

Rapid Communication

On mercurous nitrite and a basic mercurous nitrate derivative

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Mercurous nitrite, first reported by P C Ray in 1896, has a centrosymmetric structure with unsymmetrical nitrite chelation consistent with the hybridization of the metal-metal bond. When left in air with adhering mother liquor it is slowly transformed into a stable basic salt, $\text{Hg}_6(\text{OH})_2(\text{NO}_3)_4$, having a centrosymmetric zigzag structure in which each of the OH group bridges two mercurous moieties and pairs of nitrate ions cap the terminal metal atoms. In both, relatively weak intermolecular Hg-O bonding is present in the lattice. The basic salt ($n = 2$) belongs to a homologous family of general formula $\text{Hg}_2\{(\text{OH})\text{Hg}_2\}_n(\text{NO}_3)_{n+2}$.

Keywords: Inorganic chemistry, Nitrites, Nitrates, Mercurous nitrite, Basic mercurous nitrate, Crystal structure

The discovery of mercurous nitrite, $\text{Hg}_2(\text{NO}_2)_2$, by an apparently counter-intuitive reaction between metallic mercury and diluted nitric acid in 1896 by P C Ray, was the harbinger of the first research school of chemistry in India^{1,2} and immediately attracted international attention^{3,4}. The chemistry of this moderately stable, yellow crystalline solid was elaborated by Ray in a series of later papers⁵⁻⁸ and eventually led him and his students to launch a very fruitful programme on nitrites and related species^{9,10}. Through this communication we pay tribute to Ray in his 150th birth anniversary year. Herein our concerns are the structure of $\text{Hg}_2(\text{NO}_2)_2$ (**1**) and that of the white crystalline basic mercurous nitrate, $\text{Hg}_6(\text{OH})_2(\text{NO}_3)_4$ (**2**) derived therefrom. The latter is shown to belong to a homologous family of basic salts of general formula $\text{Hg}_2\{(\text{OH})\text{Hg}_2\}_n(\text{NO}_3)_{n+2}$.

Experimental

Metallic mercury and conc. nitric acid (sp. gr. 1.41) were obtained from Qualigens and Merck (India) respectively. IR spectrum was recorded using a Perkin-Elmer 783 spectrophotometer.

Ray elaborated the synthesis of (**1**) in several papers^{1,2,5-7} and we have used a scaled-down version of one of these.⁷ In a beaker of 4 cm diameter and 16 cm height, 54 g of mercury was placed followed by addition of 120 ml of dil. nitric acid (prepared by mixing 24 ml conc. nitric acid with 96 ml distilled water). The temperature was maintained throughout at 31 °C. Yellow crystalline (**1**) soon started depositing on the sides of the beaker, spreading slowly over the mercury surface. After 24 hrs the liquid and the unreacted mercury were decanted off and the yellow solid was collected.

The yellow solid thus obtained had adhering mother liquor. When left in air, it slowly transformed (nitrous odor is discernable) into a white crystalline compound. We found the transformation to be complete in a week at 31 °C. Thereafter no further changes were observed. Structure determination revealed the white solid to be the basic nitrate (**2**). A broad IR stretch assignable to O-H vibration was observed at 3458 cm^{-1} .

When the adhering mother liquor was immediately removed by absorption on filter paper, the above transformation became much slower. To arrest this complication for X-ray work, we mounted a dried crystal of (**1**) after covering it with fomblin oil followed by cooling to 100 K in a stream of cold nitrogen. For (**2**) work was done at 293 K. X-ray data were collected on a Bruker SMART APEX-II diffractometer, equipped with graphite monochromated Mo- K_α radiation ($\lambda = 0.71073 \text{ \AA}$), and were corrected for Lorentz-polarization effects. A total of 1355 reflections was collected for (**1**) out of which 588 were unique satisfying the ($I > 2\sigma(I)$) criterion and used for structure determination. For (**2**), the corresponding numbers are 7497 and 1548 respectively. Crystal data of these two complexes are given in Table 1. The structures were solved by employing the SHELXS-97 program package¹¹ and refined by full-matrix least-squares based on F^2 (SHELXL-97)¹². The hydrogen atom in (**2**) was added in the calculated position.

