

Chemical Research of Sir Prafulla Chandra Rây

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Prafulla Chandra Rây was the pathfinder and originator of chemical research in modern India. He was introduced to research by Alexander Crum Brown, a notable chemist and teacher at Edinburgh University. His doctoral work was on the chemistry of double sulphates. He received the D.Sc. degree of Edinburgh University in 1887. A year later he returned to India and in 1889 started his career as a junior professor in Presidency College, Calcutta. He was then twenty-eight. His research activities flourished in the laboratories of the college even though the facilities were inadequate. He moved to the College of Science of Calcutta University as the first Palit Professor of Chemistry in the year 1916 and the work of his school continued there with renewed vigour.

Prafulla Chandra was a synthetic chemist specially of inorganic compounds. But he also made outstanding contributions to the chemistry of thio-organic compounds. He and his students prepared many new interesting families of compounds and examined their physical properties to the extent possible at that time. He first became well known for his work on the inorganic and organic nitrites. Among metals, he had a very special fascination for mercury probably because of its importance in Ayurvedic medicines in which he was very interested. He published about two hundred original papers. The majority of his contributions until 1924 (the year when the *Journal of the Indian Chemical Society* was born) were published in the *Journal of Chemical Society* (London).

It is convenient to discuss Prafulla Chandra's research contributions under a few broad categories highlighted in *Box 1*.

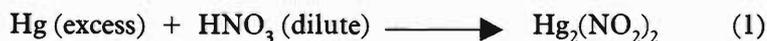
In the following sections we shall present a few selections from his many-sided experimental findings. His celebrated historical

research culminating in the creation of *History of Hindu Chemistry* has not been elaborated in this article.

Mercurous Nitrite and Related Compounds

In 1895 Prafulla Chandra reported the first synthesis of the hitherto unknown mercurous nitrite, $\text{Hg}_2(\text{NO}_2)_2$. This event was described by him in his autobiography as “the discovery of mercurous nitrite opened a new chapter in my life”. It is relevant to mention here that stable mercury(I) complexes are sparse in literature, even today, 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 undergo facile decomposition. The compound, $\text{Hg}_2(\text{NO}_2)_2$ is thus a fascinating example of a stable substance composed of two relatively unstable ions.

The preparation of $\text{Hg}_2(\text{NO}_2)_2$ was an accidental discovery. He wanted to prepare water soluble mercurous nitrate as 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 yellow crystalline $\text{Hg}_2(\text{NO}_2)_2$.



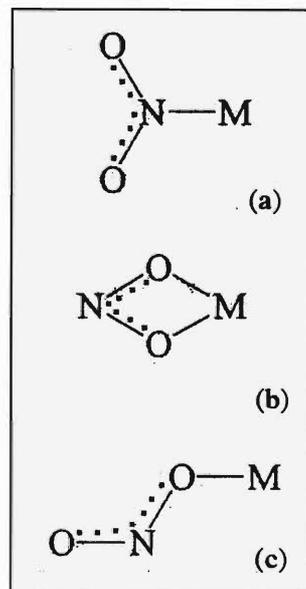
This result was first published in the *Journal of Asiatic Society of Bengal* which was immediately noticed by *Nature*. This was the beginning of a series of thorough investigations which resulted in many significant publications on this nitrite and its derivatives.

It is now known that the nitrite ion can bind to a metal ion in three different fashions (*Figure 1*) and there have been numerous structural investigations in many laboratories around the world to sort out the coordination modes. As mercury (*Figure 1a*) is a soft cation, the nitrite ions in $\text{Hg}_2(\text{NO}_2)_2$ are likely to be linked to mercury (*Figure 1a*), which exist as a dimer due to metal-metal bonding, through the soft nitrogen centers forming a linear N-

Box 1. Categories of Research Contributions

- (i) Metal nitrites with special reference to mercurous nitrite
- (ii) Ammonium nitrite and related compounds
- (iii) Chemistry of sulphur compounds
- (iv) Coordination compounds

Figure 1. Coordination modes of NO_2^- to metal.



