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Synthesis, Structure Determination, and Quantum-Chemical Characterization of an Alternate HgNCN Polymorph†

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A novel, possibly metastable form of HgNCN, designated HgNCN(II), is accessible under soft-chemical reaction conditions, and its existence has been established from combined X-ray/neutron Rietveld refinements ($P2_1/a$, $a = 6.8521(4)$ Å, $b = 6.9797(4)$ Å, $c = 5.5516(4)$ Å, $\beta = 113.212(4)°$), vibrational spectroscopy investigations, and plane-wave DFT calculations utilizing pseudopotentials. In contrast to the known mercury carbodiimide HgNCN(I) with two practically identical N–C double bonds of 1.22 Å, the true cyanamide HgNCN(II) is characterized by a short ("triple") N–C bond (1.12 Å) and a long ("single") C–N bond (1.35 Å); two Hg atoms coordinate the asymmetrically shaped NCN^{2-} unit only on the side of the C–N "single" bond. Mercury carbodiimide HgNCN(I) and mercury cyanamide HgNCN(II) are thermochemically separated from each other by such a high energy barrier that thermal decomposition prevents structural interconversion. The structure–chemical relationship of the two HgNCN phases is discussed in terms of bond-stretch and linkage isomerism.

1. Introduction

Three decades ago, the novel notion of bond-stretch isomerism was introduced by Stohrer and Hoffmann as a theoretical possibility in which molecules differ only in the length of one or more bonds.[1] At first sight, this concept seems to be counterintuitive to our usual understanding of a chemical bond; while a "normal" chemical bond involving two connected atoms is characterized by a single minimum of the potential energy surface, the bond-stretch isomerism idea relies on (at least) two distinct energy minima separated by a significant energy barrier.[2] Early on, theory showed that bond-stretch isomerism may be expected to result from an accidental crossing of energy levels; the definition was later restricted to isomers of the same spin state.[3]

The first presumed experimental evidence of bond-stretch isomerism in blue and green isomers of a crystalline organometallic molybdenum oxychloride[4] was later identified as experimental artifacts due to misinterpreted X-ray diffraction studies. Indeed, Parkin's careful 1992 analysis of all experimental findings questioned the entire existence of bond-stretch isomerism.[2] One of the last experimental cases in 1997 arose from bond-length differentiations within a metal−metal bonded trimetallic cobalt complex[5] which, however, could not be reproduced by gradient-corrected density-functional calculations.[6] Consequently, later crystallographic findings concerning small structural changes in these tricobalt complexes were interpreted as being a function of the different natures of cocrystallizing ligands.[7,8] According to the recent and most comprehensive review by Rohmer and Bénard,[9] the situation is controversial because unquestionable, clear-cut experimental evidence for bond-stretch isomerism remains a very rare event in the literature.

The notion of linkage isomerism, on the other side, is well established in coordination chemistry[10] and actually goes back to the end of the 19th century. According to textbook knowledge, linkage isomerism may arise whenever ambi-

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† Dedicated to Professor Roald Hoffmann on the occasion of his 65th birthday.

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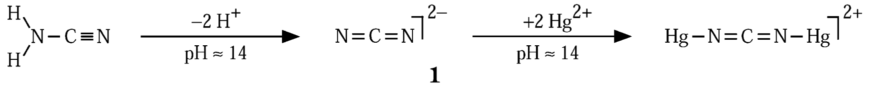
Scheme 1



dentate ligands, that is, ligands with at least two inequivalent donor atoms, are involved in chemical bonding of the same denticity to a metal atom but through different combinations of the donor atoms. The classic salts $[CoONO(NH_3)_5]Cl_2$ (red) and $[Co(NO_2)(NH_3)_5]Cl_2$ (yellow) by Jørgensen typically serve as prominent (lab course) examples[11] for this phenomenon although there are also a number of thiocyanato (M−SCN) and isothiocyanato (M−NCS) complexes which can be classified as such.

Coming back to bond-stretch isomers, a moment's reflection reveals that the chances for synthesizing these will probably increase upon combining two double-well bonds (potentials) within a single molecular entity ABC. By doing so, the energy loss on one molecular side (atoms A and B on the "left" part of the molecule locked in the high-lying energy minimum) could be balanced, at least partially, by the energy gain on the other side (atoms B and C on the "right" part locked in the low-lying energy minimum). Among those molecular entities with built-in multiple energy minima (single, double, and triple bonds using chemical terminology), cyanamides are especially good candidates for such a synthetic strategy.

