for single-crystal X-ray diffraction. Because of the insufficient quality of the obtained crystals X-ray powder diffraction investigations were performed. A sample of β-$Cd[N(CN)_2]_2$ was enclosed in a glass capillary with 0.3 mm diameter and investigated at room temperature in Debye-Scherrer geometry on a STOE Stadi P powder diffractometer with Ge(111)-monochromatized Mo-Kα$_1$ radiation.

The powder pattern was indexed with a monoclinic unit cell. The ab-initio structure determination of β-$Cd[N(CN)_2]_2$ was possible using the program EXTRA [16] for extraction of the integrated intensities and SIRPOW [17] for direct methods. The results of the subsequent Rietveld refinement performed with the program GSAS [18] are given in Figure 1. Details of the crystallographic data are listed in Table 1, the refined atomic coordinates are given in Table 2.

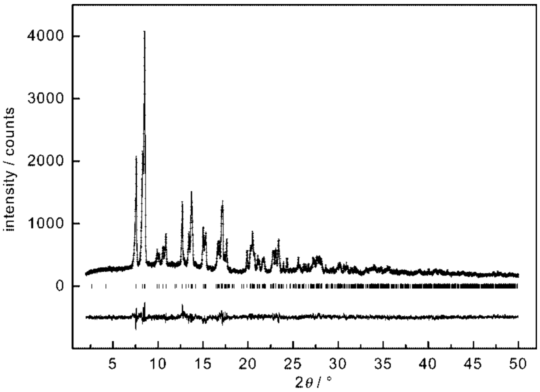


Figure 1 Observed (crosses) and calculated (line) X-ray powder diffraction patterns as well as difference profile of the Rietveld refinement of β-$Cd[N(CN)_2]_2$. The powder pattern was obtained with a STOE Stadi P powder diffractometer (λ = 70.93 pm) at 22 °C.

Table 1 Crystallographic Data for α-$Cd[N(CN)_2]_2$ and β-$Cd[N(CN)_2]_2$.

	β-$Cd[N(CN)_2]_2$	α-$Cd[N(CN)_2]_2$
M_r / g mol^{-1}	244.46	
crystal system	monoclinic	orthorhombic
space group	$P2_1/n$ (no. 14)	*Pnnm* (no. 58)
radiation λ / pm	Mo-Kα$_1$ (70.93)	
temperature / °C	22	150
lattice parameters:		
a / pm	621.60(3)	624.62(5)
b / pm	748.76(4)	752.92(6)
c / pm	770.21(5)	768.30(7)
β / °	91.784(3)	90
V / 10^6 pm^3	358.30(3)	361.32(6)
Z	2	2
ρ_c / g cm^{-3}	2.266	2.247
profile range	$2 \le 2\theta \le 50$	$6 \le 2\theta \le 35$
no. of data points	4800	2900
no. of reflections	633	131
positional parameters	15	8
profile parameters	6	4
reduced χ^2	0.794	1.920
R values		
wR_p	0.063	0.083
R_p	0.050	0.064
R_F	0.059	0.087

Table 2 Atomic coordinates and displacement factors (in pm^2) for α-$Cd[N(CN)_2]_2$ and β-$Cd[N(CN)_2]_2$.

atom	Wyckoff position	x	y	z	U_{iso}[a]
Cd (β)	2*a*	0	0	0	227(3)
Cd (α)	2*a*	0	0	0	320(10)
C1 (β)	4*e*	0.239(3)	0.365(2)	0.128(2)	200(60)
C2 (β)	4*e*	0.226(2)	0.357(2)	−0.169(2)	270(60)
C (α)	8*h*	0.268(4)	0.362(2)	0.138(2)	270(70)
N1 (β)	4*e*	0.147(2)	0.302(1)	−0.017(2)	510(90)
N1 (α)	4*g*	0.190(3)	0.300(3)	0	270(70)
N2 (β)	4*e*	0.282(2)	0.412(1)	0.275(2)	260(50)
N3 (β)	4*e*	0.291(2)	0.392(2)	−0.291(2)	350(50)
N2 (α)	8*h*	0.287(2)	0.390(2)	0.288(1)	250(50)

[a] U_{iso} is defined as $\exp(-8\pi^2 U_{iso} \sin^2\theta / \lambda^2)$.

