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The Crystal and Molecular Structure of Mercury Fulminate (Knallquecksilber) [1]

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Dedicated to Professor Rolf Huisgen

Abstract. A short survey on the fascinating history of mercury fulminate is given. The crystal structure of $Hg(CNO)_2$ has been determined using single crystal X-ray diffraction. Mercury fulminate crystallizes in an orthorhombic cell, space group *Cmce* with a = 5.3549(2), b = 10.4585(5), c = 7.5579(4) Å and Z = 4. The distances and angles in the O-N≡C-Hg-C≡N-O molecule are Hg-C 2.029(6) Å, C≡N 1.143(8) Å, N-O 1.248(6) Å and C-Hg-C 180.0(1)°, Hg-C≡N 169.1(5)°, C≡N-O 179.7(6)°. Each mercury atom is surrounded by two oxygen atoms from neighbouring $Hg(CNO)_2$ molecules with a nonbonding distance of Hg···O 2.833(4) Å. The Hg-C bond lengths in the linear $Hg(CNO)_2$ molecules are shorter than those in the tetrahedral complex $[Hg(CNO)_4]^{2-}$. This refers to a large contribution of the 6s orbital in the Hg-C bonds of $Hg(CNO)_2$. The results of the X-ray powder investigation on $Hg(CNO)_2$ are also reported.

Keywords: Mercury fulminate; Knallquecksilber; Crystal structure

Introduction

The alchemists in the 17th century, among them *Cornelius Drebbel* (1572-1633) and *Johann Kunckel von Löwenstern* (1630-1703) have known that mixtures of "spiritus vini" with mercury and silver in "aqua fortis" could explode [2]. Essentially, *Kunckel* described in his book "Laboratorium Chymicum" the violent formation of mercury fulminate from mercury nitrate and alcohol but he did not isolate it. The English chemist *Edward Howard* (1774-1816) [3, 4] succeeded in 1799 (in the beginning of the "Scientific Chemistry") to isolate mercury fulminate by treating a solution of mercury in nitric acid with ethanol. *Howard's* report [4] in 1800 on the preparation and properties was a sensation within the scientific world [2a, 3]. *Howard* originally planned to synthesize hydrochloric acid which at that time was regarded as a combination of oxygen, hydrogen and a hypothetical element "murium". As oxygen source *Howard* used nitric acid, and for hydrogen he took ethanol together with a metal (Hg) to give a metal chloride. To his surprise a violent detonation occurred when he tried to liberate hydrogen chloride from the greyish-white product by reaction with concentrated sulphuric acid.

From 1820 until 1855 *Justus von Liebig* (1803-1873) was fascinated by the chemistry of mercury and silver fulminates [5]. In 1824 *Liebig* and *Gay-Lussac* succeeded in analyzing silver fulminate as AgCNO [6]. This master piece of chemical work together with *Wöhler's* silver cyanate (AgNCO) led to the concept of isomerism. *Scholl* [7a] and *Nef* [7b] formulated fulminic acid as oxime of carbon monoxide and *Lothar Wöhler* [8] proved the monomeric nature of the fulminate ion $C{\equiv}N\text{-}O^-$.

Besides *Justus von Liebig* and *Joseph Louis Gay-Lussac* many famous chemists [2b] were engaged in the chemistry of mercury and silver fulminate: *Friedrich Wöhler*, *Jöns Jakob Berzelius*, *August Kekulé*, *Louis-Jacques Thenard*, *Claude-Louis Berthollet*, *Pierre Berthelot* [9], *Heinrich Wieland* [2b, 10], *Linus Pauling*, *Rolf Huisgen* [11]. *Berthelot* [9] reported a very exact analysis of $Hg(CNO)_2$ and studied its explosive properties ($Hg(CNO)_2 \rightarrow Hg + 2CO + N_2$). *Wieland* offered − after his own important contributions to the chemistry of fulminic acid − a widely accepted interpretation for *Howard's* formation of mercury fulminate from mercury, nitric acid and ethanol [12].