2. Solid-State Cyanamide Chemistry

Synthetic and crystallographic studies on solid-state cyanamide chemistry have enormously progressed over the past decade. Besides the classic structural investigation of Vannerberg on calcium cyanamide,[12] the recent characterizations within a constantly growing list of alkaline (Li, Na)[13−15] or alkaline-earth metal (Mg, Ca, Sr, Ba) cyanamides,[16,17] main-group element cyanamides (In, Si, Pb),[18−21] and also transition-metal (Ag) cyanamides[22,23] are especially worth mentioning. The most recent example of a transition-metal cyanamide is given by mercury cyanamide, HgNCN, synthesized and characterized by the Jansen group[24] and also, independently, within our own laboratory.[25]

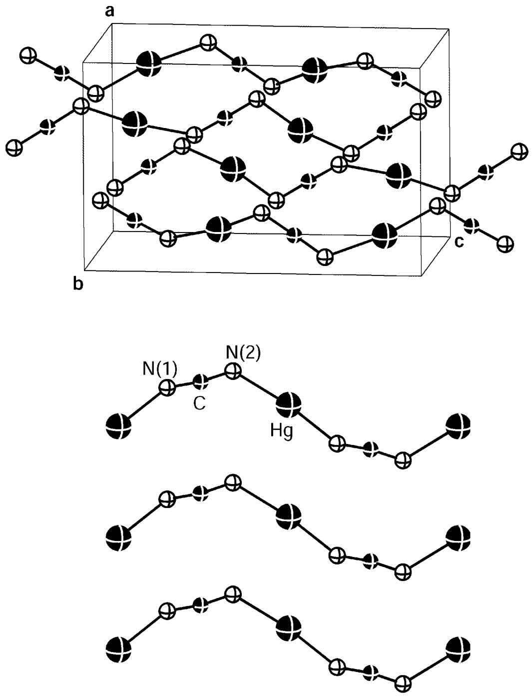


Figure 1. A look (top) into the crystal structure of HgNCN(I); schematic linkage of NCN^{2-} units and mercury atoms (bottom).

This particular mercury cyanamide is made under rather drastic conditions. The reaction starts from mercury chloride and molecular cyanamide (H_2NCN) in strongly basic (NaOH) aqueous solution (starting pH about 14). Here, the two protons of the cyanamide molecule are immediately stripped off such that the "naked" cyanamide anion may be coordinated by mercury cations (Scheme 1), eventually forming a white precipitate that is dried at 120 °C in vacuo.

The crystal structure of this mercury cyanamide, called HgNCN(I) from now on, is characterized by an almost linear, fairly symmetrical NCN^{2-} unit that is coordinated at both ends by Hg^{2+} cations (see Figure 1). More precisely, the two communicated N−C bond lengths are 1.228(9) and 1.216(8) Å within NCN^{2-}, and the N−C−N angle is reported[24] to be 172.4(7)°. Thus, the two N−C (double) bonds are identical within experimental resolution, and the small deviation from linearity is responsible for the slight symmetry reduction from $D_{\infty h}$ to C_{2v}. The shortest Hg−N bonding contacts on the "left" and "right" side of the cyanamide anion are also very similar in length (2.056(5) and 2.074(6) Å), and the N−Hg−N angle, 170(3)°, is also close to linearity.

While there is no doubt about the correctness of this particular structure determination of Jansen et al., the high symmetry of the NCN^{2-} unit in HgNCN(I) is difficult to understand. We have recently shown[21] that the absolute hardness[26] of the coordinating metal cation plays a decisive role for the shape of the cyanamide anion within a particular crystal structure. If NCN^{2-} is coordinated by chemically hard

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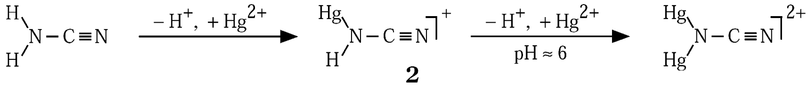
Scheme 2



cations such as alkaline or alkaline-earth metals (absolute hardnesses η between ca. 16−35 eV), one finds a symmetrical NCN^{2-} unit with two N−C double bonds. A chemically softer cation such as Pb^{2+} ($\eta = 8.46$ eV) will bond more covalently to one end of the NCN^{2-} unit and thereby force it into a less symmetrical shape, being close to one single N−C (1.30 Å) and one triple C−N bond (1.16 Å).[21] The crystal structure of Ag_2NCN by Jansen et al.[23,25] is another nice example for this rule of thumb, the differing bond lengths being 1.19 and 1.27 Å because of the very soft silver cation ($\eta = 6.7$ eV). Why, then, do we find a symmetrical NCN^{2-} unit within HgNCN(I), keeping in mind the low hardness of Hg^{2+} ($\eta = 7.7$ eV), lying between those of Pb^{2+} and Ag^{+}?