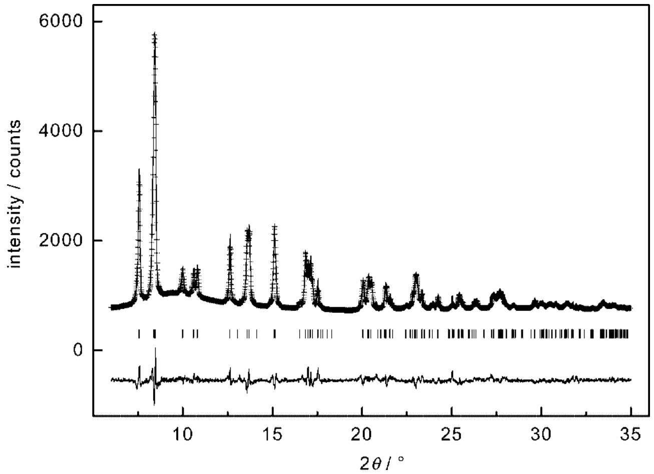


Figure 2 Observed (crosses) and calculated (line) X-ray powder diffraction patterns as well as difference profile of the Rietveld refinement of α-Cd[N(CN)$_2$]$_2$. The powder pattern was obtained with a STOE Stadi P powder diffractometer (λ = 70.93 pm) at 150 °C.

The diffraction data of α-Cd[N(CN)$_2$]$_2$ were collected at 150 °C with a STOE Stadi P powder diffractometer with monochromatized Mo-Kα_1 radiation using a graphite heating equipment. The obtained diffraction pattern of the high-temperature phase is very similar to that of M^{II}[N(CN)$_2$]$_2$ (M = Mg, Cr, Mn, Co, Ni, Cu), and it could be indexed with similar lattice constants and in the same space group (*Pnnm*) as these dicyanamides. Therefore, all these compounds were assumed to be isotypic. The Rietveld refinement was successful using the atomic coordinates of Mg[N(CN)$_2$]$_2$ as starting values (Figure 2). Information about the crystallographic details and the atomic coordinates are given in Tables 1 and 2.

Further details of the crystal structure investigations reported in this paper may be obtained from the Fachinformationszentrum Karlsruhe, D−76344 Eggenstein-Leopoldshafen, Germany, by quoting the depository numbers CSD−413334 (α-Cd[N(CN)$_2$]$_2$) and CSD−413333 (β-Cd[N(CN)$_2$]$_2$).

The comparison of the structural data of both phases exhibits their structural relation: The cell volumes of monoclinic β-Cd[N(CN)$_2$]$_2$ and orthorhombic α-Cd[N(CN)$_2$]$_2$ are quite similar (ca. 360 · 10^6 pm^3). Additionally, the lattice parameters *a*, *b*, and *c* resemble each other, the angle *β* (β-Cd[N(CN)$_2$]$_2$) differs only slightly from 90°. This situation is comparable to that found for α- and β-Na[N(CN)$_2$] and the phase transition between these two polymorphs [19].

Results and Discussion

The crystal structures of both α- and β-Cd[N(CN)$_2$]$_2$ consist of Cd^{2+} and bent [N(CN)$_2$]$^-$ ions. The dicyanamide anions are nearly planar (point symmetry: C$_1$) in β-Cd[N(CN)$_2$]$_2$ and exactly planar in α-Cd[N(CN)$_2$]$_2$ (point symmetry: C$_s$). In Figure 4 the changes of the atomic parameters during the phase transition are given.

The distances and angles are similar to that of other dicyanamides (Table 3). The distances C-N from the bridging N atoms are longer (121 − 134 pm) than those to the terminal N atoms (107 −118 pm). The N-C-N angles are almost linear (159 − 176°), whereas the C-N-C angles are 115 − 118°. The distances from the terminal N-atoms to the Cd^{2+} ions are 226 − 245 pm (β-Cd[N(CN)$_2$]$_2$) and 226 − 255 pm (α-Cd[N(CN)$_2$]$_2$). These values are comparable to the Cd-N distances found in Cd(CN)$_2$ (220 pm) [20], CdCN$_2$ (238 pm) [21] and in {Cd(dadpm)[N(CN)$_2$]$_2$}$_n$ (232−238 pm) [6].

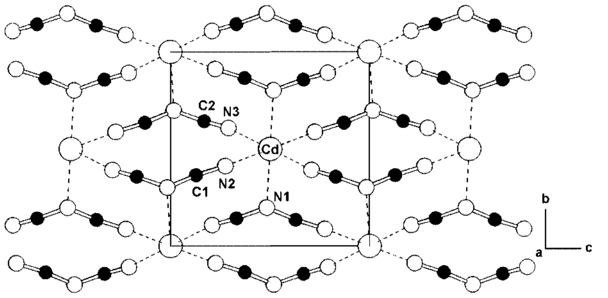


Figure 3 Crystal structure of β-Cd[N(CN)$_2$]$_2$ (view along [100]).

