

Mercury Cyanamide / Carbodiimide Networks: Synthesis and Crystal Structures of $\text{Hg}_2(\text{NCN})\text{Cl}_2$ and $\text{Hg}_3(\text{NCN})_2\text{Cl}_2$

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Mercury Cyanamide / Carbodiimide Chloride, Inorganic Polymer, 2D Network

We report about the synthesis and crystal structure determination of $\text{Hg}_2(\text{NCN})\text{Cl}_2$ ($P2_1/c$ (No. 14), $Z=4$, $a=806.7(1)$, $b=907.1(2)$, $c=788.0(1)$ pm, $\beta=106.446(3)^\circ$, 1374 independent reflections, 67 variables, $R_1=0.0463$) and $\text{Hg}_3(\text{NCN})_2\text{Cl}_2$ ($Pca2_1$ (No. 29), $Z=4$, $a=702.0(2)$, $b=1078.5(2)$, $c=1050.3(2)$ pm, 1977 independent reflections, 71 variables, $R_1=0.0380$). Both compounds contain infinite -Hg-NCN-Hg- zigzag chains which are linked by additional Hg atoms to result in two-dimensional frameworks characterized by 20-membered rings sharing edges. The remarkably flexible structural backbone $[\text{Hg}_3(\text{NCN})_2]^{2+}$ hosts additional Cl^- anions and HgCl_2 molecules in $\text{Hg}_2(\text{NCN})\text{Cl}_2$ but only Cl^- anions in $\text{Hg}_3(\text{NCN})_2\text{Cl}_2$, by that reaching a high packing efficiency in both cases. While $\text{Hg}_2(\text{NCN})\text{Cl}_2$ exclusively contains carbodiimide $\text{N}=\text{C}=\text{N}^{2-}$ species, $\text{Hg}_3(\text{NCN})_2\text{Cl}_2$ is the first structural example of an inorganic network built up from both carbodiimide $\text{N}=\text{C}=\text{N}^{2-}$ and cyanamide $\text{N}-\text{C}\equiv\text{N}^{2-}$ groups.

1. Introduction

Over the last decade, synthetic and crystallographic as well as theoretical studies on solid-state cyanamide chemistry have progressed enormously. Besides the relatively simple crystal chemistry of the cyanamides involving alkaline or alkaline-earth metal cations [1 - 3], which is easily understood in terms of electrostatic interactions, effects of covalent bonding in the main-group and transition-metal representatives allow for greater structural varieties. For example, we mention chain structures formed in Ag_2NCN [4], in mercury carbodiimide $\text{HgNCN}(\text{I})$ [5] and in mercury cyanamide $\text{HgNCN}(\text{II})$ [6]; in addition, there are three-dimensional bonding arrangements in $\text{In}_{2.24}(\text{NCN})_3$ [7], ZnNCN [8] and in $\text{Si}(\text{NCN})_2$ [9], which bear striking resemblance with interpenetrating networks such as of the β -cristobalite (SiO_2) type.

When it comes to the *aufbau* of crystalline porous materials, various organic or inorganic spacer ligands coordinating to metal cations have been explored; here, N-containing spacers such as pyridine and cyano ligands were typically and successfully used [10]. On the other side, the probably smallest N, N'-type ligand — the NCN^{2-} anion, either in carbodiimide $\text{N}=\text{C}=\text{N}^{2-}$ or in cyanamide $\text{N}-\text{C}\equiv\text{N}^{2-}$ form — had not been expected to form pore or chan-

nel structures. It is also clear that the metal cation plays a decisive role for the total structure since its preferences for coordination number, coordination geometry and chemically matching ligands must be taken into account. For Hg(II), twofold linear coordination is observed throughout [11] but there are also some examples of 4- and 6-coordinated Hg(II) centers with longer interatomic distances [12]. To the best of our knowledge, no metal-cyanamide polymeric networks have been reported so far.

In an attempt to grow high-quality HgNCN single crystals by slow diffusion, we unexpectedly found two such inorganic polymers involving Hg^{2+} and NCN^{2-} in crystalline form. Here, we describe both synthesis and crystal structures of $\text{Hg}_2(\text{NCN})\text{Cl}_2$ and $\text{Hg}_3(\text{NCN})_2\text{Cl}_2$ and further discuss the coordination situation as well as the two-dimensional frameworks observed in the two compounds. The seemingly rather flexible coordination of the NCN^{2-} anion and Hg^{2+} cation allows for differing capacities to host guest species within the framework.