Mercury fulminate was widely used as primary explosive for nearly a hundred years. In the beginning of the 20th century the annual production of mercury fulminate only in Germany was about 100 000 kg per year [2a, 13]. *A. Nobel* [2a, 14] used this energetic compound as a component in his recent developed metal blasting cap detonator to initiate dynamite. The wide application of dynamite was only possible when the use of $Hg(CNO)_2$ as primary explosive guaranteed a safe ignition [13]. For this purpose it is now replaced by lead azide which is more stable on storage [15].

To our knowledge a detailed X-ray crystal structure determination of mercury fulminate has not been carried out. *Miles* [16] reported a good method for the crystallization of

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mercury fulminate and performed first investigations on the crystal structure of mercury fulminate with single crystals already in 1931. He correctly derived the holohedric orthorhombic crystal class and also the lattice parameters (a = 5.48, b = 7.71, c = 10.43 Å, V = 441 Å^3. But no atomic positions of the constituent atoms were given.

About twenty years later, *Suzuki* [17] performed a single crystal investigation on mercury fulminate. He could set Hg atoms correctly in the positions of a face centred lattice with a total of only 49 reflections, indexed using the cell parameters given by *Miles* [16]. However, due to the wrong space group, the positions of the C, N and O atoms could not be located and a bent CNO-Hg-ONC structure was proposed as it was generally assumed at that time.

Within the last decades, two results of X-ray powder investigations have also been published. The first was presented by the *International Centre for Diffraction Data* (ICCD) as powder diffraction file 00-002-0287 for mercury fulminate, $HgC_2N_2O_2$, determined with *CuKα1* radiation (λ = 1.540598 Å). It contained 22 d-values for non-indexed reflections [18]. These data were obtained from Canadian Industries Limited as private communication. The lattice parameters obtained by this d-values were calculated by least squares fit and correspond to a = 5.398(5), c = 10.214(4) and c = 7.630(10) Å. The result of the second X-ray powder investigation on mercury fulminate was published 1981 by *Brown* and *Swallowe* [19]. In this case, *NiKα* radiation was used (λ = 1.6592 Å) with longer wave length in comparison to that with Cu radiation. The precision of the obtained values is lower in this case since mercury fulminate strongly absorbs X-ray radiation. As a consequence, the obtained lattice parameters calculated by least squares fit show higher standard deviations (a = 5.44(3), b = 10.38(4), c = 7.75(5) Å).

Here we report the results of the X-ray investigations of single crystals as well as powders of $Hg(CNO)_2$. The single crystal investigation reveals − as expected − almost linear O-N-C-Hg-C-N-O bonds, similar to those in mercury cyanide NC-Hg-CN [20]. *Liebig* already recognized the close similar between metal fulminates and metal cyanides [5, 21]. In analogy, the correct structure for fulminic acid is H-C≡N-O [2d, 22, 23] and not C≡N-OH. Furthermore, the fulminate ligand forms transition metal complexes that are very similar to those of cyanide [5, 24]. The X-ray structure determination of two polymorphic forms of silver fulminate [25] revealed very interesting structures containing CNO bridges and three centred Ag-C-Ag bonds in hexameric units or infinite chains. The structures of the metal complexes $[(Ph_3P)_2Pt(CNO)_2]$ [26], $[Ph_3PAuCNO]$ [27], $[Au(CNO)_2]^-$ [28][1)], $[M(CNO)_4]^{2-}$ (M = Ni, Pt, Zn) [29][2)],$[Hg(CNO)_4]^{2-}$ [30][1)] as well as $[Co(CNO)_6]^{3-}$ [31][1)] with almost linear M-C≡N-O bonds were determined using X-ray diffraction. Density functional theory (DFT) calculations for these fulminato complexes are in good agreement with the observed structural parameters [32]. In contrast, a recent DFT calculation predicts bent CNO-Hg-ONC units in mercury fulminate [33], a structure which to our surprise is still present in the literature.

Experimental Section

Synthesis

$Hg(CNO)_2$ was synthesized by dissolving 1 g of mercury in 12 g of nitric acid (ρ = 1.4 g cm^{-3}) and adding 11 g of ethanol to this solution in two portions [34]. It is important to add the first half of ethanol before the red brown gases have disappeared. *Caution*: Mercury fulminate is sensitive to impact and friction and is easily detonated by sparks and flames. Before use it should be stored under water and with exclusion of light.