3. Synthesis and Characterization of HgNCN(II)

To synthesize an alternative, less symmetrical form of HgNCN, we have therefore used considerably softer acid−base conditions. The room-temperature synthesis starts from solutions of mercury chloride and molecular cyanamide, too, but small amounts of aqueous ammonia (as compared to NaOH) are slowly added in order to establish a pH value around 6. The underlying idea, namely a stepwise replacement of the two protons of H_2NCN by mercury atoms, is schematically outlined in Scheme 2.

As a matter of fact, there results a white precipitate in practically quantitative yield which we will denote HgNCN(II) from now on. Both HgNCN(I) and HgNCN(II) give identical chemical compositions on the basis of standard CHN analyses using a Perkin-Elmer 240B elemental analyzer; the calculated contents are 11.65 (N) and 4.99 (C), while the experimental ones are 11.52(5)/11.64(5) and 4.91(5)/4.92(5) for HgNCN(I) and HgNCN(II), respectively. H and Cl contaminations are not present.

3.1 Diffractional Studies. Because attempts to grow single crystals of HgNCN(II) were unsuccessful, the structure determination had to be based on powder methods, just like for HgNCN(I). The X-ray diffraction data were recorded at room temperature using a calibrated STOE STADI-P powder diffractometer with strictly monochromatized Cu $K\alpha_1$ radiation and a flat sample holder ($15 \leq 2\theta \leq 100°$, 0.01° step width). In contrast to Jansen's orthorhombic HgNCN(I), the strongly different X-ray powder diagram of HgNCN(II) could be indexed[27] using a monoclinic unit cell. The structure was solved using direct methods[28] and refined by a Rietveld analysis.[29] At the very beginning, two competing structural models (one in space group *Cm*, the other one in $P2_1/a$) gave practically identical results on the basis of the X-ray data although electronic structure calculations strongly favored the primitive unit cell in which the mercury atoms acquire an almost linear coordination by N atoms.

Table 1. Crystallographic Data for HgNCN(II)

chemical formula: HgNCN	formula weight: 240.61 g/mol
$a = 6.8521(4)$ Å	space group: $P2_1/a$ (No. 14)
$b = 6.9797(4)$ Å	λ(X-ray) = 1.54056 Å
$c = 5.5516(4)$ Å	$\rho_{calcd} = 6.55$ g/cm^3
$\beta = 113.212(4)°$	μ(X-ray) = 110.22 mm^{-1}
$V = 244.02$ Å^3	R_p(X-ray) = 0.084
$Z = 4$	R_{Bragg}(X-ray) = 0.027
$T = 20(1)$ °C	

Table 2. Positional Parameters (all atoms on Wyckoff position 4e) and Isotropic Displacement Parameters for HgNCN(II) with Standard Deviations in Parentheses

atom	*x*	*y*	*z*	B_{iso} (Å^2)
Hg	0.7578(10)	0.1338(9)	0.9949(11)	1.11(5)
N(1)	0.2180(10)	0.1267(28)	0.1846(13)	1.7(2)
N(2)	0.2996(14)	0.1220(27)	0.6536(14)	1.6(2)
C	0.2313(32)	0.1197(38)	0.4342(24)	2.8(3)

This choice was then fully corroborated by subsequent time-of-flight (TOF) neutron data showing that the whole structure (in contrast to the Hg substructure) does not possess a *C*-centering but must be described with a primitive unit cell (and space group $P2_1/a$). The TOF neutron data were recorded at room temperature at the POLARIS diffractometer at ISIS, Rutherford Laboratories, U.K. For the refinement, we used the data of bank A ($0.5 \leq d \leq 8.3$ Å, 5373 data points) and bank E ($0.2 \leq d \leq 4.0$ Å, 5523 data points) together with the X-ray data.