2. Experimental Section

2.1 Synthesis

Two 0.1 molar aqueous solutions of HgCl_2 and H_2NCN were filled into a “U-form” glass the left and right parts

Table 1. Crystallographic data for Hg₂(NCN)Cl₂.

Formula; molar mass	Hg ₂ (NCN)Cl ₂ ; 512.11 g/mol
Crystal color and form	Colorless hexagon
Lattice constant	$a = 806.7(1)$ pm $b = 907.1(2)$ pm $c = 788.0(1)$ pm $\beta = 106.446(3)^\circ$
Cell volume	$553.0(2) \cdot 10^6 \text{ pm}^3$
Space group; Z	$P2_1/c$ (No. 14); 4
X-ray density	6.151 g/cm^3
$F(000)$	856
Diffractometer	Bruker SMART CCD diffractometer with Mo- K_α radiation, graphite monochromator
Temperature	293(1) K
No of reflections	4569 ($R_{\text{eq}} = 0.0557$)
Independent refls	1374
Octants; max. θ	$-10 \leq h \leq 10, -11 \leq k \leq 12,$ $-10 \leq l \leq 10; 28.30^\circ$
Absorption coeff.	56.280 mm^{-1}
Abs. correction	numerical, indexed faces:
Crystal dimension	$(100) \leftrightarrow (\bar{1}00), -0.014 \leftrightarrow 0.019 \text{ mm}$ $(010) \leftrightarrow (0\bar{1}0), -0.022 \leftrightarrow 0.020 \text{ mm}$ $(001) \leftrightarrow (00\bar{1}), -0.042 \leftrightarrow 0.055 \text{ mm}$
Structure solution	Direct Methods (SHELXS-97)
Structure refinement	Least-squares method on F^2 , Full matrix
No. of intensities	1374
No. of variables	67
No. of restraints	0
Weighting scheme	$w = 1/[\sigma(F_0^2)(0.0581P)^2]$, where $P = (\max(F_0^2, 0) + 2F_0^2)/3$
Min., max. residual electron density	$-1.478, 6.961 \text{ e/\AA}^3$ (proximity of Hg)
R_1, wR_2	0.0463, 0.1103
Goodness of fit	0.888

of which were separated from each other by a $d = 2$ cm pottery filter of 4A type. The glass was held at room temperature for 1 d after which a white powder, later identified as HgNCN(II), precipitated at both sides. Upon washing, two differently shaped types of colorless crystals were found within the main phase HgNCN(II). Those of a regular hexagon form were later identified to be Hg₂(NCN)Cl₂ and predominate on the side of the HgCl₂ solution; the rectangular plates are formed by Hg₃(NCN)₂Cl₂ and show up mainly on the H₂NCN side. After drying in air, some selected crystals turned out to be suitable for X-ray single crystal measurement.

2.2. Single crystal structure determination

Selected crystals of Hg₂(NCN)Cl₂ ($0.033 \times 0.042 \times 0.097 \text{ mm}^3$) and Hg₃(NCN)₂Cl₂ ($0.07 \times 0.04 \times 0.02 \text{ mm}^3$) were mounted on the tips of glass fibers. A set

Table 2. Positional parameters and isotropic displacement parameters (U_{eq} in pm^2 , a third of the trace of the orthogonalized U_{ij} tensor) for Hg₂(NCN)Cl₂ (standard deviations in parentheses).

Atom	W.-Site	x	y	z	U_{eq}
Hg(1)	4e	0.1093(1)	0.82183(8)	0.2337(1)	259(2)
Hg(2)	2d	1/2	0	1/2	239(3)
Hg(3)	2b	1/2	0	0	541(5)
Cl(1)	4e	0.4907(7)	0.7527(6)	0.2527(7)	306(11)
Cl(2)	4e	0.8009(6)	0.0217(6)	0.0761(7)	319(12)
N(1)	4e	0.234(2)	0.990(2)	0.399(2)	225(36)
C	4e	0.135(3)	0.086(2)	0.424(2)	228(46)
N(2)	4e	0.035(2)	0.176(2)	0.453(2)	271(38)

of X-ray intensities was collected for each compound with a Bruker SMART-CCD diffractometer using graphite-monochromatized Mo- K_α radiation at $T = 20(1)^\circ\text{C}$ and the aid of the SMART and SAINT software packages [13].