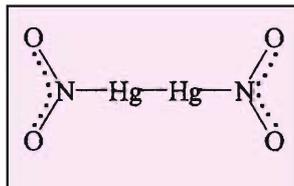


Figure 2. Structure of $\text{Hg}_2(\text{NO}_2)_2$.

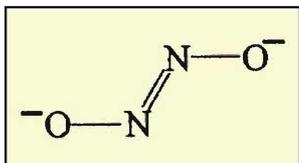
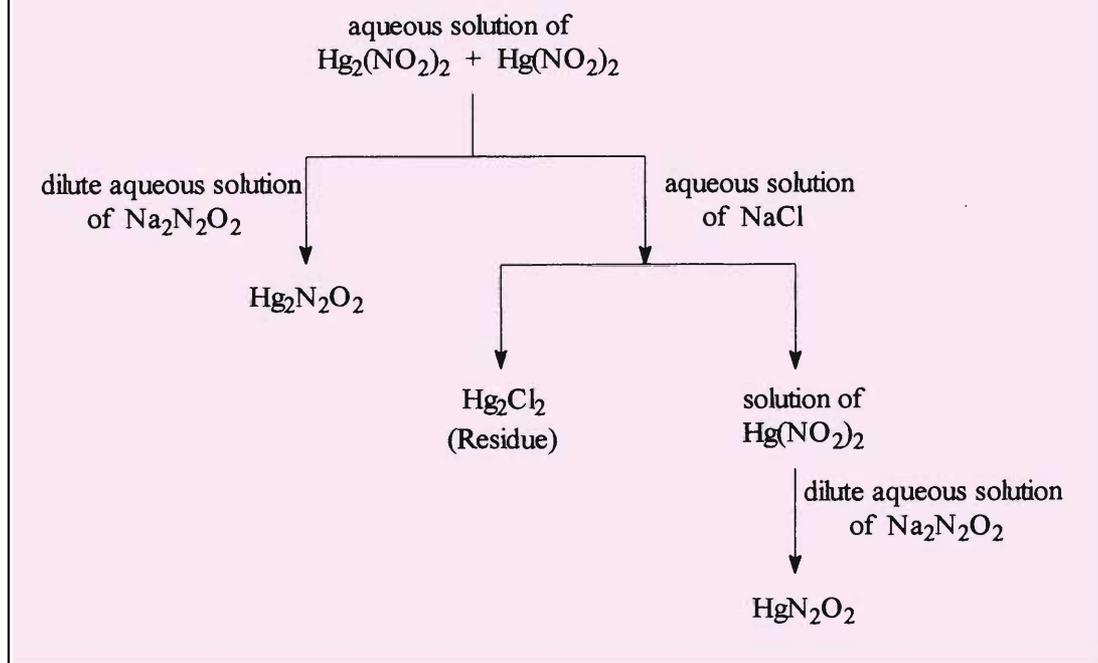


Figure 3. Structure of hyponitrite anion $(\text{N}_2\text{O}_2)^{2-}$.

Hg-Hg-N chain (Figure 2). It was not possible to make such a proposal in Prafulla Chandra's time because structural principles were in their infancy. A direct experimental proof of the structure of the above nitrite is still awaited.

Subsequently, Prafulla Chandra became interested in the chemistry of hyponitrites. Structure of the hyponitrite anion $(\text{N}_2\text{O}_2)^{2-}$ is shown in Figure 3. The hyponitrites were prepared by reacting the corresponding nitrite with aqueous solution of sodium hyponitrite, $\text{Na}_2\text{N}_2\text{O}_2$. The reaction of mercury with nitric acid was used to prepare a solution containing a mixture of mercurous nitrite ($\text{Hg}_2(\text{NO}_2)_2$) and mercuric nitrite ($\text{Hg}(\text{NO}_2)_2$). From this mixture, he isolated the corresponding hyponitrites in the pure form by following the scheme shown in Box 2. A simpler procedure for the direct synthesis of mercuric hyponitrite from mercuric nitrite was invented later using KCN as the reducing agent. The hyponitrites of mercury were found to be thermally more stable than the corresponding nitrites and nitrates.