Results and discussion

The formation of mercurous nitrite in a nitric acid environment is somewhat surprising at the first instance, but this has been rationalized by Ray^{1,7} and

Table 1—Crystal data for (1) and (2)

	(1)	(2)
Empirical formula	Hg ₂ N ₂ O ₄	H ₂ Hg ₆ N ₄ O ₁₄
Molecular mass	493.20	1485.60
Temperature (K)	100	293K
Crystal system	Monoclinic	Monoclinic
Space group	P2 ₁ /c	P2 ₁ /n
<i>a</i> (Å)	4.405(5)	8.2141(8)
<i>b</i> (Å)	10.433(5)	10.0641(9)
<i>c</i> (Å)	6.246(5)	10.1665(10)
β (°)	109.104(5)	113.070(2)
<i>V</i> (Å ³)	271.2(4)	773.23(13)
<i>Z</i>	2	2
<i>D</i> _{calcd} (g/cm ³)	6.040	6.381
Cryst. dimen. (mm)	0.13 × 0.13 × 0.14	0.13 × 0.14 × 0.15
Goodness-of-fit	1.07	0.92
Final <i>R</i> indices	0.0500;	0.0312;
[<i>I</i> > 2σ(<i>I</i>)] <i>R</i> ₁ ; <i>wR</i> ₂	0.1280	0.0765

others^{13,14} in terms of the observable initial reductive generation of nitrous acid by the metal. In 1966 the synthesis of (1) and its decomposition to an unidentified product was briefly reported¹⁵. The X-ray structure of (1) has been reported at 298 K at two different levels of accuracy^{16,17}. We have examined the structure of this historic compound at 100 K. In this context, we note that not too many anhydrous salts of the bare mercurous ion with anions of oxo-acids are known and only a few of these have been structurally characterized¹⁸.

Basic mercurous nitrates are relatively complex species usually derived via hydrolysis of normal mercurous nitrate. Ray⁷ contributed to this field but the nature of some of the species could be derived only from structural work done in more recent years¹⁹⁻²³. These however, do not include (2) reported by us herein as the product to which (1) is converted when left in air. The pathway of this transformation in terms of the possible roles of adhering mother liquor, atmospheric oxygen and moisture is under scrutiny.

The lattice of (1) consists of discrete Hg₂(NO₂)₂ molecules which are centrosymmetric and planar. A molecular view is shown in Fig. 1a and relevant bond parameters are listed in Table 2. The nitrite ion is chelated in an unsymmetrical fashion. The near collinearity of the relatively strong Hg1-O1 bond (2.201(13) Å) with the Hg1-Hg1a bond is evidently dictated by the hybridization in the metal-metal bond. The length of the Hg1-O2 bond (2.613(13) Å) is then dependent on the O1-N1-O2 angle. Since the van der Waals radii²⁴ of both O and Hg are 1.5 Å, all Hg-O contacts of length < 3.0 Å are indicative of at least some chemical bonding. In this study, all Hg-O distances (*d*) in the range 2.5 Å < *d* < 3.0 Å are shown

Table 2—Bond distances and bond angles of (1)^a

Bond lengths (Å)		Bond angles (°)	
Hg1-O1	2.201(3)	O1-Hg1-O2	49.6(5)
Hg1-O2	2.613(13)	Hg1-O1-N1	107.9(11)
Hg1-Hg1a	2.540(3)	Hg1a-Hg1-O1	177.0(4)
Hg1-O1 (inter)	2.840(14)	Hg1-O2-N1	88.2(11)
Hg1-O2 (inter)	2.925(14)	Hg1a-Hg1-O2	132.9(3)
O1-N1	1.250(2)	O1-N1-O2	114.3(16)
O2-N1	1.209(2)		

^a(inter) in parenthesis means intermolecular, all other bond parameters are intramolecular.