In both cases, a total sphere of data was collected to allow for absorption corrections by means of face-indexing (Hg₂(NCN)Cl₂) and the empirical SADABS method (Hg₃(NCN)₂Cl₂). The crystal structures were then solved by Direct Methods and refined by alternating cycles of (difference) Fourier syntheses and full-matrix least-squares refinements with SHELXS-97 and SHELXL-97 [14]*.

3. Results

3.1. The crystal structure of Hg₂(NCN)Cl₂

All relevant crystallographic data of the final refinement of Hg₂(NCN)Cl₂ are summarized in Table 1 whereas Tables 2 and 3 offer the positional and isotropic as well as anisotropic displacement parameters; important bond distances and angles are given in Table 4.

The coordination motifs in Hg₂(NCN)Cl₂ are offered in Fig. 1 by means of labeled displacement ellipsoids. The Hg(1) atom is bonded to two nitrogen atoms from crystallographically identical NCN²⁻ units in a nearly linear arrangement, that is Hg(1)-N(1) = 207.0(16) pm, Hg(1)-N(2) = 207.4(16) pm and N(1)-Hg-N(2) = 172.4(7)^o. The Hg(1)s together with the NCN²⁻ units form infinite zigzag chains along the b axis, the NCN²⁻ unit acting as a μ -bridging ligand. Hg(2), sitting on the center of inversion

*Details may be obtained from: Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), by quoting the registry numbers CSD-412608 (Hg₂(NCN)Cl₂) and CSD-412609 (Hg₃(NCN)₂Cl₂).

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Hg(1)	258(4)	207(4)	283(4)	-35(4)	28(3)	-47(4)
Hg(2)	145(5)	270(6)	278(6)	-36(5)	22(4)	-3(5)
Hg(3)	196(6)	931(14)	478(9)	-57(9)	65(6)	-140(8)
Cl(1)	362(28)	258(28)	292(26)	-19(22)	84(22)	32(24)
Cl(2)	236(26)	294(29)	384(30)	36(24)	17(23)	-10(23)
N(1)	180(80)	166(87)	358(99)	-10(73)	124(73)	-27(72)
C	358(123)	178(104)	125(100)	53(77)	34(92)	7(93)
N(2)	184(82)	291(97)	280(90)	51(84)	29(71)	52(83)

Table 4. Selected interatomic distances (pm) and bond angles (°) for Hg₂(NCN)Cl₂.

Hg(1)-N(1)	207.0(16)	Hg(1)-N(2)	207.4(16)
Hg(2)-N(1)	206.6(16) (2×)	Hg(2)-Cl(1)	295.9(5) (2×)
Hg(3)-Cl(2)	233.8(5) (2×)	N(1)-C	124(3)
C-N(2)	122(3)		
N(1)-Hg(1)-N(2)	172.4(7)	N(1)-Hg(2)-N(1)	180
C-N(1)-Hg(1)	113.5(14)	C-N(1)-Hg(2)	123.5(15)
C-N(2)-Hg(1)	124.4(15)	Hg(2)-N(1)-Hg(1)	123.0(8)
N(1)-C-N(2)	177(2)	Cl(2)-Hg(3)-Cl(2)	180
Cl(1)-Hg(2)-Cl(1)	180		

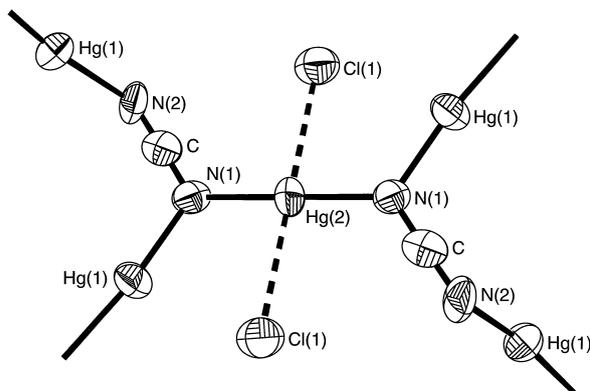


Fig. 1. Thermal ellipsoid plot (90% probability) of the atomic coordinations in Hg₂(NCN)Cl₂; the incorporated HgCl₂ molecule has been omitted for clarity.

symmetry, is also bonded linearly to two N(1) nitrogen atoms; thus, Hg(2)-N(1) = 206.6(16) pm and N(1)-Hg(2)-N(1) = 180° by space group symmetry. Remarkably, it is the Hg(2) atom which links the above-mentioned zigzag chains made from Hg(1) and NCN²⁻ units (Fig. 1). Also, the four Hg-N distances are almost identical (207 pm) and agree very well with those found in related materials (205 - 211 pm) [11, 15].

