Mercury Azides and the Azide of Millon's Base**

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The reaction between calomel Hg_2Cl_2 (Greek: *kalos* = beautiful, *melas* = black) and ammonia was already known to the alchemists, and attempts to discover the nature of the black precipitate have been made at all stages of chemical history.[1] Today we know that numerous mercurous (Hg^I) and mercuric (Hg^{II}) halides readily undergo a condensation reaction with ammonia resulting, in the case of Hg_2Cl_2, in the disproportion to elemental Hg and $HgCl_2$ followed by the successive formation of the fusible precipitate $[Hg(NH_3)_2]Cl_2$, the infusible precipitate $[HgNH_2]Cl$, and finally the chloride of Millon's base $[Hg_2N]Cl$ along with the formation of NH_4Cl. The parent compound nitridodimercury hydroxide, Millon's base $[Hg_2N]OH\cdot 2H_2O$, was discovered between 1830–1850 by Millon in the reaction of HgO and NH_3.[2] Like most binary transition-metal–nitrogen compounds, mercury–nitrogen species form a class of highly endothermic compounds. Difficulties in the isolation and handling of such nitrogen-rich compounds arise from their extremely low energy barriers, which often lead to explosive decomposition.[3] To increase the barrier to explosion organic substituents can be introduced, such as in $RHgN_3$ (R = alkyl, phenyl).[4] The first mercury azide $Hg_2(N_3)_2$ was obtained by Curtius as early as 1890 upon combining aqueous solutions of mercury(I) salts with alkali-metal azides, or in the reaction of the free acid HN_3 with elemental mercury.[5b] Pioneering work by Dehnicke and Beck in the 1960s led to the vibrational characterization of $Hg_2(N_3)_2$,[6a] α-$Hg(N_3)_2$[6a] and $[Ph_4P][Hg(N_3)_3]$.[7] To date, structural data of binary mercury azides are only available for $Hg_2(N_3)_2$ from X-ray powder diffraction studies,[6b] and α-$Hg(N_3)_2$ from isotropically refined single-crystal X-ray analysis.[6e] Furthermore, a second highly labile modification of mercury(II) azide, β-$Hg(N_3)_2$ has been observed but could not be isolated or characterized so far.[5a,8] Besides

these azides, the neutral nitrido compounds Hg_3N[9] and Hg_2N_3 (but without any unequivocal characterization for both),[10] and the cationic framework $[Hg_2N]^+ = {}^3_\infty[Hg_{4/2}N]^+$[11–13] in a number of salts of Millon's base have been described.[2] We were intrigued by the idea of combining the cationic $[Hg_2N]^+$ framework with the azide anion generating the binary azide salt of Millon's base $[Hg_2N]N_3$ which would be the first characterized nitrido-metal azide featuring a three-dimensional network structure. It should be noted, that to date, only molecular nitrido-metal azide species, such as the $[NM(N_3)_4]^-$ anion (as $[Ph_4As]^+$ or $[Ph_4P]^+$ salts, M = Mo, W)[14a,b] and the 24-membered uranium nitrogen ring $(UNUN_3)_4$ in $[Cp'_2U(\mu-N)U(\mu-N_3)Cp'_2]_4$ (Cp' = C_5Me_5, C_5Me_4H) are known.[14c]

A first indication for the existence of such a nitridodimercury azide can be found in the work of Curtius who reported on the reaction of mercury(I) azide with ammonia resulting in a black precipitate, that is why he named $Hg_2(N_3)_2$ "Stickstoffkalomel" ("*nitrogen calomel*") in accord with the reaction of calomel Hg_2Cl_2.[5b] Later Strecker et al. reported on the analogous reaction using mercury(II) azide yielding an yellow explosive powder which they called ammonia-basic mercuric azide.[15] However, since neither spectroscopic nor structural data are available, a systematic study is desirable to further confirm the existence of $[Hg_2N]N_3$.