Crystal structure of β-Cd[N(CN)$_2$]$_2$

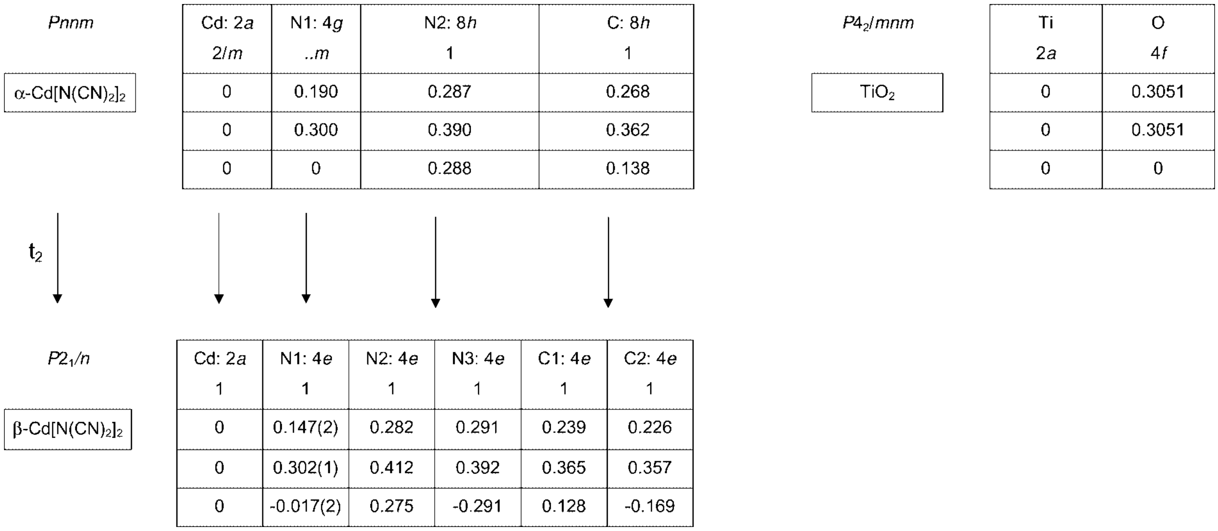
The crystal structure of β-Cd[N(CN)$_2$]$_2$ can be derived from the rutile structure type (Figure 4). It crystallizes in a subgroup (*P*2$_1$/*n*) of the space group of α-Cd[N(CN)$_2$]$_2$ (*Pnnm*). The phase transition between the two polymorphs can be described as a translationengleiche transition of index 2 (t2). During heating the local point symmetry of the dicyanamide ions changes from C$_1$ to C$_s$ and the angle *β* of the monoclinic crystal system changes to 90°, leading to an orthorhombic structure (Figures 4 and 5). In β-Cd[N(CN)$_2$]$_2$ the Cd^{2+} ions are coordinated by both terminal N atoms N2 and N3 as well as bridging N atom N1 (Scheme 1, mode 5).

Crystal structure of α-Cd[N(CN)$_2$]$_2$

α-Cd[N(CN)$_2$]$_2$ crystallizes isotypically with the dicyanamides of divalent metals M^{II}[N(CN)$_2$]$_2$ (M = Mg, Cr, Mn, Co, Ni, Cu). By replacing the dicyanamide ions by their centres of gravity these crystal structures can be derived directly from the rutile structure type (space group *P*4$_2$/*mnm*) by a translationengleiche transition of index 2. With respect to the ionic radii of the metal ions M^{2+} (CN: 6) (Mg^{2+}: 86, Cr^{2+}: 87, Mn^{2+}: 81, Co^{2+}: 79, Ni^{2+}: 83, Cu^{2+}: 87 pm) it is unexpected that the cadmium salt in spite of the large ion radius of Cd^{2+} (109 pm) forms the same structure as the dicyanamides mentioned above. In α-Cd[N(CN)$_2$]$_2$ the Cd^{2+} ions are octahedrally coordinated by six N atoms, the dicyanamide ions [N(CN)$_2$]$^-$ are bound to three Cd^{2+} ions. Analogously to β-Cd[N(CN)$_2$]$_2$ the anions exhibit the same coordination mode 5 (see Scheme 1).