The experimentally determined structure is thus based on a combined X-ray and neutron data Rietveld refinement which was performed against three data sets (one X-ray powder data set with 278 reflections and two TOF neutron bank sets with 534/665 reflections; weighting scheme 0.4 ÷ 0.3 ÷ 0.3) using a pseudo-Voigt X-ray and a tabulated TOF neutron profile.[30] Two phases were refined, namely HgNCN(II) (main phase, 94.8%) and HgNCN(I) (5.2%). The residual values concerning the data from X-rays/neutron bank A/neutron bank E arrive at 0.084/0.050/0.045 (R_p), 0.107/0.071/0.060 (R_{wp}), and 0.027/0.049/0.045 ($R_{Bragg}(F)$ of HgNCN(II)). The final structural parameters are given in Tables 1 and 2 while an overview of the Rietveld refinements is shown in Figure 2. All atomic sites are fully occupied; the bond lengths and angles (see discussion later) were calculated by including all available statistical uncertainties as implemented within the *ORFFE* computer program.[31]

HgNCN(II) crystallizes with a layerlike structure along the monoclinic *a* direction (see Figure 3). In sharp contrast to HgNCN(I), the cyanamide group of HgNCN(II) exhibits two different N−C bond lengths, namely a long N(1)−C ("single") bond of 1.353(17) Å and a short C−N(2) ("triple")

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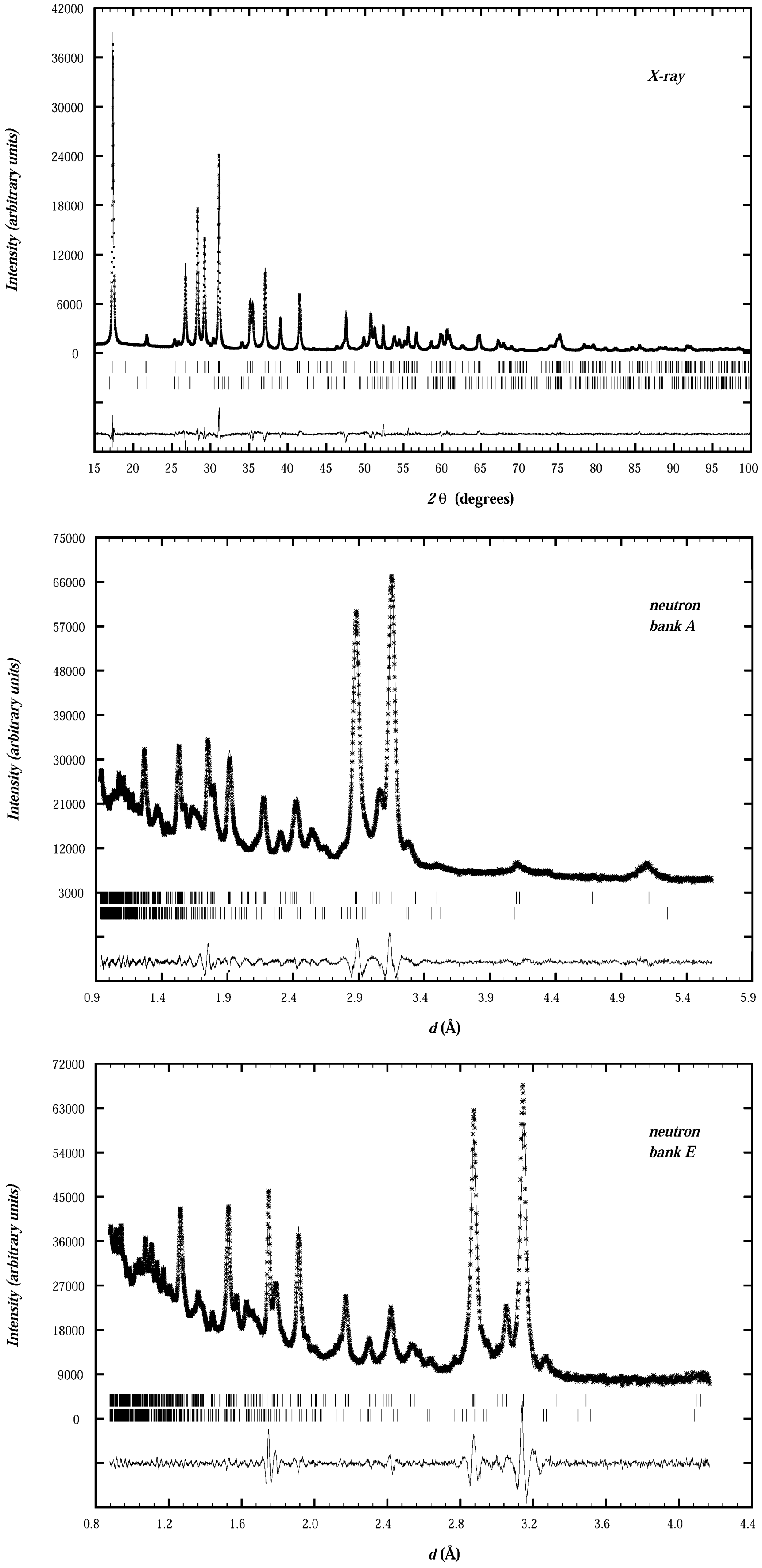