Following our interest in binary element–nitrogen compounds we report herein on the synthesis and full characterization of the azide salt of Millon's base $[Hg_2N]N_3$ (Figure 1) and the isolation and characterization of β-$Hg(N_3)_2$. Furthermore, the single-crystal structure of $Hg_2(N_3)_2$ was determined for the first time (Figure 2). For comparison and to get a precise set of structural data the single-crystal structure of α-$Hg(N_3)_2$ was also elucidated (Figure 3).

In accordance with literature, both $Hg_2(N_3)_2$ and α-$Hg(N_3)_2$ are easily prepared by precipitation from aqueous solutions of mercury(I) or mercury(II) nitrate, respectively, with sodium azide at ambient temperature.[16] After washing them with water and drying in air or in vacuum, both compounds are obtained as stable microcrystalline colorless solids in almost quantitative yields. The phase purity was confirmed by IR/Raman spectroscopy, ICP (inductively coupled plasma) and powder X-ray diffraction.[16] In analogy to the preparation of β-$Pb(N_3)_2$, a second metastable modification of mercury(II) azide, β-$Hg(N_3)_2$ can be obtained by slow diffusion of aqueous NaN_3 into a solution of mercury(II) nitrate which is separated by a layer of aqueous $NaNO_3$.[17,5a] Thereby, needle-like crystals of β-$Hg(N_3)_2$ start to form in the lower mercury(II) nitrate layer which is always accompanied by spontaneous explosions during crystal growth finally leading to a mixing of the layers and the fast precipitation of α-$Hg(N_3)_2$. **Caution!** Slow crystallization during the preparation of α- or β-$Hg(N_3)_2$ leads to the formation of

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large crystals which are extraordinarily sensitive to all kinds of provocation (e.g. even detonate in solution) and therefore should be avoided by all means. Nevertheless, with extreme care, we were able to manually isolate some specimens of β-Hg(N_3)_2 under the microscope which allowed the characterization by vibrational spectroscopy, single-crystal X-ray diffraction, and the determination of the melting point.

As illustrated in Scheme 1, several synthetic routes to the azide salt of Millon's base [Hg_2N]N_3 were applied. The best synthetic method starts from a saturated solution of Hg(N_3)_2

$$2\,Hg_2(N_3)_2 \xrightarrow[\substack{-2\,Hg \\ -3\,NH_4N_3}]{\substack{NH_{3(aq)} \\ H_2O}} [Hg_2N]N_3 \xleftarrow[\substack{-3\,NH_4N_3}]{\substack{NH_{3(aq)} \\ H_2O}} 2\,Hg(N_3)_2$$

$$[Hg_2N]N_3 \uparrow \substack{NaN_3 \;\; -NaX \\ H_2O \;\; X^- = NO_3^-,\,Br^-}$$

$$[Hg_2N]X$$

Scheme 1. Different synthetic routes to [Hg_2N]N_3.

in water at ambient temperature which is added dropwise to an aqueous solution of ammonia under exclusion of light. Hg_2(N_3)_2 can also be used, since it disproportionates quickly into Hg and Hg(N_3)_2 in polar solvents, but in this case elemental Hg has to be separated. The solvent was removed by decantation and the resulting yellow precipitate (black in case of Hg_2(N_3)_2) was washed several times with water until the washing solution gave no precipitate with silver nitrate. The solid was dried carefully at 70°C for several hours in vacuo which yielded nitridodimercury azide [Hg_2N]N_3 as an yellow solid in 60% yield. However, as shown by powder X-ray diffraction studies, [Hg_2N]N_3 obtained by these procedures, always consisted of two phases: a hexagonal (α) and a cubic (β) phase. Pure cubic β-[Hg_2N]N_3 suitable for structure analysis from powder X-ray diffraction data was obtained by heating a mixture of crystalline Hg(N_3)_2 and a concentrated ammonia solution in a PTFE autoclave for three weeks at 180°C. Note that an excess of Hg(N_3)_2 led to the deposition of large crystals of Hg_2(N_3)_2 rather than [Hg_2N]N_3.[18]