Single Crystal Preparation

Single crystals of sufficient quality for the structure determination were obtained from aqueous ammonia, water, ethanol solutions (1:1:1) [16] and dried on filter paper with the exclusion of light. Small crystals of rhombic habitus with well-developed faces were selected under a polarization microscope and then cooled to 100 K using a *Cryojet Controller* of an *Oxford Xcalibur3 CCD* single crystal diffractometer from *Oxford Diffraction*.

Powder Preparation

For X-ray powder experiments freshly prepared microcrystalline mercury fulminate was used. After drying on filter paper, a *Lindemann* capillary (d = 0.5 mm) was carefully filled in order to prevent grinding.

Single Crystal X-ray Diffraction Experiments

A single crystal of mercury fulminate (0.05 × 0.05 × 0.01 mm) was measured using an *Oxford Xcalibur3 CCD* single crystal diffractometer from *Oxford Diffraction* (*MoKα* radiation, graphite monochromator, λ = 0.71073 Å). The temperature (100 K) of the single crystal was maintained using a *Cryojet Controller* from *Oxford Diffraction*. The conditions limiting possible reflections were hkl: h + k = 2n, h0l: l = 2n, hk0: h = 2n yielding the space group *Cmce* (No. 64, former space group *Cmca*). The derived centre of symmetry of this space group is in agreement with morphological studies of *Miles* [16]. A total of 4428 data were collected in the 2-Theta range up to 55.0° according to a reflection range from −6 < h < 6, −13 < k < 13, −9 < l < 9. The data were corrected for absorption. After merging, 257 unique reflections with a redundancy of seventeen remained resulting in an reliability index R_{int} = 4.18 %. The structure was solved using *SHELXS-97* [35a] and refined using *SHELXL-97* [35b]. A summary of the crystallographic data for mercury fulminate obtained by the single crystal investigation is shown in Table 1. The positional parameters and the thermal displacement parameters are listed in Table 2. Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karslruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-606; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD 417930.

[1)] as $[Ph_4As]^+$ salt; [2)] as $[(C_3H_7)_4N]^+$ salts

Table 1 Crystallographic Data for $Hg(CNO)_2$ obtained by a Single Crystal Investigation at 100 K.

Formula	$Hg(CNO)_2$
Formula Weight	284.63
Temperature / K	100
Crystal System	orthorhombic
Space Group	*Cmce*
a / Å	5.3549(2)
b / Å	10.4585(5)
c / Å	7.5579(4)
Volume / Å^3	423.27(3)
Z	4
Absorption Coefficient / mm^{-1}	36.220
Density calc. / g / cm^3	4.467
F(000)	488
2 Theta / °	55.0
Index Ranges	$-6 < h < 6$; $-13 < k < 13$; $-9 < l < 9$
Reflections Collected	4428 [R_{int} = 0.0418]
Reflections Unique	257
Parameters	23
GOOF	0.906
R_1 / wR_2 [$I > 2\sigma(I)$]	0.0111 / 0.0241
R_1 / wR_2 (all data)	0.0202 / 0.0250
Largest Rest. Peak / e·Å^{-3}	0.478

Notes. Standard deviation in parentheses.

Table 2 Atomic Coordinates and Thermal Displacement Parameters /Å^2 for $Hg(CNO)_2$ at 100 K obtained from a Single-Crystal Investigation.

atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
Hg	0	0	0	0.0148 (1)	0.0141 (1)	0.0209 (2)	−0.0032 (3)	0	0	0.0166 (1)
C	0	0.8186 (6)	0.0951 (8)	0.0126 (3)	0.0213 (3)	0.0220 (3)	0.0013 (2)	0	0	0.0187 (1)
N	0	0.7109 (5)	0.1210 (6)	0.0122 (2)	0.0263 (3)	0.0144 (2)	0.0040 (2)	0	0	0.0176 (1)
O	0	0.5932 (4)	0.1481 (6)	0.0245 (2)	0.0193 (2)	0.0299 (2)	0.0104 (2)	0	0	0.0246 (9)

Notes. Standard deviation in parentheses

X-ray Powder Experiments

An X-ray powder investigation of the micro crystalline $Hg(CNO)_2$ was performed on a *Huber G644 Guinier Diffractometer* using *MoKα1* radiation (λ = 0.7093 Å, quartz monochromator). The angle calibration of the diffractometer was performed using electronic grade germanium (a = 5.6575 Å). In the 2θ-range 1000 data points were collected with a counting time of 100 seconds for each increment (0.04°) between 6 and 46°.