Figure 2. Rietveld refinements of the crystal structure of HgNCN(II) based on X-ray (top) and neutron intensities (middle and bottom); each part of the figure depicts (from top to bottom) measured and fitted diffraction patterns, the Bragg reflections of HgNCN(II) and HgNCN(I), and the difference between measured and calculated intensities.

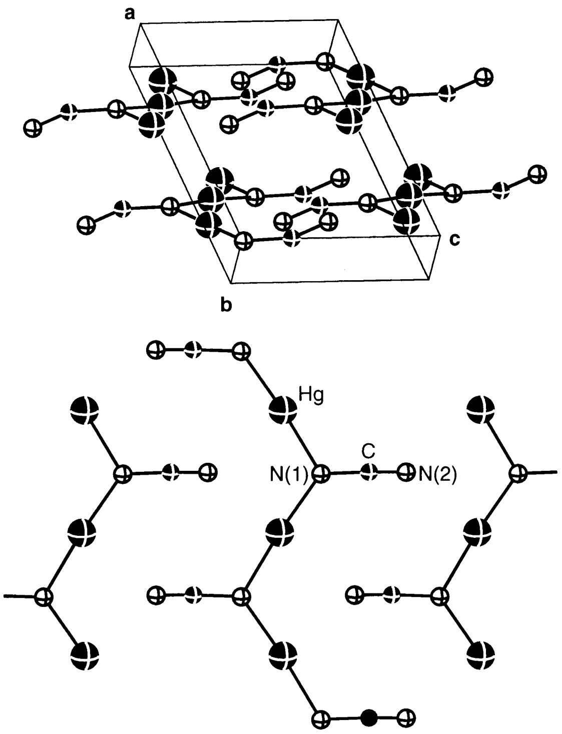

Figure 3. A look (top) into the crystal structure of HgNCN(II); schematic linkage of NCN^{2-} units and mercury atoms (bottom).

bond of 1.120(14) Å. This scenario results from the fact that only one end of the NCN^{2-} unit is covalently bonded to neighboring Hg atoms; the N−C bond lengths themselves are in excellent accordance with similar structural investigations of higher accuracy.[32]

While N(1) has two such Hg−N bonding interactions at 2.051(18) and 2.110(18) Å, the corresponding Hg−N interatomic distances of N(2) at the "loose" end of the NCN^{2-} unit lie at 2.646(16) and 2.785(16) Å, that is, in the nonbonding region. The N−C−N angle arrives at 160.7(2.1)° which is significantly more kinked than in HgNCN(I) and even more than in related compounds.[32] We note, however, that the central carbon atom shows a somewhat enlarged thermal displacement parameter such that the exact size of this N−C−N angle must be regarded with some caution: an N−C−N angle artificially set to linear during the Rietveld refinement is clearly unstable although the refinement does not worsen significantly, showing that even the high TOF resolution limit has been reached.

As expected, the marked preference of the mercury atom for linear two-coordination is nicely reflected by the N−Hg−N angle of 174.7(7)°. Including the four second-nearest Hg−N contacts (between 2.65(2) and 2.96(1) Å), the coordination motif of Hg is a strongly distorted octahedron.

3.2 Vibrational Spectroscopy and Energetics. The different geometries of the cyanamide groups within HgNCN(I) and HgNCN(II) find their expression in the vibrational spectra of the two modifications. The IR measurements were performed using a Fourier transform Avatar 360 E.S.P. spectrometer (Nicolet) with KBr disks, and the Raman spectra were recorded using a Bruker IFS 66v/S spectrophotometer (FRA 106/S, Nd:YAG laser, $\lambda = 1064$ nm, 75−80 mW) with 256 scans and samples run as powders in spinning capillary tubes. Both kinds of data are presented in Figure 4.