After washing the product and drying at 70°C in vacuo, cubic anhydrous β-[Hg_2N]N_3 was afforded as pale yellowish powder. Pure hexagonal α-[Hg_2N]N_3 suitable for powder X-ray diffraction was obtained by treating α-[Hg_2N]Br, which was generated from HgBr_2 and NH_3 in H_2O at ambient temperature,[13] with a concentrated aqueous solution of NaN_3. This Br^-/N_3^- exchange in the α-[Hg_2N]^+ framework took about 300 days when the precipitate was periodically filtered and suspended again in a freshly prepared, concentrated aqueous NaN_3 solution every 30 days. In contrast, the same exchange procedure took only four days starting from β-[Hg_2N]NO_3 but again yields only a mixture of the cubic and hexagonal phase. However, both exchange reactions avoid the use of explosive mercury azides and therefore the NO_3^-/N_3^--exchange represents a slightly less-hazardous procedure for the preparation of [Hg_2N]N_3.

α-[Hg_2N]N_3 and β-[Hg_2N]N_3 were obtained as yellow polycrystalline solids, which were not suitable for single-crystal structure elucidation, and were characterized by

Table 1: Selected structural data from single crystal and powder X-ray analyses (distances [Å], angles [°]), melting points [°C], IR and Raman data [cm⁻¹], and NBO partial charges[19] [e].[a]

	Hg_2(N_3)_2[i]	α-Hg(N_3)_2[i]	β-Hg(N_3)_2[i]	β-[Hg_2N]N_3
Hg-N_α[b]	2.161(4)	2.062[h]	2.084[h]	2.0604(1)
N_α-N_β	1.213(6)	1.217	1.211	1.226(6)
N_β-N_γ	1.144(6)	1.141	1.140	1.226(6)
Hg-Hg[c]	2.5331(3)	4.372	3.914	3.3647(1)
N_α-N_β-N_γ	176.6(5)	175.1	174.9	180
Hg-N_α-N_β	118.9(3)	116.5	114.5	–
Hg-Hg-N_α	178.8(1)	–	–	–
N_β-N_α-N_α-N_β	180	145.6	24.13	–
m.p.	225[d]	195–200[e]	180–185[e]	283[d]
$\nu_{as,N3}$(IR)[f]	2084	2089	2046	1959
	2064	2044	–	–
$\nu_{as,N3}$(Ra)[f]	2124	2127	2109	n. a.[g]
	2066	2094	2069	–
		2071	2059	
q(Hg)	0.748	1.279	1.278	–
q(N_α)	−0.816	−0.752	−0.750	–
q(N_β)	0.219	0.219	0.220	–
q(N_γ)	−0.152	−0.107	−0.109	–

[a] The phase purity of all species was verified by a Rietveld refinement. [b] For [Hg_2N]N_3 this distance corresponds to the nitrido mercury distance in [Hg_2N]^+, Hg···N_azide distances are 2.931 and 3.464 Å. [c] Closest Hg···Hg distances; [d] M.p. = T_{decomp}. [e] Sublimation, no decomposition up to 360°C observed. [f] The presence of more than one azido ligand results in in-phase and out-of-phase coupling. [g] n.a. = not active, owing to ideal $D_{\infty h}$ symmetry Raman inactive. [h] If there are more than one azide ligands, the average value is given. [i] Hg_2(N_3)_2 corresponds to the *trans*-C_{2h}, α-Hg(N_3)_2 to the *trans*-C_2 and β-Hg(N_3)_2 to the *cis*-C_{2v} isomer in the gas-phase computation.[16]