Hg(3) is not involved in the Hg-NCN bonding but linearly coordinated by two Cl⁻ at a distance of Hg(3)-Cl(2) = 233.8(5) pm and an angle of Cl(2)-

Table 3. Anisotropic displacement parameters (pm²) for Hg₂(NCN)Cl₂ (standard deviations in parentheses). The components U_{ij} refer to a displacement factor of the form $\exp\{-2\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{23}klb^*c^*)\}$.

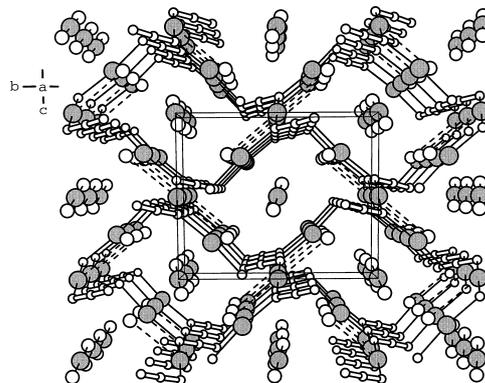


Fig. 2. Packing of Hg₂(NCN)Cl₂; the big circles are Hg atoms, the medium circles Cl⁻ anions and the small units NCN²⁻ anions.

Hg(3)-Cl(2) = 180° by space group symmetry. Since this is very similar to the situation in pure HgCl₂ (Hg-Cl: 227 and 229 pm, Cl-Hg-Cl: 178.6°) [16], the notion of an isolated molecular HgCl₂ species is justified; the one additional interaction of Cl(2) with Hg(1) is insignificant (305.5(5) pm). In addition, there is a free Cl⁻ anion in the leftover coordination sites around Hg(2) at 295.9(5) and around Hg(3) at 309.5(5) pm.

Coming back to the NCN²⁻ unit, the individual distances of N(1)-C = 124(3) pm and C-N(2) = 122(3) pm as well as the N(1)-C-N(2) angle of 177(2)° show it to be a carbodiimide species, similar to the one found in HgNCN(I) [5]. We note, however, that N(2) is one-coordinate but N(1) is two-coordinate to Hg (see also Discussion).

The total structural motif of Hg₂(NCN)Cl₂ is shown in Fig. 2. Mercury atoms and carbodiimide units form an unprecedented two-dimensional network from Hg(1)-NCN-Hg(1) chains cross-linked by Hg(2) atoms. As a result, there are 20-membered rings stacked on top of each other along the *a*

Table 5. Crystallographic data for $\text{Hg}_3(\text{NCN})_2\text{Cl}_2$.

Formula; molar mass	$\text{Hg}_3(\text{NCN})_2\text{Cl}_2$; 752.73 g/mol
Crystal color and form	Colorless rectangular prism
Lattice constant	$a = 702.0(2)$ pm $b = 1078.5(2)$ pm $c = 1050.3(2)$ pm
Cell volume	$795.1(3) \cdot 10^6 \text{ pm}^3$
Space group; Z	$Pca2_1$ (No. 29); 4
X-ray density	6.288 g/cm^3
$F(000)$	1256
Diffractometer	Bruker SMART CCD diffractometer with Mo- K_α radiation, graphite monochromator
Temperature	293(1) K
No of reflections	9910 ($R_{\text{eq}} = 0.0924$)
Independent refls	1977
Octants; max. θ	$-9 \leq h \leq 9, -14 \leq k \leq 14,$ $-14 \leq l \leq 13; 28.32^\circ$
Absorption coeff.	58.386 mm^{-1}
Abs. correction	multi-scan (SADABS)
Twin structure	inversion twin, BASF = 0.47(2)
Structure solution	Direct Methods (SHELXS-97)
Structure refinement	Least-squares method on F^2 , Full matrix
No. of intensities	1977
No. of variables	71
No. of restraints	1 (floating origin)
Weighting scheme	$w = 1/[\sigma(F_o^2)(0.0139P)^2]$, where $P = (\max(F_o^2, 0) + 2F_o^2)/3$
Min., max. residual electron density	-1.539, 1.821 $\text{e}/\text{Å}^3$ (proximity of Hg)
R_1, wR_2	0.0380, 0.0651
Goodness of fit	1.015

axis. The channels thus formed are filled with HgCl_2 molecules and Cl^- anions.