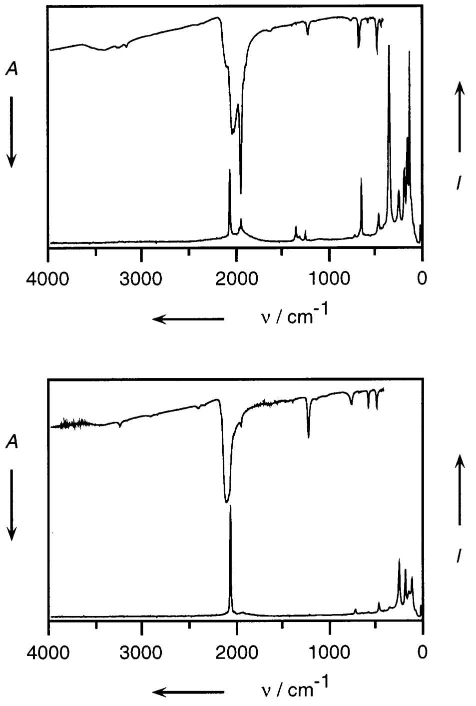

Figure 4. Infrared and Raman spectra of HgNCN(I) (top) and HgNCN(II) (bottom). In both graphs, the infrared absorptions (axes on the left) and the Raman intensities (axes on the right) are given in arbitrary units.

As has been reported before,[24] the symmetric stretching mode is already IR-observable for HgNCN(I) at 1219 cm^{-1} but stronger so for HgNCN(II), also at 1219 cm^{-1}, because of the lowered symmetry. The asymmetric stretching frequency is already split for HgNCN(I) (2031 and 1948 cm^{-1}), and the splitting is even larger in HgNCN(II) (2097 and 1949 cm^{-1}). We also find the deformation vibration of HgNCN(I) at 616 cm^{-1}.

The N−C bonds in the two differing polymorphs may also be numerically analyzed by the bond-valence concept.[33] Taking a bond distance of 1.22 Å as the most appropriate choice for a formal N−C double bond,[21] the bond orders in the NCN^{2-} unit of HgNCN(I) arrive at 1.96 and 2.02, summing up to 3.98; on the other side, the bond orders of the "triple" and "single" N−C bonds in HgNCN(II) then come to 2.62 and 1.40, summing up to 4.02. Thus, C−N bonding seems to be nicely adjusted in both anions. In addition, a primitive bond energy calculus suggests that the symmetrical HgNCN(I) might be the energetically stable modification because it contains two N−C double bonds (bond energy 616 kJ/mol) compared to one triple N−C (892 kJ/mol) and one single C−N bond (305 kJ/mol),[34] which results in a maximum 35 kJ/mol energy difference keeping

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(32) The differentiation of the two bond lengths compares very favorably with recent X-ray single-crystal studies on Co/Ni complexes with cyanamide as a neutral ligand. Here, the short N−C bond was found to be 1.12 Å while the longer one arrived at 1.33 Å; the N−C−N angle was 166°. For further information, see: Liu, X.; Kroll, P.; Dronskowski, R. *Z. Anorg. Allg. Chem.* **2001**, *627*, 1682.

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in mind that the notions of a single and a triple N−C bond are simplifying exaggerations. We mention, however, that this calculus does *not* hold for the energetic sequence of the isolated molecules H_2NCN (cyanamide) and HNCNH (carbodiimide) taking into account high-quality quantum chemical calculations[35] and experimental evidence.

In addition, the crystallographic density of HgNCN(I), 6.79 g/cm^3, is 3.5% higher than the one of HgNCN(II), 6.55 g/cm^3; usually, but not always, higher stability goes with better packing. Third, it has proven impossible for us to synthesize 100% pure HgNCN(II) because there is always a contamination with traces (about 5%) of HgNCN(I), also visible (and refinable) in the powder diffraction diagrams of supposedly pure HgNCN(II).

The question of the relative energetics of HgNCN(I) and HgNCN(II) could, in principle, be experimentally answered by an accurate differential thermal analysis or calorimetric measurement. Very unfortunately, both polymorphs decompose, prior to interconversion, around 230 °C, yielding metallic Hg and a white C/N-containing polymer of unknown structure and composition. Thus, the energy barrier between I and II is certainly larger than the thermal energy at that temperature. Nonetheless, it is possible to catalyze the conversion of HgNCN(II) into HgNCN(I) by keeping the solid inside a 1 M solution of NaOH for about 8 h at 60 °C. This finding also points to the direction of HgNCN(I) being the thermodynamically stable phase. We are presently preparing a set of calorimetric measurements necessary for a definite thermochemical assignment of the two polymorphs.