powder diffraction (Rietveld refinement), ICP-OES, IR and Raman spectroscopy (Table 1).[16] Since both compounds are highly explosive, standard elemental analysis could not be carried out but the mercury content was determined by iodometric titration[20] and ICP-OES (inductively coupled plasma optical emission spectroscopy).[16] Both species are air stable but hygroscopic and almost insoluble in common polar and unpolar solvents. Like Hg_2(N_3)_2[5b,6a,b] or α- and β-Hg(N_3)_2,[5,6,17] α-[Hg_2N]N_3 and β-[Hg_2N]N_3 are sensitive to heat, shock, and especially friction, properties which are greatly influenced by the crystallinity. With increasing crystallinity, samples of all the azides tend to become more sensitive. As shown by DSC (differential scanning calorimetry) studies, [Hg_2N]N_3 is thermally stable up to 283°C (β-[Hg_2N]N_3) and 313°C (α-[Hg_2N]N_3). At this temperature a smooth decomposition under release of molecular nitrogen and elemental mercury is observed on slow heating rates (cf. Hg_2(N_3)_2 decomposes at about 225°C, Table 1). On fast heating in a closed vessel a heavy detonation occurs which is accompanied by a bright blue flashlight. In contrast, pure α- and β-Hg(N_3)_2 sublime under argon at temperatures of about 180–205°C on slow heating. In the absence of argon, the slow formation of yellow HgO is observed at these temperatures. While all the species are remarkably stable in air or even in water for several months, β-Hg(N_3)_2 is found to completely convert into α-Hg(N_3)_2 within hours in aqueous solution.

Table 1 summarizes the characterization of all the binary mercury azides. Two well-resolved ¹⁴N NMR resonance

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signals were found in the spectrum (run in [D$_6$]DMSO) at 300 K for α-Hg(N$_3$)$_2$, while it was impossible to obtain NMR data for [Hg$_2$N]N$_3$ owing to its low solubility. It was also impossible to detect Hg$_2$(N$_3$)$_2$ in [D$_6$]DMSO because it disproportionates into Hg(N$_3$)$_2$ and Hg within minutes. Thus the spectrum of Hg(N$_3$)$_2$ was always observed. As expected, the ^{14}N spectrum of α-Hg(N$_3$)$_2$ shows a sharp signal at $\delta = -133$ ppm ($\Delta\nu_{1/2} = 65$ Hz) for the N$_\beta$ atoms and a medium-sharp resonance signal at $\delta = -261$ ppm ($\Delta\nu_{1/2} = 690$ Hz) for the N$_\gamma$ atoms in accord with literature values for covalently bound azido groups (e.g. -137 ($\nu_{1/2} = 71$ Hz) and $\delta = -260$ ppm ($\nu_{1/2} = 632$ Hz) for Bi(N$_3$)$_3$).[21] The observation of only one set of azide signals and the absence of the N$_\alpha$ resonance indicate strong quadrupole relaxation effects and a rapid ligand exchange on the NMR timescale.[22] The ^{199}Hg NMR spectrum of Hg(N$_3$)$_2$ exhibits one sharp signal at $\delta = -1745$ ppm in [D$_6$]DMSO (-1785 ppm in D$_2$O, cf. HgCl$_2$ in water $\delta = -1560$ ppm).[23]

At the M06-2X/aug-cc-pvTZ level of theory, two isomers were found for Hg$_2$(N$_3$)$_2$ (*cis-C$_{2v}$* and *trans-C$_{2h}$*) and Hg(N$_3$)$_2$ (*cis-C$_{2v}$* and *trans-C$_2$*), which are almost equal in energy ($\Delta G^{298} < 1$ kcal mol^{-1}).[16] Owing to a very flat potential the conversion occurs almost barrier free by rotation. The charge distribution for all four azides is characterized by alternating net charges along the Hg$^{(\delta+)}$-N$^{(\delta-)}$-N$^{(\delta+)}$-N$^{(\delta-)}$ units with a large positive charge at the Hg atom (Table 1). The ionic bonding between the Hg$_2^{2+}$/Hg^{2+} and the azido ligands as well as the covalent bonding between $^+$Hg–Hg$^+$ in Hg$_2$(N$_3$)$_2$ becomes clearly visible in the electron localization function (ELF) which also displays distorted lone pairs located on the N$_\alpha$ atoms (see Figure 2 for Hg$_2$(N$_3$)$_2$ and Figure S23[16] for Hg(N$_3$)$_2$).