Box 2. Preparation of $\text{Hg}_2\text{N}_2\text{O}_2$ and HgN_2O_2



Prafulla Chandra also synthesised numerous nitrites of alkali, alkaline earth and coinage metals as well as double nitrites such as those containing both mercury and alkaline earth metals. Thermal decomposition of the compounds was thoroughly investigated. Other physicochemical properties such as relative stability, molecular volume and molecular conductivity were studied. Contrary to the view held earlier, Prafulla Chandra established beyond doubt that nitrites were stable substances.

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Ammonium Nitrite and Alkylammonium Nitrites

One of the very notable contributions of Prafulla Chandra in the field of nitrite chemistry was the synthesis of ammonium nitrite in pure form via double displacement between ammonium chloride and silver nitrite, (2).



Ammonium nitrite, so formed, was sublimed at 32-33°C under reduced pressure to afford crystalline colourless needles. It had all along been believed that ammonium nitrite undergoes fast thermal decomposition yielding N_2 and H_2O .



Prafulla Chandra established that this reaction is far less facile than thought. He carried out a series of experiments to show that pure ammonium nitrite is indeed stable and it can be sublimed without decomposition even at 60°C. The stability of this salt in its vapour state was firmly established by vapour density measurements. He presented the results in a meeting of the Chemical Society in London and the scientific audience including William Ramsay was greatly impressed. *Nature* (August 15, 1912) immediately highlighted the successful preparation of 'ammonium nitrite in tangible form' and the determination of the vapour density of 'this very fugitive salt'. The details of these experiments were published in the *Journal of Chemical Society*, London in the same year.

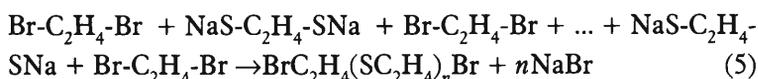
His success with ammonium nitrite prompted Prafulla Chandra to develop the chemistry of alkylammonium nitrites. He prepared a family of such compounds by double displacement of alkylamine hydrochlorides and silver nitrite.



in cold aqueous solution. The relative stability of these compounds were studied and compared. He then proceeded to work on mercury alkyl- and mercury alkylaryl-ammonium nitrites.

Organic Sulphur Compounds

In the College of Science, Prafulla Chandra made major contributions to the chemistry of organic sulphur compounds. He synthesised new compounds and studied their interactions with the salts of mercury. Moreover, ligating properties of some of these thio-compounds were investigated. Long-chain sulphur species, sulphur-containing condensed heterocycles and thioketones are some of the systems that he synthesised. For example, as a by-product of the synthesis of 1,4-dithian (Figure 4) from dithioethylene glycol and ethylene bromide, he isolated the long chain compound, $\text{BrC}_2\text{H}_4(\text{SC}_2\text{H}_4)_{48}\text{Br}$ (5), which was 'the first instance of a crystalline organic sulphur compound of such high molecular weight as 3068'.



He also worked on the synthesis of condensed heterocyclic systems. Of these, the synthesis of triethylene tri- and tetrasulphides from simple reactions of ethylene dibromide and alcoholic KSH (6) are noteworthy. Potassium permanganate oxidation of the tetrasulphide to the corresponding sulphone compound (7) was also examined. A brief report of his work on the synthesis of thiocamphor and other cyclic thioketones was published in *Nature* in 1934. Thiocamphor (Figure 5) was synthesized in a good yield by the simultaneous action of dry H_2S and dry HCl gas at 0°C on a solution of camphor in absolute