3.3 Quantum-Chemical Studies. To provide a more quantitative answer, electronic structure calculations of density-functional type were performed using the Vienna ab initio simulation package (VASP),[36,37] plane-wave basis sets, and ultrasoft pseudopotentials. The exchange-correlation energy was treated by the local density approximation (LDA) as parametrized by Perdew and Zunger[38] on the basis of results of Ceperley and Alder;[39] additionally, we used the generalized-gradient approximation (GGA) of Perdew and Wang.[40] The structures of both HgNCN(I) and HgNCN(II) were fully optimized using a cutoff of 400 eV for the expansion of the wave function into the plane wave basis set. The Brillouin zone integrations were performed using the scheme of Monkhorst and Pack.[41] A 2 × 4 × 4 mesh for the orthorhombic *Pbca* structure of HgNCN(I) resulted in 4 special *k* points. The monoclinic $P2_1/a$ structure of HgNCN(II) demanded 16 special *k* points from a total set of 4 × 4 × 4. The interatomic forces were allowed to relax to values below 0.02 eV/Å, stresses below 1 kbar. Even finer grids for the *k* point sampling and even larger plane wave basis sets confirmed the convergence of structural properties at this level of accuracy. The total energy differences were converged to values smaller than 0.5 kJ/mol HgNCN.

The geometries of HgNCN(I) and HgNCN(II) are satisfactorily reproduced using either the LDA or the GGA; the theoretical lattice parameters do not deviate from the experimental ones by more than about 0.3 Å (rms) using the LDA and about 0.4 Å using the GGA. Both structures are stable configurations, as expected. For HgNCN(I), the bond distances and angles of the NCN^{2-} unit and the coordinating Hg atoms are reproduced within 0.01 (LDA) or 0.02 Å (GGA) and 2°/3° (LDA/GGA). The structure of HgNCN(II) is more demanding, though. The short N−C ("triple") bond of 1.12 Å comes out longer (1.19/1.20 Å using the LDA/GGA), and the long N−C ("single") bond of 1.35 Å comes out shorter (1.27/1.28 Å), probably because of a large amount of electronic correlation. One of the two shortest Hg−N(1) bonds is very well described within a 0.01 Å error bar while the other one is underestimated by 0.04/0.07 Å (LDA/GGA). The experimental N(1)−C−N(2) angle, 161°, however, comes out almost linear (178°) for both LDA and GGA. As recently shown by us[21,42] the N−C−N bending force-field is extremely shallow and very hard to model computationally. Nonetheless, the calculations show that HgNCN(I) is more stable by about 7 kJ/mol than HgNCN(II) on the basis of either the LDA or the GGA, supporting the experimental and structural hints.

To gain more confidence into this admittedly small energetic difference and further test the utilized pseudopotentials, we have redone all of the described calculations by means of the projector-augmented-wave (PAW) method, an all-electron pseudopotential hybrid,[43] within VASP.[44] These significantly more sophisticated calculations confirm HgNCN(I) to be the stable polymorph by roughly twice the mentioned energy value, namely 13 kJ/mol. Also, the local geometries (interatomic distances, bond angles) remain almost unchanged. In addition, a pure all-electron plane-wave band-structure calculation without any pseudopotentials (LAPW)[45] based on the experimental geometries yields an even larger difference of 86 kJ/mol in favor of HgNCN(I).Thus, all solid-state DFT calculations point in the same direction, indicating that HgNCN(II) is a metastable phase.[46]

Indicating where theory needs to proceed, we can try to model one possible transient geometry of HgNCN (see Figure 5) by computational means, and this optimized structure (space group *C*2/*m*), characterized by a symmetrical linkage of the NCN^{2-} units to four neighboring mercury atoms, eventually turns out to be a relative minimum on the energy hypersurface. As expected, it is less stable than HgNCN(II)

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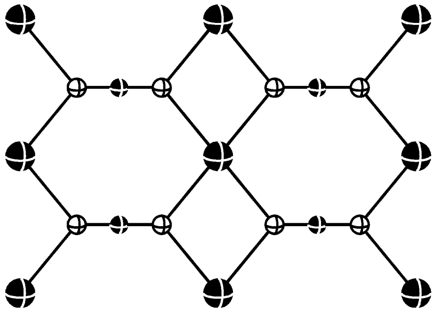

Figure 5. Schematic linkage of NCN^{2-} units and mercury atoms in a possible three-dimensional monoclinic transition structure lying between the structures of HgNCN(I) and HgNCN(II).

by roughly 16 kJ/mol (GGA and ultrasoft pseudopotentials), the aforementioned energy barrier. Within this metastable structure, the N−C double bond comes to 1.24 Å, and Hg is octahedrally coordinated by N (4 × 2.42 Å, 2 × 2.55 Å) because the linear NCN^{2-} unit actually tilts out of the paper plane by ca. 23°.