The vibrational spectra of Hg^I and Hg^{II} azides feature the presence of azido ligands as shown by the asymmetrical stretching mode in the range 2127–2044 cm^{-1}, the symmetrical stretching mode at 1373–1178 cm^{-1} and the deformation mode at 666–570 cm^{-1}.[3,16] The asymmetric stretching mode of β-[Hg$_2$N]N$_3$ is observed at significantly lower wave number with 1959 cm^{-1} (cf. 1971 cm^{-1} in α-[Hg$_2$N]N$_3$) which is to our knowledge the lowest value ever found. This result, together with the fact that the $\nu_{as,N3}$ is not Raman active clearly indicates the presence of a $D_{\infty h}$ symmetric N$_3^-$ ion which only interacts electrostatically with the [Hg$_2$N]$^+$ framework. The Hg–N stretching modes in mercury(I) and mercury(II) azide are found in the range 434–339 cm^{-1} (661–706 cm^{-1} in [Hg$_2$N]N$_3$) in accord with our computations.[16]

The structures of α-[Hg$_2$N]N$_3$ and β-[Hg$_2$N]N$_3$ were studied by means of powder diffraction and Rietveld refinements. The powder pattern of β-[Hg$_2$N]N$_3$ could be indexed in agreement with the cubic space group $Fd\bar{3}m$ with $a = 9.5167(1)$ Å and a volume of 861.90(4) Å^3 (Figure 1). Integral reflection intensities were extracted by the Pawley method and the structure was solved by charge-flipping which initially yielded the Hg positions. All further N atoms could be located by successive difference Fourier syntheses. The cubic Millon's base is isostructural to the *anti-β-cristobalite* type (SiO$_2 = {}^3_\infty[\text{SiO}_{4/2}]$). The Hg–N distance in the NHg$_4$ tetrahedra is 2.0604(1) Å in cubic β-[Hg$_2$N]N$_3$ (cf. 2.040(13) Å in [Hg$_2$N]NO$_3$).[5c] The N$_3^-$ ions are located in the cavities and
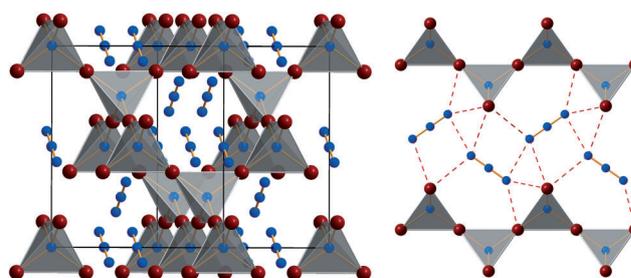

Figure 1. Left: Perspective view of the unit cell of β-[Hg$_2$N]N$_3$. Right: Coordination environment of the azide anions in β-[Hg$_2$N]N$_3$. Disorder of the azide anions not displayed. Red Hg, blue N.

compensate the charge.[24] The refined N–N distance is 1.226(6) Å (cf. 1.18840(8) Å, determined by laser velocity modulation spectroscopy in the gas phase).[25] Each azide ion points to the face of one NHg$_4$ tetrahedron resulting in three Hg···N interactions of 2.941(6) Å, along with four further weak contacts of 3.466(6) Å to adjacent Hg atoms. The closest terminal N···N distance is very short at 2.741(9) Å (cf. Σr_{vdW}(N-N) = 3.1 Å)[26] which leads to a zigzag chain-like arrangement of the azide ions in the NHg$_2$ lattice (Figure 1, right). α-[Hg$_2$N]N$_3$ crystallizes in the hexagonal space group $P6_3/mmc$. Although the azide ions are so severely disordered in the hexagonal modification, that their positions cannot be refined, its cationic [Hg$_2$N]$^+ = {}^3_\infty[$NHg$_{4/2}]^+$ framework clearly corresponds to the *anti*-tridymite structure type, another modification of SiO$_2$.