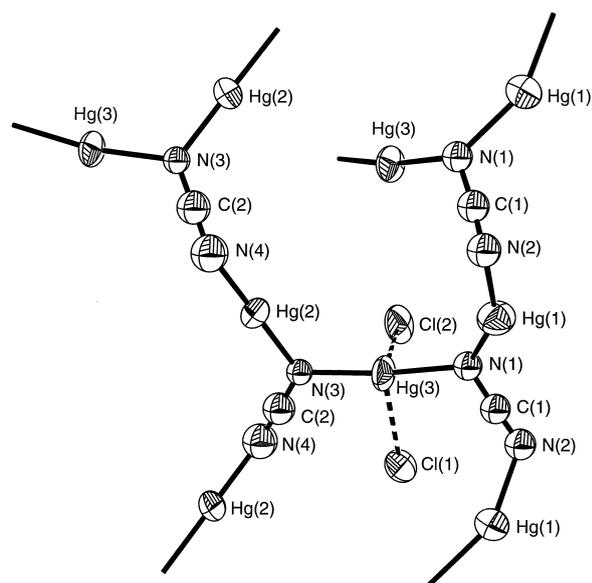
3.2. The crystal structure of $\text{Hg}_3(\text{NCN})_2\text{Cl}_2$

Upon refinement in the acentric space group $Pca2_1$, it was realized that the individual crystal (just like all others) was an inversion twin. The corresponding twin refinement converged to a batch scale factor of 0.47(2), i. e., approximately equal contributions of the two twin compounds. By doing so, R_1 reduced from 0.0433 to 0.0380 by slightly changing the spatial parameters of the light atoms only. Due to the very strong absorption, a refinement including anisotropic displacement parameters for Hg and Cl and isotropic ones for N and C turned out to be the most reasonable.

The crystallographic data of $\text{Hg}_3(\text{NCN})_2\text{Cl}_2$ are summarized in Table 5, and Tables 6 and 7 offer po-

Table 6. Positional parameters (all atoms on 4a) and isotropic displacement parameters (U_{eq} in pm^2 , a third of the trace of the orthogonalized U_{ij} tensor) for $\text{Hg}_3(\text{NCN})_2\text{Cl}_2$ (standard deviations in parentheses).

Atom	x	y	z	U_{eq}
Hg(1)	0.7065(1)	0.08577(7)	0.95711(7)	296(2)
Hg(2)	0.98652(9)	0.44557(6)	0.00562(8)	236(2)
Hg(3)	0.23031(9)	0.20550(6)	0.64448(7)	247(2)
Cl(1)	0.0697(6)	0.2006(4)	0.8980(5)	275(9)
Cl(2)	0.6336(6)	0.2972(4)	0.0809(5)	324(11)
N(1)	0.155(2)	0.017(1)	0.603(1)	193(31)
C(1)	0.105(2)	0.956(2)	0.702(2)	209(38)
N(2)	0.044(2)	0.906(2)	0.788(1)	231(34)
N(3)	0.150(2)	0.385(1)	0.158(1)	164(28)
C(2)	0.159(2)	0.440(2)	0.260(2)	255(41)
N(4)	0.182(2)	0.498(2)	0.357(2)	316(40)

Fig. 3. Thermal ellipsoid plot (90% probability) of the atomic coordinations in $\text{Hg}_3(\text{NCN})_2\text{Cl}_2$.

sitional and isotropic as well as anisotropic displacement parameters (Hg, Cl). Important interatomic distances are listed in Table 8.

Fig. 3 shows the individual atomic coordinations in $\text{Hg}_3(\text{NCN})_2\text{Cl}_2$ using displacement ellipsoids. Hg(1) is bonded to N(1) at 213.0(14) pm and to N(2) at 211.4(15) pm; the widened Hg-N bond lengths find their expression in the significantly kinked bond angle N(1)-Hg-N(2) of $151.1(6)^\circ$. Just like in $\text{Hg}_2(\text{NCN})\text{Cl}_2$, there are infinite zigzag chains built from Hg(1) and NCN^{2-} units along the c axis. A

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Hg(1)	365(4)	285(4)	239(4)	13(4)	-38(3)	26(3)
Hg(2)	280(3)	207(3)	220(3)	37(3)	-18(3)	41(3)
Hg(3)	321(3)	114(3)	305(4)	-13(3)	11(3)	-33(3)
Cl(1)	350(23)	244(23)	231(21)	-76(20)	25(19)	8(19)
Cl(2)	396(25)	133(22)	442(28)	-40(23)	99(23)	-49(21)

Table 7. Anisotropic displacement parameters (pm²) for Hg₃(NCN)₂Cl₂ (standard deviations in parentheses). The components U_{ij} refer to a displacement factor of the form $\exp\{-2\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{23}klb^*c^*)\}$.