4. Discussion and Structural Classification

Summarizing, there exist two polymorphs of HgNCN containing a differently shaped NCN^{2-} unit. Ignoring the small (and energetically unimportant) difference in the N−C−N angle, both isomers differ from each other only in the N−C bond lengths on the “left” and “right” side of the molecular anion, which results from differing coordinations by mercury atoms. Thus, both isomers could well be phrased, if one is willing to regard the solid as an infinite molecule, as bond-stretch isomers; the isolated molecule HgNCN is unknown! Having said this, we must also ask whether the alternative concept of linkage isomerism can be used for the present finding. It is obvious that the linkage is truly different in HgNCN(I) and HgNCN(II); the NCN^{2-} unit, however, can surely not be designated an ambidentate ligand a priori. If we compare it with, say, NCS^- and SCN^-, it is clear that NCN^{2-} only changes into a quasiambidentate ligand by the changing chemical functionalities of the two N atoms because of bond stretching (left) and bond shortening (right) upon coordination to Hg within HgNCN(II).

A literature search concerning the closely related azides in the fields of (organometallic) coordination and (inorganic) solid-state chemistry yields interesting findings for the N_3^- unit, too. Differing linkages have indeed been reported, but only for different compositions. For example, while the manganese compound $[NEt_4][Mn_2(N_3)_3(CO)_6]$ contains 1,1-μ coordinated N_3^- ions with somewhat shorter (1.24 ± 1 Å) and longer (1.14 ± 3 Å) N−N bonds,[49] the copper phase $[BPh_4][Cu_2(N_3)_2(Me_5dien)_2]$ exhibits a regular, 1,3-μ coordinated N_3^- unit (two N−N bonds around 1.16 Å)[50] such that isomerism would clearly be an inappropriate wording. With respect to extended binary azides, the N_3^- unit is nearly always found with a $D_{\infty h}$ geometry,[51] and the N−N bond length is around 1.18 Å including rigid-body corrections based on reliable neutron data.[52] Whenever a binary azide is subject to a phase transformation, the different polymorphs contain identically shaped N_3^- units, though.[51,53] Within lead azide,[54] only one of the four linear N_3^- anions in the asymmetric unit is a bit distorted (N−N bond lengths of 1.21 and 1.15 Å), but this anion cannot be dubbed a separatable isomer. α-$Hg(N_3)_2$, finally, contains Hg atoms which are linearly coordinated by linear, symmetrical N_3^- units;[55] if the N_3^- geometry in the extremely explosive β-$Hg(N_3)_2$ (with unknown structure because of obvious reasons) is not fundamentally different, the case of HgNCN seems to be a singular one with respect to isomerism.

Concerning the continuity of the bond-stretch and linkage isomerism concepts, it is indeed possible that both notions are equally appropriate for HgNCN (adopting a liberal attitude toward the described NCN^{2-} question of ambidenticity for linkage isomerism). Also, because we do not know how to draw a persistent line between the two concepts, we prefer to leave the semantic decision to the chemical community. For obvious structural reasons, however, we would finally like to propose that HgNCN(I) should better be called mercury carbodiimide in the future while mercury cyanamide is the appropriate designation for HgNCN(II).

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(46) For the sake of completeness, we have also performed reference calculations on the hypothetical molecules $H_2N{-}Hg{-}N{=}C{=}N{-}Hg{-}NH_2$ (carbodiimide) and $(H_2N{-}Hg{-})_2N{-}C{\equiv}N$ (cyanamide) using both DFT and post-Hartree−Fock schemes plus full structural optimizations.[47] The B3LYP functional energetically prefers the carbodiimide form by 30 kJ/mol, but the order reverses using MP2 such that the cyanamide is more stable (11 kJ/mol); this comes out even more pronounced by a higher correlated method such as QCISD (15 kJ/mol). These findings manifest that the carbodiimide molecule appears to be the much more correlated species, in agreement with prior, independent electron correlation increments for carbon−nitrogen bonds.[48] Even the described state-of-the-art QCISD molecular calculation, however, does not fully reproduce the shortness of the N−C triple bond found experimentally in the solid state (1.21 vs 1.12 Å).

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