The *Guinier* diffractogram was analysed by the *Rietveld* technique using the program *FullProf* [36]. The diffractogram was refined by profile matching [37] in the space group *Cmce* with reliability indices R = 6.36 % and R_{wp} = 8.91 %. The corresponding lattice parameters are a = 5.470(3), b = 10.376(5) and c = 7.700(4) Å at 295 K. Using the positional parameters derived by the single crystal investigation and applying soft distance constraints for Hg-C, C-N and N-O (2.03, 1.14, 1.25 Å), the *Guinier* diffractogram could be refined to R = 8.91 % and R_{wp} = 11.70 %. The *Rietveld* plot for the refinement is shown in Figure 1. The crystallographic data for the powder investigation at room temperature are summarized in Table 3.

The analysis of the *Guinier* powder data by applying the *Rietveld* technique does not allow for a decision whether the fulminate group is bonded via C-Hg-C or O-Hg-O due to the small scattering contribution of the light non-metal atoms in comparison to mercury. The scattering contribution of the atoms at small diffraction angles is related to the squares of their total electron numbers:

80^2 (one mercury atom) : $2{\cdot}6^2$ (two carbon atoms): $2{\cdot}7^2$ (two nitrogen atoms) : $2{\cdot}8^2$ (two oxygen atoms) = 6400 : 72 : 98 : 128 ≈ 100 : 1.1 : 1.5 : 2.0. In comparison to mercury, the scattering contribution of the C-, N- and O-atoms in mercury fulminate lies between 1 and 2 %. The nitrogen atoms in $Hg_2(N_3)_2$ next to mercury could not be located for the same reason by *Meyer* et al. [38]. A reliable decision between C-Hg-C and O-Hg-O bonding in mercury fulminate can be made on the basis of precise single crystal X-ray diffraction data. The reliability indices R_1 / wR_2 [$I > 2\sigma$ (I)] for C-Hg-C bonding are 0.0111 / 0.0241 (Table 1) in comparison to those obtained when O-Hg-O bonding is assumed (R_1 / wR_2 [$I > 2\sigma$ (I)] 0.0362 / 0.0576).

Table 3 Crystallographic Data for $Hg(CNO)_2$ obtained by X-Ray Powder Investigation at 295 K with Mo Kα1 radiation.

Temperature / K		295	
a / Å		5.470(3)	
b / Å		10.376(5)	
c / Å		7.700(4)	
volume / Å^3		437.0(3)	
Hg (x,y,z)	0	0	0
C (x,y,z)	0	0.818(3)	0.095(3)
N (x,y,z)	0	0.711(3)	0.123(3)
O (x,y,z)	0	0.593(3)	0.149(3)
R		0.0868	
R_{wp}		0.114	
R_{Bragg}		0.151	

Notes. Standard deviation in parentheses

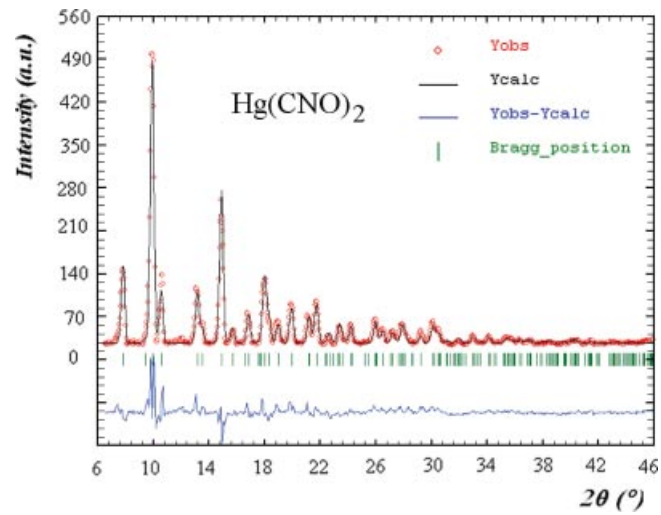

Fig. 1 *Rietveld* plot of the *Guinier* diffractogram for Mercury Fulminate obtained at 295 K using *MoKα1* radiation in the 2-Theta-range from 6−46°.

