Molecule of the Month

Mercurous Nitrite*

Rajarshi Ghosh

Rajarshi Ghosh is an Assistant Professor at the Department of Chemistry, The University of Burdwan, Burdwan. His current research interest is on synthesis and characterization of coordination molecules with special reference to structural studies and biological applications.

Yellow crystalline mercurous nitrite was first reported by P C Rây[1] in 1896. In 1966, Allred *et al* reported that using Rây's method, they had isolated the compound but that it turned into some 'unidentified solid' immediately. This resulted in a controversy that lasted four decades on whether it was possible to isolate mercury(I) nitrite or not. In 2011, A Chakravorty *et al*, on the 150th birth anniversary of Rây, delineated the synthesis as well as X-ray structural characterization of mercurous nitrite.

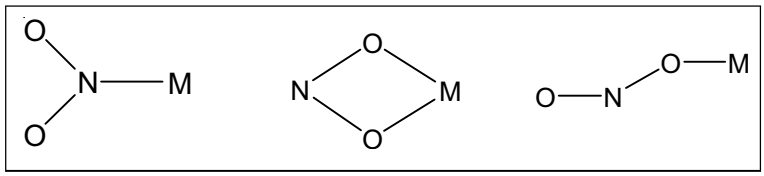
Modern chemical education as well as research in India was pioneered by the many-faceted personality, P C Rây. After completion of his studies in India and abroad he joined Presidency College, Calcutta (now known as Kolkata) as a junior professor in 1889. Very soon he became a popular teacher among his students with his amiable lectures along with scientific demonstrations and historical anecdotes. Along with teaching at Presidency College, Rây took up research work very seriously [1]. Inspite of inadequate facilities available, he synthesized mercurous nitrite in the year 1896 [2a, 2b]. "He isolated the crystals and after a quantitative analysis was convinced that it was a new compound, mercurous nitrite, which can be prepared in the laboratory very easily" [1]. Immediately, this discovery attracted national and international attention [2–4].

The reason for the interest in mercurous nitrite $Hg_2(NO_2)_2$ was that stable mercury(I) complexes are sparse in the literature owing to the instability of mercury(I) towards disproportionation to mercury(II) and metallic mercury in solution. Moreover, the nitrite ion is not very stable and can easily undergo decomposition. But it is to the credit of Rây that he could isolate the compound and perform its quantitative estimation. Preparation of $Hg_2(NO_2)_2$ [2] was an accidental discovery. Rây was trying to prepare water

[1] See *Resonance,* Vol.6, No.1, 2001.

* A tribute to P C Rây on his 152nd birth anniversary.

Keywords
P C Rây, mercurous nitrite, coordination complex, X-ray structures.



Scheme 1. Different binding modes of NO_2^-

soluble mercurous nitrate which is an intermediate for the synthesis of calomel, Hg_2Cl_2. Accordingly, dilute aqueous nitric acid (1:4) was reacted with excess mercury. To his surprise, this resulted in the formation of a yellow crystalline $Hg_2(NO_2)_2$ (see equation (1)). This result was first published in *Journal of Asiatic Society of Bengal* [2a].

$$Hg\ (excess) + HNO_3\ (dilute) \rightarrow Hg_2(NO_2)_2 \qquad (1)$$

In 1966, R A Potts and A L Allred [5] wrote, "This compound was reported by Rây, and an attempt was made to prepare it by his method. The described yellow crystals were obtained, but they slowly decomposed with an odor of nitrogen dioxide over them, leaving an unidentified solid." Things remained unclear until 2011. A Chakravorty *et al* at the Indian Association for the Cultivation of Science in Kolkata isolated and characterized the 'mercurous nitrite' and the 'unidentified solid' [5]. Chakravorty *et al* [6] reported the synthesis of the compound following Rây's method [2] and proved that the compound was actually a coordination complex instead of an ionic compound, but with the same elemental composition.