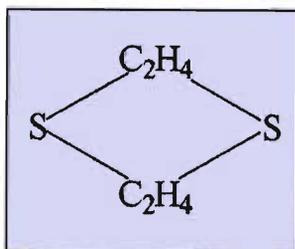
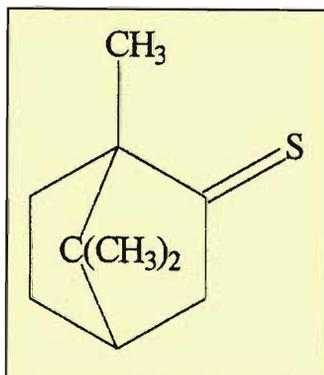
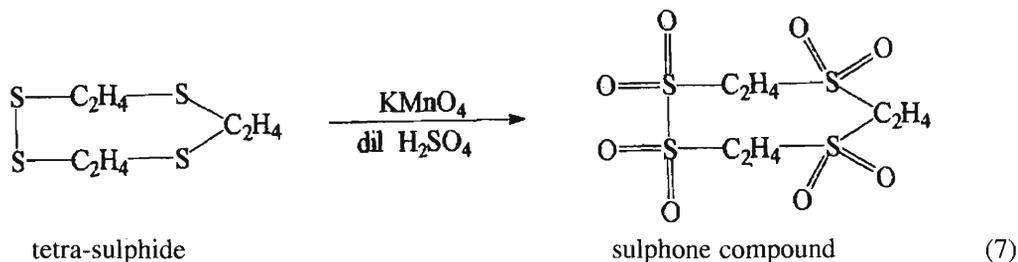
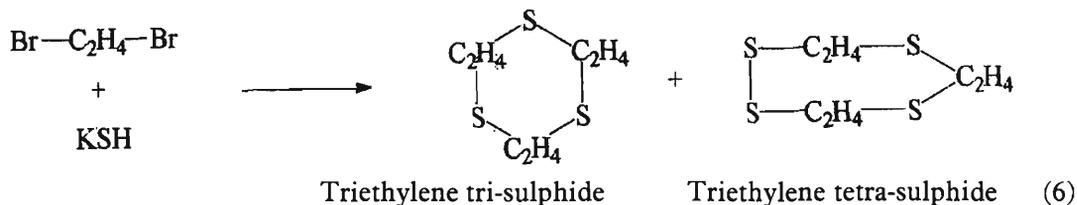


Figure 4. Structure of 1,4-dithian.

Figure 5. Structure of thiocamphor.





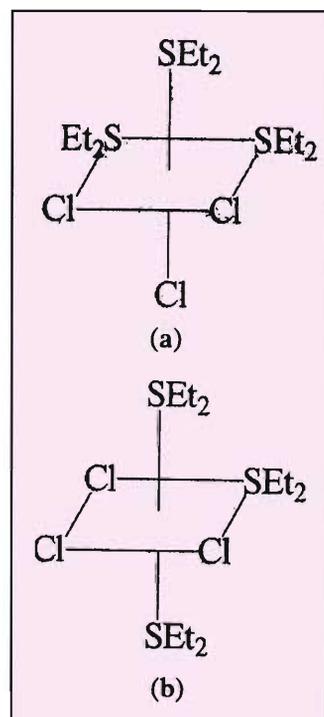
alcohol. This method was extended later to synthesize cyclic thioketones containing different ring systems.

Coordination Compounds

Prafulla Chandra made extensive contributions to the coordination chemistry of the heavier transition metal ions like platinum, iridium and gold. Particularly noteworthy are his studies on organic sulphides such as methyl sulphide, ethyl sulphide, diethyl sulphide and diethyl disulphide as ligands. Complexes of different types were isolated and their compositions were deduced based on elemental analysis and molar conductance.

From the reaction of diethyl sulphide with iridium tetrachloride he isolated two isomers of composition $\text{IrCl}_3 \cdot 3\text{Et}_2\text{S}$, one orange and another red. The orange compound is now known to have the pseudooctahedral meridional geometry (Figure 6a) and not the facial geometry (Figure 6b) assigned by Prafulla Chandra. This work indeed represents the isolation of the first mixed halide octahedral thioether compound of the generic type $\text{MX}_3(\text{R}_2\text{S})_3$ which now has rich chemistry ($\text{M}=\text{Ir}(\text{III}), \text{Rh}(\text{III}), \text{Os}(\text{III})$ and $\text{Ru}(\text{III})$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$) representing the efforts of many later workers in different countries. The first seed was

Figure 6. a) Pseudooctahedral meridional geometry and b) facial geometry.