Hg$_2$(N$_3$)$_2$ crystallizes in the monoclinic space group $P2_1/n$ with two formula units per cell. As displayed in Figure 2, the solid-state structure mainly consists of Hg$_2$(N$_3$)$_3$ molecules with equal Hg-N1/Hg-N1' distances as a result of symmetry (2.161(4) Å, cf. Σr_{cov}(Hg-N) = 2.04 Å[27] and 2.18(2) from powder diffraction data).[6b] In addition three further weak Hg···N van der Waals interactions are found (Hg1-N1^{ii} 2.801(4), Hg1-N1^{iii} 2.875(4), Hg1-N3^{iv}
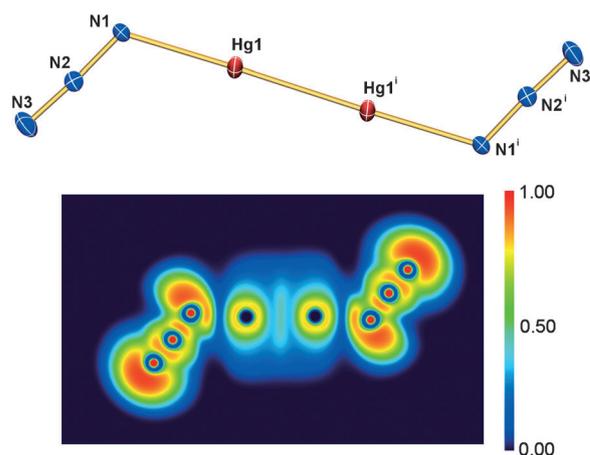

Figure 2. Top: ORTEP drawing of Hg$_2$(N$_3$)$_2$. Thermal ellipsoids set at 50% probability at 173 K. Selected structural data are summarized in Table 1. Symmetry code (i) $-x+2$, $-y$, $-z+1$. Bottom: Two-dimensional cross section through the molecule plane of the electron localization function (ELF).

2.961(5) Å, Σr_{vdW}(Hg-N) = 3.10 Å).[28] The Hg1-Hg1′ distance is 2.5331(3) Å in accord with the published distance of 2.544(3) Å[6b] (cf. Hg_2F_2 2.508(1), Hg_2Cl_2 2.526(6),[29] and Σr_{cov}(Hg-Hg) = 2.66 Å).[27] As observed for Hg_2X_2 (X = halogen), the N1-Hg1-Hg1′-N1′ unit is almost linear (deviation < 1.2°, Figure 2), while the N2-N1-Hg1 angle amounts to 118.9(3)° and the Hg-N_3 unit adopts the typical *trans*-bent structure with a N1-N2-N3 angle of 176.6(5)°.

α-$Hg(N_3)_2$ crystallizes in the orthorhombic space group $Pca2_1$ with one independent molecule per asymmetric unit (Figure 3). The primary coordination sphere of the Hg atom consists of two slightly trans-bent azido ligands with a N1-Hg-

slightly longer than that observed in α-$Hg(N_3)_2$ (Table 1). In analogy to α-$Hg(N_3)_2$, the overall coordination sphere of the Hg^{2+} ion can be described as distorted pentagonal bipyramidal with five Hg···N intermolecular interactions to five adjacent azido groups at distances between 2.632(4) (Hg1···N4[i]) and 3.196(5) Å (Hg1···N1[v]) (Figure 3). While the intermolecular interactions in α-$Hg(N_3)_2$ lead to the formation of layers parallel (010), which are further interconnected to a three-dimensional network, the secondary Hg···N interactions in β-$Hg(N_3)_2$ lead to the formation of a channel-like structure along [001] with considerably shorter Hg···Hg distances (3.9138(2), cf. 4.3722(2) Å in α-$Hg(N_3)_2$).[16]