Results and Discussion

From the results of this structural investigation it is obvious that crystals of mercury fulminate consist of discrete monomeric molecules ONC-Hg-CNO which are C-Hg-C bonded.

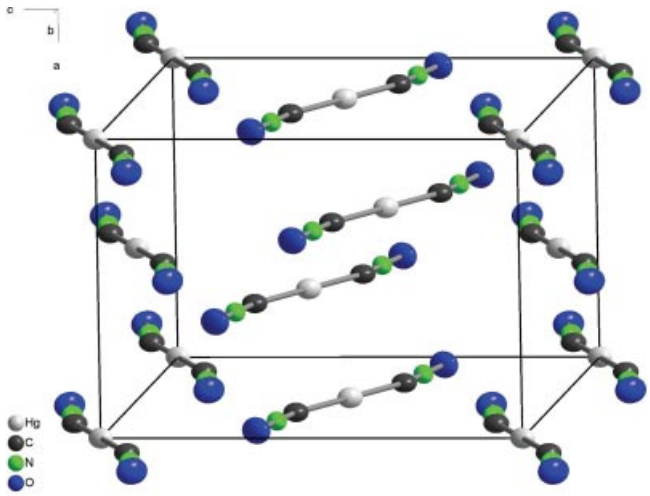

Fig. 2 Representation of the unit cell of mercury fulminate along [010]. The anisotropic thermal displacement parameters are shown at the 50 % probability level.

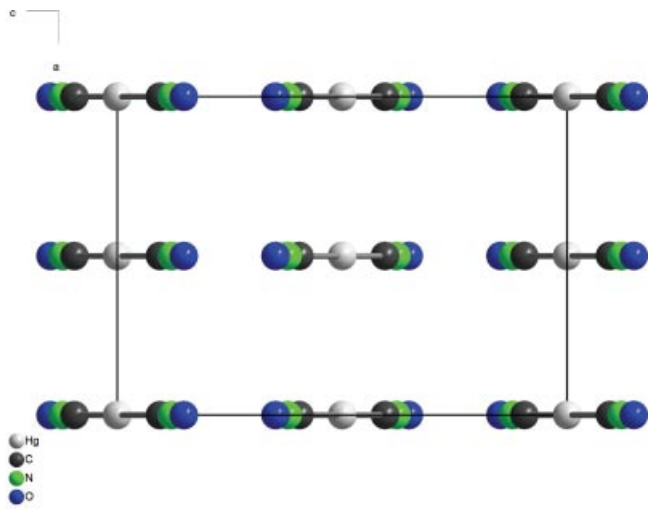

Fig. 3 Planar layers of mercury fulminate molecules at x = 0 and x = 0.5. The anisotropic thermal displacement parameters are shown at the 50 % probability level.

Figure 2 shows a view along [010] on the structure of mercury fulminate.

The mercury atoms have the positions of a face-centred lattice at (0,0,0), (0,0.5,0.5), (0.5,0.5,0) and (0.5,0,0.5) arranging the discrete mercury fulminate molecules at layers with x = 0 and x = 0.5 in the b-c-plane. Figure 3 shows planar layers of mercury fulminate molecules lying at x = 0 and x = 0.5 along [010].

One discrete mercury fulminate molecule is shown in Figure 4 with bond lengths and bond angles.

The fulminate group CNO consists of a short carbon-nitrogen and a longer nitrogen-oxygen bond. The carbon-nitrogen bond length is 1.143(8) Å. This refers to a triple bond, since the tabulated bond length C≡N is 1.11 Å and that for C=N is 1.22 [39]. The nitrogen-oxygen bond with a

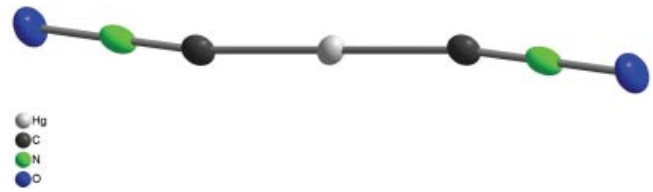

Fig. 4 Representation of one mercury fulminate molecule with bond lengths and bond angles. The anisotropic thermal displacement parameters are shown at the 50 % probability level. Selected bond lengths /Å and angles / °: Hg-C 2.029(6), C-N 1.143(8), N-O 1.248(6), C-Hg-C 180.0(2), Hg-C-N 169.1(5), C-N-O 179.7(6).