Table 8. Selected interatomic distances (pm) and bond angles (°) for Hg₃(NCN)₂Cl₂.

Hg(1)-N(2)	211.4(15)	Hg(1)-N(1)	213.0(14)
Hg(1)-Cl(2)	267.4(5)	Hg(1)-Cl(1)	290.2(5)
Hg(2)-N(4)	205.2(16)	Hg(2)-N(3)	207.3(13)
Hg(2)-Cl(1)	293.2(5)	Hg(3)-N(3)	211.5(13)
Hg(3)-N(1)	214.4(14)	Hg(3)-Cl(2)	282.0(4)
Hg(3)-Cl(1)	289.2(5)	Hg(3)-Cl(1)	294.5(5)
C(1)-N(2)	113(2)	C(1)-N(1)	128(2)
N(3)-C(2)	123(2)	C(2)-N(4)	120(2)
N(1)-Hg(3)-N(3)	168.2(5)	N(3)-Hg(2)-N(4)	178.2(6)
N(1)-Hg(1)-N(2)	151.1(6)	Hg(1)-N(1)-Hg(3)	121.7(6)
Hg(2)-N(3)-Hg(3)	117.2(6)	C(1)-N(1)-Hg(1)	116.2(12)
C(1)-N(1)-Hg(3)	113.0(12)	C(1)-N(2)-Hg(1)	116.3(13)
C(2)-N(3)-Hg(2)	123.5(13)	C(2)-N(3)-Hg(3)	118.6(13)
C(2)-N(4)-Hg(2)	136.2(14)	N(1)-C(1)-N(2)	174(2)
N(3)-C(2)-N(4)	175(2)		

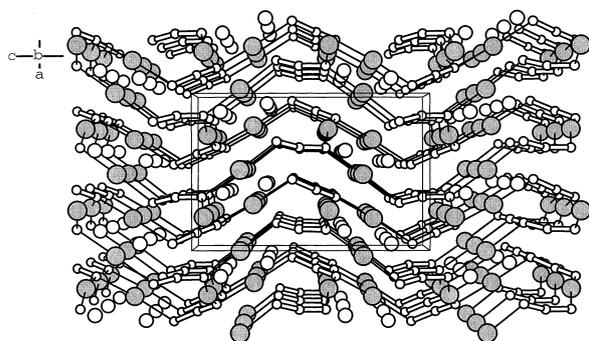


Fig. 4. Same as in Fig. 2 but for Hg₃(NCN)₂Cl₂.

similar role is played by Hg(2) but with shorter bond lengths (Hg(2)-N(3) = 207.3(13), Hg(2)-N(4) = 205.2(16) pm) and, consequently, an almost linear angle of N(3)-Hg(2)-N(4) = 178.2(6)°. Additionally, the Hg(3) atoms connect the two zigzag chains by two bonds to N(1) at 214.4(14) pm and to N(3) at 211.4(14) pm; the bridging angle N(1)-Hg(3)-N(3) is 168.2(6)°. Also, there are two wide contacts of (almost) free chlorine ions to Hg, namely Cl(1) and Cl(2) at 267 - 295 pm.