NO_2^- can bind to metal ions in different ways (*Scheme* 1). From X-ray structural characterization it appeared that one of the O atoms of the two NO_2^- ligands was coordinated (*Scheme* 1c) to each Hg(I) and there is Hg(I)-Hg(I) bonding (*Figure* 1). But the

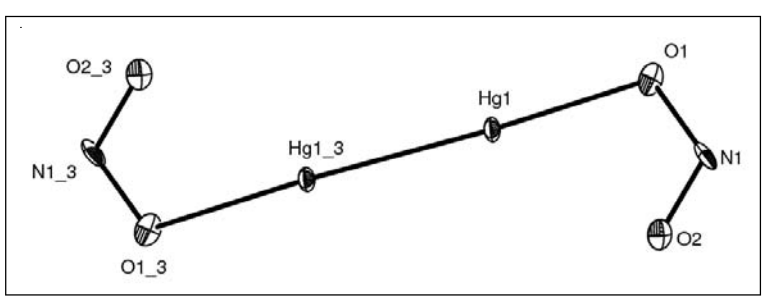


Figure 1. X-ray structure of bis(nitrito-κ O-)dimercury (Hg-Hg)(I).
[CIF file (No.422481) is obtained from Inorganic Crystal Structure Database].
Note that the two (O1 and O2) are co-ordinated differently to Hg1. The Hg1–O2 distance is 2.613Å, which is less than the sum of the van der Waals radii of Hg (1.5Å) and O(1.5Å) indicating chemical interaction between the two.

reason for the combination of soft Hg(I) with hard O centres is not clear yet. Hence, according to the work by Chakravorty [6], the compound synthesized by Rây should be named as (according to IUPAC nomenclature) bis(nitrito-κO-)dimercury(Hg-Hg)(I). The 'unidentified solid' reported by Allred [5] appeared as a white crystalline basic mercurous nitrate, $Hg_6(OH)_2(NO_3)_4$ which was derived from bis(nitrito-κ O-)dimercury(Hg-Hg)(I) (previously called $Hg_2(NO_2)_2$). The former basic nitrate is shown to belong to a homologous family of basic salts with the general formula $Hg_2\{(OH)Hg_2\}_n(NO_3)_{n+2}$. When the yellow crystalline $Hg_2(NO_2)_2$ was left exposed to air, it slowly transformed (nitrous odor is discernable) into a white crystalline compound. It was found that the transformation is completed in a week at 31ºC. Thereafter no further changes were observed. The single crystal X-ray structural characterization of both the compounds confirmed their composition and oxidation states of mercury in each species. Thermal ellipsoid plot of $Hg_2(NO_2)_2$ is given in *Figure* 1.

Interestingly, though the efforts of Allred *et al.* [5] were unsuccessful in the preparation of $Hg_2(NO_2)_2$, their idea regarding the structure of the mercurous salt has been proved to be true by Chakravorty *et al* [6]. According to Allred [5], "If this compound $[Hg_2(NO_2)_2]$ does exist, the nitrite anion would be expected to be bonded to the mercury(I) through the oxygen, nitrito-, rather than the nitrogen, nitro-." The X-ray structure (*Figure* 1) reported by Chakravorty *et al* [6] proved that this speculation of Allred was absolutely correct.

Revisit of the synthesis and characterization of Rây's 'mercurous nitrite' (presently bis(nitrito-κ O-)dimercury(Hg-Hg)(I)) by Chakravorty *et al* has actually ended a long puzzle, which originated from Allred's paper [5].

Suggested Reading

[1] N R Dhar, *Acharya Prafulla Chandra Ray*: *Life and achievements*, Indian Chemical Society, pp.21–23, 1972.

[2] (a) P C Rây, *J Asiatc Soc Bengal*, Vol.65, p.1, 1896; (b) P C Rây, *Z. Anorg. Chem*, Vol.12, p. 365, 1896; (c) P C Rây, *J. Chem. Soc.* Vol.71, p.337, 1897.

[3] Noted in *Nature*, 54, p.83, 1896.

[4] P C Rây, *Life and Experiences of a Bengali Chemist*, The Asiatic Society, Calcutta, Vol.1, p.114, 1996.

[5] R A Potts and A L Allred, *Inorganic Chemistry*, Vol.5, pp.1066–1071, 1966.

[6] S Samanta, S Goswami and A Chakravorty, *Indian J. Chem.*, Vol.50A, pp.137–140, 2011.

Address for Correspondence
Rajarshi Ghosh
Department of Chemistry
The University of Burdwan
Burdwan 713 104, India.
Email:
rajarshi_chem@yahoo.co.in