In conclusion, we present for the first time a comprehensive study of the azide salt of Millon's base along with the isolation of the highly labile β-$Hg(N_3)_2$. While the structural elucidation of $[Hg_2N]N_3$ and the metastable β-$Hg(N_3)_2$ fills an open gap in azide chemistry, the azide salt of Millon's base represents the first example of binary nitrido–metal azide consisting of a three-dimensional cationic network structure which incorporates the azide ions in the cavities and are only loosely bound by electrostatic forces.

Figure 3. Top: ORTEP drawing of α-$Hg(N_3)_2$ (left) and β-$Hg(N_3)_2$ (right). Thermal ellipsoids set at 50% probability at 173 K. Selected structural data are summarized in Table 1. Bottom: Coordination sphere around Hg^{2+} in α-$Hg(N_3)_2$ (left, symmetry codes: (i) $x-0.5$, $-y+1$, z; (ii) $-x+2$, $-y+1$, $z+0.5$; (iii) $-x+2$, $-y$, $z+0.5$; (iv) $-x+2$, $-y+1$, $z-0.5$; (v) $x+0.5$, $-y$, z) and around Hg^{2+} in β-$Hg(N_3)_2$ (right, symmetry code: (i) $-x$, y, $z+0.5$; (ii) x, $-y$, $z-0.5$; (iii) $-x+0.5$, $-y+0.5$, $z+0.5$; (iv) $-x$, y, $z-0.5$; (v) $-x-1$, y, $z-0.5$).

N4 angle of 173.0(2)° (cf. 175(1)° isotropically refined single-crystal X-ray analysis[6e]) and two slightly different Hg–N distances (Hg–N1 2.048(5), Hg–N4 2.076(4) Å) which are somewhat shorter than that observed in $Hg_2(N_3)_2$ (2.161(4) Å) but in agreement with those previously reported (Hg-N1 2.04(2), Hg-N4 2.14(2) Å).[6e] Five Hg···N intermolecular interactions with five adjacent azido groups are observed at distances between 2.764(5) (Hg1···N4[i])–3.138(6) Å (Hg1···N6[v]). Including these van der Waals interactions, the overall coordination sphere of the Hg^{2+} ion corresponds to a distorted pentagonal bipyramid (Figure 3).

β-$Hg(N_3)_2$ crystallizes in the orthorhombic space group $Iba2$ with four formula units per cell. The coordination environment of the Hg atom is displayed in Figure 3. In contrast to α-$Hg(N_3)_2$, the two azido ligands are arranged in a *cis* conformation with respect to the Hg atom (N2-N1-N4-N5 24.13, cf. 145.6° in α-$Hg(N_3)_2$) with an almost linear N1-Hg-N4 angle of 178.3(2)° and there are two very different Hg–N distances (Hg–N1 2.069(4), Hg–N4 2.098(4) Å) which are

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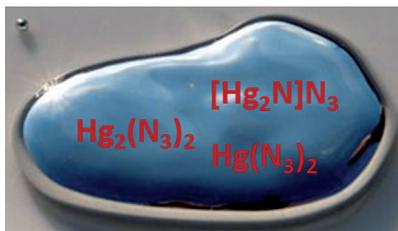
Communications

Mercury Azides

H. Lund, O. Oeckler, T. Schröder,
A. Schulz,* A. Villinger* —— ▮▮▮▮–▮▮▮▮

Mercury Azides and the Azide of Millon's
Base

[Hg$_2$N]N$_3$

Hg$_2$(N$_3$)$_2$

Hg(N$_3$)$_2$

Always look on the bright azide of life:
The synthesis of Millon's base azido salt
[Hg$_2$N]N$_3$, and the metastable β-Hg(N$_3$)$_2$,
along with their full characterization is
possible for the first time and closes an
open gap in azide chemistry.