Thermal Behavior

Thermoanalytical measurements were performed with a DSC 25 (Mettler) as well as with a DSC 141 (Setaram) in



α-Cd[N(CN)$_2$]$_2$	Cd: 2*a* 2/*m*	N1: 4*g* ..*m*	N2: 8*h* 1	C: 8*h* 1
	0	0.190	0.287	0.268
	0	0.300	0.390	0.362
	0	0	0.288	0.138

TiO$_2$	Ti 2*a*	O 4*f*
	0	0.3051
	0	0.3051
	0	0

β-Cd[N(CN)$_2$]$_2$	Cd: 2*a* 1	N1: 4*e* 1	N2: 4*e* 1	N3: 4*e* 1	C1: 4*e* 1	C2: 4*e* 1
	0	0.147(2)	0.282	0.291	0.239	0.226
	0	0.302(1)	0.412	0.392	0.365	0.357
	0	-0.017(2)	0.275	-0.291	0.128	-0.169

Figure 4 Group – sub-group relation between α- and β-Cd[N(CN)$_2$]$_2$ (left) in comparison to the atomic coordinates of rutile (right). The indices of the translationengleiche (t) transitions as well as the unit cell transformations are given.

Table 3 Bond distances (in pm) and angles (in °) in α-Cd[N(CN)$_2$]$_2$ and β-Cd[N(CN)$_2$]$_2$.

	β-Cd[N(CN)$_2$]$_2$ (22 °C)	α-Cd[N(CN)$_2$]$_2$ (150 °C)
Cd-N1	244.6(1) (2x)	254.8(2) (2x)
Cd-N2	226.5(1) (2x)	226.3(1) (4x)
Cd-N3	225.6(1) (2x)	–
C-N1	–	125.5(2)
C-N2	–	117.7(2)
C1-N1	132.7(2)	–
C1-N2	120.7(2)	–
C2-N1	134.0(2)	–
C2-N3	106.6(2)	–
N1-C-N2	–	158.8(3)
N1-C1-N2	166.1(2)	–
N1-C2-N3	176.2(2)	–
C-N1-C	–	115.0(3)
C1-N1-C2	117.7(2)	–

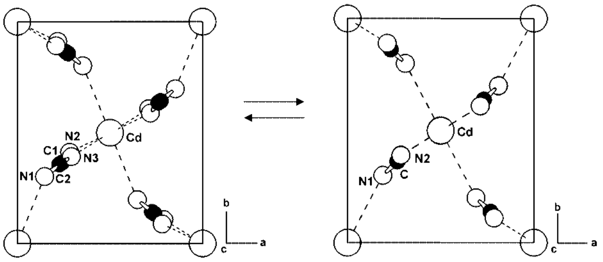


Figure 5 Crystal structure of β-Cd[N(CN)$_2$]$_2$ (view along [001], left) and of α-Cd[N(CN)$_2$]$_2$) (view along [001], right).

order to analyze the phase transition of β- into α-Cd[N(CN)$_2$]$_2$. Samples of β-Cd[N(CN)$_2$]$_2$ were heated from room temperature to 500 °C using closed alumina crucibles (heating rate: 10 °C · min^{-1}). Neither during heating nor during subsequent cooling any remarkable thermal effect was observed. According to the observed reversible character of the displacive phase transition between α-Cd[N(CN)$_2$]$_2$ and β-Cd[N(CN)$_2$]$_2$, the heat of reaction seems to be very small.

After heating the compounds to 500 °C and subsequent cooling to room temperature the products were characterized by IR spectroscopy. The spectra neither show the typical signals of the dicyanamide ion [N(CN)$_2$]$^-$ nor that of the isolated tricyanomelaminate ions [C$_6$N$_9$]$^{3-}$. The spectra show broad signals belonging to C≡N and C=N bonds which can indicate a further polymerization of the dicyanamide ions to extended C-N networks of unknown structure. Similar spectra were observed for the thermolysis products of the divalent dicyanamides M[N(CN)$_2$]$_2$ (M = Mg, Ca, Sr, Ba, Pb, Co, Ni) [10, 11, 22]. Temperature-dependent X-ray measurements were performed on a STOE Stadi P powder diffractometer (Mo-Kα_1 radiation) with a computer controlled STOE furnace. By heating above 310 °C a sample of Cd[N(CN)$_2$]$_2$ became X-ray amorphous.

Acknowledgments. Financial support by the Fonds der Chemischen Industrie, the Bundesministerium für Bildung und Forschung, and the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

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