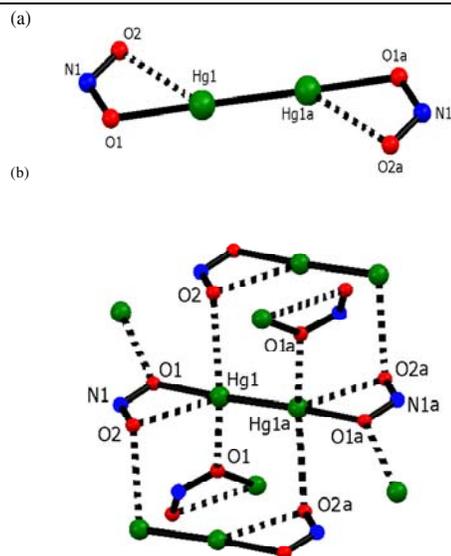


Fig. 1— (a) Molecular view of discrete Hg₂(NO₂)₂ (1); (b) Molecular view of Hg₂(NO₂)₂ (1) showing intermolecular interactions.

as dotted lines in Figs 1 and 2. Intermolecular Hg-O bonds of this type in the lattice of Hg₂(NO₂)₂ are shown in Fig. 1b (distances are in Table 2). In effect, every oxygen atom is linked to two mercury atoms belonging to two different molecules. Our results are in general agreement with those reported previously^{16,17}.

The zigzag molecular structure of monoclinic basic nitrate (2) is shown in Fig. 2a and selected bond parameters are listed in Table 3. It is centrosymmetric and has three crystallographically independent Hg atoms; the center of inversion lies at the midpoint of the Hg3-Hg3a bond. Two nitrate ions cap each of the two terminal mercury atoms. The fragment excluding the nitrate ions is nearly perfectly planar (plane A) and the nitrate O1 and O1a atoms also lie on this plane. The planar nitrate chelate rings incorporating N1 (plane B) and N2 (plane C), make dihedral angles of 60.7° and 77.0° with plane A respectively. The dihedral angle between the two

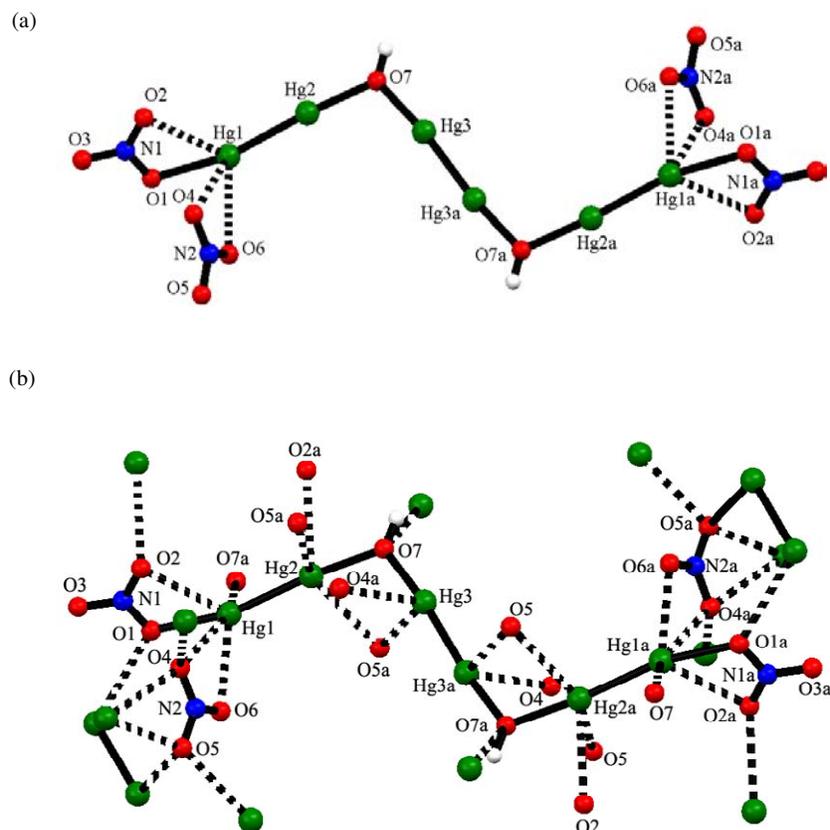


Fig. 2—(a) Molecular view of discrete $\text{Hg}_6(\text{OH})_2(\text{NO}_3)_4(\mathbf{2})$; (b) Molecular view of $\text{Hg}_6(\text{OH})_2(\text{NO}_3)_4(\mathbf{2})$ showing intermolecular interactions.