The lack of inversion symmetry in Hg₃(NCN)₂Cl₂ is reflected by the presence of two symmetry-inequivalent NCN²⁻ groups. Whereas the almost

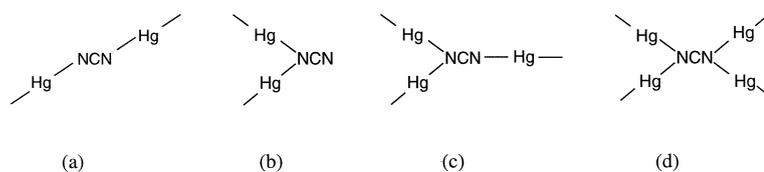
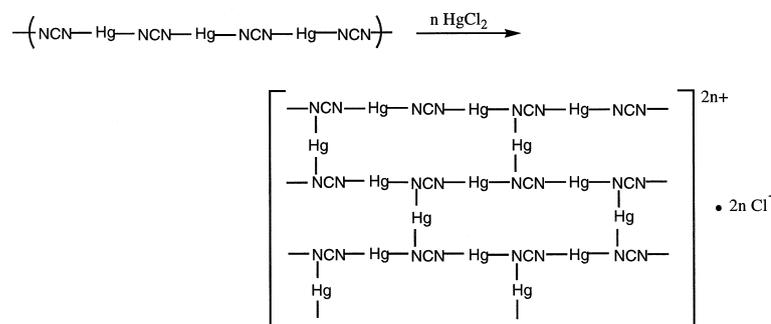
linear (174(2)°) N(1)-C(1)-N(2) group can be considered a cyanamide unit because of the two different bond lengths, N(1)-C(1) = 128(2) and C(1)-N(2) = 113(2) pm, which are close to a single and triple C-N bond, the N(3)-C(2)-N(4) group is also linear (175(2)°) but contains two C-N double bonds: N(3)-C(2) = 123(2) and C(2)-N(4) = 120(2) pm; the structural designation of N(3)-C(2)-N(4) as a carbodiimide species is justified. We mention that this is the first occurrence of both cyanamide (known from the structures of PbNCN [17] and HgNCN(II) [6]) and carbodiimide units (known from HgNCN(I) [5]) in the same crystal structure of an inorganic network.

Fig. 4 presents the whole crystal structure. Mercury atoms and NCN²⁻ units form also 20-membered rings, but the cavities are much smaller than those in Hg₂(NCN)Cl₂ since only chloride ions need to be hosted in the channels.

4. Discussion

The structural chemistry of systems with NCN²⁻ and Hg²⁺ units has been characterized so far by two binding modes, schematically given in Scheme 1: mode (a) is found in mercury carbodiimide, HgNCN(I), mode (b) in mercury cyanamide, HgNCN(II). To generate the novel structural networks observed in Hg₂(NCN)Cl₂ and Hg₃(NCN)₂Cl₂, the new binding mode (c) is necessary. The binding mode (d) has, so far, never been observed experimentally, but quantum-chemical calculations from first principles suggest this coordinative scenario as one possible (and energetically high-lying) transition structure when going from (a) to (b) [6].

The structural analysis makes it clear that the title compounds are characterized by a stoichiometrically identical [Hg₃(NCN)₂]²⁺ cationic backbone which is built up from 20-membered rings. Thus, the chemical formulas could be rewritten as Hg₂(NCN)Cl₂ = 1/2 · { [Hg₃(NCN)₂]Cl₂ · HgCl₂ } and as Hg₃(NCN)₂Cl₂ = [Hg₃(NCN)₂]Cl₂. While the N-

Scheme 1. The coordination modes between NCN^{2-} and Hg^{2+} .Scheme 2. The $[\text{Hg}_3(\text{NCN})_2]^{2+}$ framework.

C-N and -N-Hg-N- bond distances and angles are relatively constant for both compounds, the cavities (and channels) thus formed seem to be remarkably flexible; flexible enough, at least, to adapt to either Cl^- , HgCl_2 , or a combination of the two. It remains to be seen whether the backbone can host other species such as Br^- , HgBr_2 *etc.* as well.

The generation of the backbone itself is schematically depicted in Scheme 2.

As stated before, the new binding mode (c) is needed to set up the 20-membered rings composed of NCN^{2-} and Hg^{2+} . While the sketch alludes to the notion of an open material, an inspection of the packing efficiency yields an astonishing result. Based on the tabulated [18] volume increment of Hg^{2+} ($8 \text{ cm}^3/\text{mol}$), it is possible to calculate an average volume increment, on the basis of the crystal structures of HgNCN(I) and HgNCN(II) , for the NCN^{2-} unit, namely $28.1 \text{ cm}^3/\text{mol}$; thus, NCN^{2-} is similar in spatial requirement to S^{2-} ($29 \text{ cm}^3/\text{mol}$). Including the value for Cl^- ($20 \text{ cm}^3/\text{mol}$), the theoretical molar volume of $\text{Hg}_2(\text{NCN})\text{Cl}_2$ should be $84.1 \text{ cm}^3/\text{mol}$ — the experimental volume is even

smaller by 1%, though. Likewise, $\text{Hg}_3(\text{NCN})_2\text{Cl}_2$ should require $120.2 \text{ cm}^3/\text{mol}$ but is more dense by 0.4%; as it seems, the packing efficiency is clearly optimized.