Table 4 Bond lengths /Å and angles / ° in mercury fulminates and cyanides

	Hg-C	C≡N	N-O	Hg-C≡N	C≡N-O	C-Hg-C
$Hg(CNO)_2$	2.029	1.143	1.248	169.1	179.7	180.0
$[Hg(CNO)_4]^{2-}$ [30]	2.16	1.13	1.25	170	178	102-118
	2.21	1.14	1.26	172	179	
$Hg(CN)_2$ [20]	2.015	1.137	–	177.0	–	175
$[Hg(CN)_4]^{2-}$ [40]	2.17	1.14	–	178	–	108
	2.19					111

value of 1.248(6) Å is remarkably longer. Here the tabulated bond length for N=O is 1.17 Å and that for N-O is 1.45 Å [39]. Within the limitations of error, the atomic arrangement of the bonds C-N-O and C-Hg-C in the fulminate group is linear (179.7(6)°) and (180.0(2)°), respectively. However, the angle N-C-Hg (169.1(5)°) deviates from linearity by eleven degrees.

The distances and angles of the $Hg(CNO)_2$ molecules (Table 4) are in the same range as for other metal fulminates [5, 26−31]. A very similar structure has been determined for the linear isoelectronic gold complex $[Au(CNO)_2]^-$ [28]. Of interest is the comparison of the linear $Hg(CNO)_2$ with the tetrahedral $[Hg(CNO)_4]^{2-}$ [30]. As with the mercury cyanides [20, 40] (Table 2) the Hg-carbon distance in the neutral linear compounds are considerably shorter than in the tetrahedral complexes which is certainly due to a larger contribution of the 6s orbital in the Hg-C bonds [41]. Remarkably, the Hg-C and C≡N bond lengths in the mercury fulminates and cyanides are very similar (Table 4). In conclusion, the formula O-N≡C-Hg-C≡N-O well describes the bonding in the mercury fulminates.

In order to achieve a higher space filling, the fulminate molecules in the layers at x = 0 and x = 0.5 are rotated against each other by an angle of 41.5°. Figure 5 shows one layer with five discrete monomeric molecules. However, such an arrangement also leads to two mercury-oxygen contacts at 2.833(4) Å. The tabulated *van-der-Waals* radii for mercury and also for oxygen are 1.5 Å [39] leading to a *van-der-Waals* distance of about 3.0 Å. The measured Hg-O distance of 2.83 Å is slightly shorter than the *van-der-Waals* distance indicating some weak interactions. Similar contacts appear in the corresponding cyanide $Hg(CN)_2$ with mercury-nitrogen distances of 2.742 (3) Å [20].

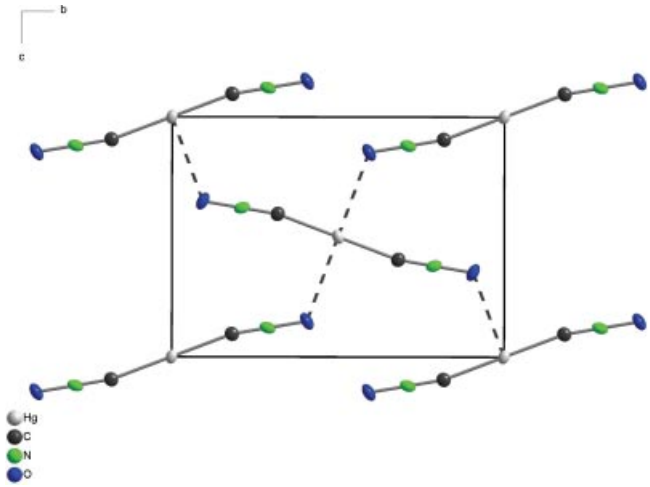

Fig. 5 View along [100] on one layer of mercury fulminate molecules. In this orientation, two oxygen atoms form interatomic distances Hg···O of 2.833(4) Å, smaller than the calculated *vander-Waals* distance of 3.0 Å. The anisotropic thermal displacement parameters are shown at the 50 % probability level.