By the interaction of chloroplatinic acid with thio-organic compounds, numerous platinum complexes were synthesised by Profulla Chandra and different oxidation states were assigned to the metal ion.

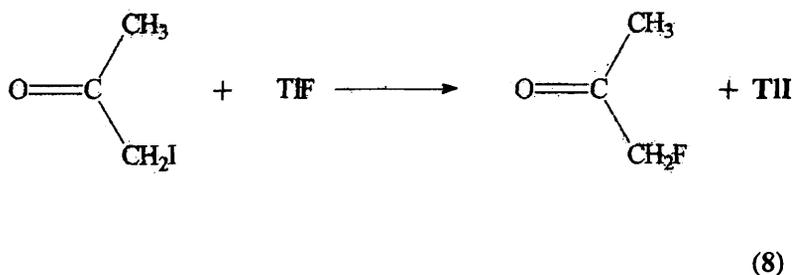
however shown by Profulla Chandra. The red isomer of $\text{IrCl}_3 \cdot 3\text{Et}_2\text{S}$ was shown by later workers to be a salt of type $[\text{IrCl}_2(\text{Et}_2\text{S})_4]^+ + [\text{IrCl}_4(\text{Et}_2\text{S})_2]^-$.

By the interaction of chloroplatinic acid with thio-organic compounds, numerous platinum complexes were synthesised by Profulla Chandra and different oxidation states were assigned to the metal ion. Similar studies were carried out on gold compounds. However, the proposed structures and the oxidation states of such species deserve further scrutiny.

Other Activities

In Presidency College, Profulla Chandra began his research activities by chemical examination of certain fats and oils like ghee, butter and mustard oil, used as cooking media in India. The purpose was to create standards and identify the adulteration of foodstuffs in metropolitan cities of India. He published a long report on this work in the *Journal of the Asiatic Society of Bengal* in 1894.

Much later in the College of Science, he developed certain methods for facile fluorination of organic compounds using thallos fluoride as the fluorinating agent. For example, one-pot synthesis of monofluoroacetone from the reaction of monoiodoacetone and anhydrous thallos fluoride (8) was successfully achieved in a high yield. He also isolated methyl fluoroformate and fluoroacetals using the same principle of halide substitution.



Conclusion

The above account reveals the versatility of Prafulla Chandra's research activities. Most importantly, he initiated chemical research in modern India and was successful in developing the first research school of chemistry that in time spread far and wide. In his obituary notice, *Nature* (July 15, 1944) wrote "it was by the enthusiasm for research with which he inspired his students that he will best be remembered".

Suggested Reading

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A Tailor-made Integral Matrix

An $n \times n$ integral matrix with n given integers as its eigenvalues is trivially obtained by considering a diagonal matrix with these diagonal entries. If one is also given n non-zero integral vectors, how can one make up a matrix which has integer entries and which has these vectors as its eigenvectors? Here is a simple way. First, note that if $\mathbf{a}, \mathbf{b} \in \mathbf{Z}^n$ are integer vectors considered as columns, and if $\mathbf{a}^t \mathbf{b} \neq -1$, then the matrix $I + \mathbf{a}\mathbf{b}^t$ is invertible; it has the inverse $I - s\mathbf{a}\mathbf{b}^t$ where $s = \frac{1}{1 + \mathbf{b}^t \mathbf{a}}$. Further, \mathbf{a} and \mathbf{b} may be so chosen that $\mathbf{b}^t \mathbf{a} = 0$ because this only means that $(I + \mathbf{a}\mathbf{b}^t)^{-1} = I - \mathbf{a}\mathbf{b}^t$. If we are given n integers and n non-zero integral vectors \mathbf{a}, \mathbf{b} satisfying $\mathbf{b}^t \mathbf{a} = 0$, let us form the diagonal matrix A with the given integers as its diagonal entries and let us consider the matrix $B = (I + \mathbf{a}\mathbf{b}^t)A(I + \mathbf{a}\mathbf{b}^t)^{-1}$. We see that B is actually an integral matrix. Moreover, the eigenvalues of B are exactly those of A and the columns of $I + \mathbf{a}\mathbf{b}^t$ are eigenvectors of B .

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