It is not known, up to now, whether compounds of the above kind may serve useful in the synthesis of functional materials exhibiting cavities of diverse shapes and sizes. The rational design of such coordination networks continues to be a challenging goal for crystal engineers [10, 19]. Samples of $\text{Hg}_2(\text{NCN})\text{Cl}_2$ might nonetheless be subjected to the attempt of exchanging the hosted HgCl_2 molecular species ($48 \text{ cm}^3/\text{mol}$) against (substituted) hydrocarbons of similar size. In any case, the existence of $\text{Hg}_2(\text{NCN})\text{Cl}_2$ and $\text{Hg}_3(\text{NCN})_2\text{Cl}_2$ shows that it is possible to generate new channels and cavities using NCN^{2-} .

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- [1] N.-G. Vannerberg, *Acta Chem. Scand.* **16**, 2263 (1962).
 [2] a) M. Becker, J. Nuss, M. Jansen, *Z. Anorg. Allg. Chem.* **626**, 2505 (2000); b) M. Becker, M. Jansen, *Solid State Sciences*, **2**, 711 (2000).
 [3] U. Berger, W. Schnick, *J. Alloys Compd.* **206**, 179 (1994).
 [4] a) F. P. Bowden, H. M. Montagu-Pollock, *Nature* **191**, 556 (1961); b) M. Becker, J. Nuss, M. Jansen, *Z. Naturforsch.* **55b**, 383 (2000).
 [5] a) S. K. Deb, A. D. Yoffe, *Trans. Faraday Soc.* **55**, 106 (1958); b) M. Becker, M. Jansen, *Z. Anorg. Allg. Chem.* **626**, 1639 (2000).

- [6] X. Liu, P. Müller, P. Kroll, R. Dronskowski, *Inorg. Chem.* **41**, 4259 (2002).
- [7] R. Dronskowski, *Z. Naturforsch.* **50b**, 1245 (1995).
- [8] M. Becker, M. Jansen, *Acta Crystallogr.* **C57**, 347 (2001).
- [9] R. Riedel, A. Greiner, G. Miehe, W. Dreßler, H. Fueß, J. Bill and F. Aldinger, *Angew. Chem. Int. Ed.* **36**, 603 (1997).
- [10] a) M. S. Zaworotko, *Chem. Commun.* 1 (2001); b) B. Holliday, C. Mirkin, *Angew. Chem. Int. Ed.* **40**, 2022 (2001); c) A. K. Cheetham, G. Férey, T. Loiseau, *Angew. Chem. Int. Ed.* **38**, 3268 (1999).
- [11] D. Breiting, K. Brodersen, *Angew. Chem. Int. Ed.* **9**, 357 (1970).
- [12] D. Bebout, A. DeLanoy, D. Ehmann, M. Kasner, D. Parrish, R. Butcher, *Inorg. Chem.* **37**, 2952 (1998).
- [13] SADABS, SMART and SAINT, Bruker AXS Inc., Madison Wisconsin, USA.
- [14] G. M. Sheldrick, SHELXS97 and SHELXL97, University of Göttingen, Germany.
- [15] a) H. Schumann, J. Cottfriedsen, S. Dechert, F. Girgsdies, *Z. Anorg. Allg. Chem.* **626**, 747 (2000); b) N. Masciochi, G. A. Ardizzoia, A. Maspero, G. Lamonica, A. Sironi, *Inorg. Chem.* **38**, 3657 (1999).
- [16] V. Subramanian, K. Seff, *Acta. Crystallogr.* **B36**, 2132 (1980).
- [17] X. Liu, A. Decker, D. Schmitz, R. Dronskowski, *Z. Anorg. Allg. Chem.* **626**, 103 (2000).
- [18] W. Biltz, *Raumchemie der festen Stoffe*, Verlag von Leopold Voss, Leipzig (1934).
- [19] a) L. R. MacGillivray, J. L. Atwood, *Nature* **389**, 469 (1997); b) P. Holy, J. Závada, I. Císarová and J. Podlaha, *Angew. Chem. Int. Ed.* **38**, 381 (1999).