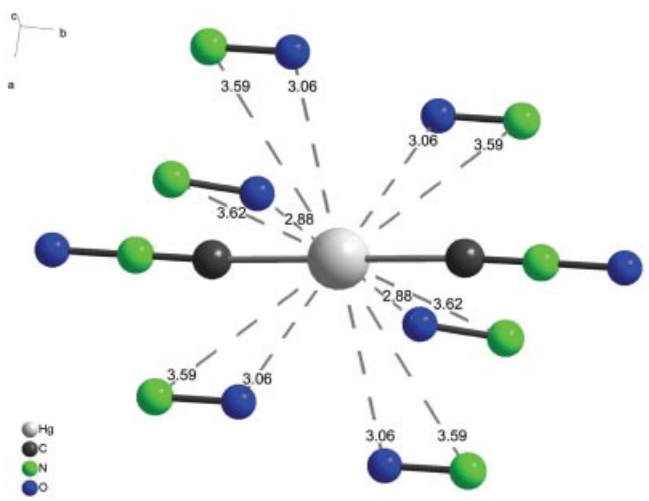

Fig. 6 Distorted polyhedron built up by six oxygen and six nitrogen atoms. The two chemically bonded fulminate groups are also shown. The distances to the central Hg atom are given in Å. The anisotropic thermal displacement parameters are shown at the 50 % probability level.

Considering the two surrounding layers, four additional mercury-oxygen contacts with distances of 3.06 Å are present. This results in six Hg···O distances. There are also six Hg-N distances (four times at 3.59 Å and two times at 3.62 Å).These twelve atoms centred by a mercury atom build up a distorted polyhedron with four atoms at the top, four atoms in the middle and four atoms at the bottom. If these four atoms were arranged symmetrically as parallel squares one would obtain a cuboctahedron. The real polyhedron is far away from this situation, however. Figure 6 shows the distorted polyhedron around one mercury atom and the two fulminate groups.

It is interesting to compare the crystal structure of mercury fulminate $Hg(CNO)_2$ with that of mercury azide (with the analogous formula) $Hg(NNN)_2$. Both the fulminate and the azide anion are linear and contain 16 valence electrons resulting in one negative charge. The crystal structure of mercury azide was determined by *Müller* in 1973 [42]. $Hg(N_3)_2$ crystallizes with four molecules per unit-cell as does the mercury fulminate. Both structures are not isotypic. $Hg(N_3)_2$ crystallizes in the non-centrosymmetric space group $Pca2_1$, $Hg(CNO)_2$ in the centrosymmetric space group *Cmce*. However, the unit-cell volume of the azide is V = 421.1(3) $Å^3$ [42], whereas that of the fulminate equals to 437.6 $Å^3$ (Table 3) at room temperature. As a consequence, the azide is packed more densely (4 %) compared to the fulminate. But the most striking difference is the bonding angle of the azide group to the mercury atom which is due to the totally different hybridization of the atom directly bonded to the mercury atom (C: sp / N: sp^3). According to this, an oxygen bonded fulminate would lead to a bent M-O-N≡C group similar as in the corresponding azide $Hg(N_3)_2$. There are two crystallographic different azide groups in $Hg(N_3)_2$ with N-N-Hg angles of 111(2) and 120(2)° [42]. In $Hg(CNO)_2$ the two fulminate groups are crystallographic identical and have bond angles N-C-Hg of 169.1(5)°. In addition, the atomic arrangement of N-N-N group in the the azide anions deviate with bond angles of 171(3) and 176(2) from linearity. This is also true for the atomic arrangement N-Hg-N with a bond angle of 175(1)°. Quite a puzzle are the Hg-N bond distances of the two crystallographically different azide groups. One Hg-N distance is 2.04(2) whereas the other is 2.14(2) Å [42].

In summary, the molecular and crystal structure of the historically important mercury fulminate has now been solved, more than 300 years after its discovery.

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