Table 3—Bond distances (Å) and bond angles ($^\circ$) of $(\mathbf{2})^a$

Bond lengths (Å)				Bond angles ($^\circ$)	
Hg1-O1	2.261(7)	O3-N1	1.224(9)	Hg1-O1-N1	106.2(5)
Hg1-O2	2.742(6)	O4-N2	1.241(10)	Hg1-O2-N1	84.0(5)
Hg1-O4	2.755(7)	O5-N2	1.259(11)	O1-N1-O2	119.7(7)
Hg1-O6	2.676(7)	O6-N2	1.221(9)	Hg2-Hg1-O1	167.64(18)
Hg2-O7	2.119(6)	Hg1-O7a (inter)	2.709(11)	Hg2-Hg1-O2	121.23(13)
Hg3-O7	2.105(7)	Hg2-O2a (inter)	2.916(9)	Hg1-Hg2-O7	172.47(18)
Hg1-Hg2	2.5122(5)	Hg2-O5a (inter)	2.772(12)	Hg3a-Hg3-O7	173.40(17)
Hg3-Hg3a	2.5078(5)	Hg2-O5a (inter)	2.807(10)	Hg2-O7-Hg3	109.19(10)
O1-N1	1.267(10)	Hg3-O5a (inter)	2.863(11)		
O2-N1	1.229(10)	Hg3-O4a (inter)	2.733(6)		

^a(inter) in parenthesis means intermolecular, all other bond parameters are intramolecular.

chelate rings is 68.3° . The shortest Hg-O bonds are those with the hydroxide ligand (2.119(6) Å) and (2.105(7) Å), the nitrate Hg1-O1 bond being somewhat longer at (2.261(7) Å). The latter bond is approximately collinear with the Hg1-Hg2 bond (O1-Hg1-Hg2, $167.64(18)^\circ$). All other nitrate Hg-O bonds have lengths > 2.5 Å. The Hg1-Hg2 and Hg3-Hg3a bonds are nearly equal in length at ~ 2.51 Å which is slightly shorter than that observed in **(1)**. The angle at the hydroxo ion Hg2-O7-Hg3, is 109.1° , the distance between Hg2 and Hg3 being 3.442(1) Å. Intermolecular Hg-O contacts (< 3 Å) are abundant as

can be seen in Fig. 2b and Table 3. The bond parameters in the present complex are comparable to those reported in two other basic mercurous nitrates, viz., $(\text{Hg}_2)_2(\text{OH})(\text{NO}_3)$ **(3)**^{21,22} and $(\text{Hg}_2)_5(\text{OH})_4(\text{NO}_3)_6$ **(4)**^{20,22}.

We would like to point that **(2)**, **(3)** and **(4)** belongs to a homologous family of general formula, $\text{Hg}_2\{(\text{OH})\text{Hg}_2\}_n(\text{NO}_3)_{n+2}$. The values of n in **(2)**, **(3)**, and **(4)**, are respectively 2, 1 and 4. The systems with $n = 3$ does not appear to have structurally characterized. Further, one may also expect higher ($n > 4$) homologues to exist. The $n = 0$ case corresponds to normal mercurous nitrate which has

been characterized structurally both in anhydrous²³ and hydrated¹⁹ forms.

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Supplementary data

Crystallographic data for complexes (1) and (2) have been deposited with the Inorganic Crystal Structure Database, ICSD Nos. 422481 and 422482, respectively. These data can be obtained free of charge from Inorganic Crystal Structure Database via http://www.fiz-karlsruhe.de/request_for_deposited_data.html.

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