

# THE CHEMICAL RESEARCHES OF ACHARYA PRAFULLA CHANDRA RAY

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## Abstract

This article sketches the germination of Prafulla Chandra's interest in chemistry in Presidency College, its progressive growth in Edinburgh University and finally its culmination in his research laboratories in Calcutta (Presidency College and later in the University College of Science). From those of his contributions which have stood the test of time, a selected few like the ones on nitrites, on mercury complexes, on sulfur ligand related chemistry, on platinum metal chemistry and more will be highlighted. Certain difficulties and mistakes on the way will be noted. Mention will be made of his school of chemistry and of his diversified activity profile.

**Key words:** Double Salts, Coordination Compounds, Iridium, Isomorphism, Mercury, Nitrites, Thioethers, Thiols.

## 1. INTRODUCTION

Prafulla Chandra was born on August 02, 1861 into a Jaminder family in a village now in Bangladesh. It was an eventful era in the history of India. His school and early college education took place in Calcutta. He had inherited a genuine and lasting love for literature and history from Harish Chandra his erudite father and friend who maintained a good private library. He would grow up to be a man with varied interests and he would say 'diversified work has been my recreation, the chief solace of my life'. He taught himself to read half-a-dozen languages. He became a social worker, an ascetic, a philanthropist who gave away his all.

And he became a worshiper of chemistry, in his words "almost by mistake". He initiated chemical research in India by Indians. He became the *guru* of the first research school of chemistry in the country, the first historian of chemistry in ancient and medieval India, a champion of the

Indian Chemical Industry and the founder of the Indian Chemical Society. He was honoured many times during his lifetime within and outside the country. In the International Year of Chemistry (2011) the Royal Society of Chemistry announced the award of the International Chemical Landmark "To commemorate the life and achievements of Acharya P. C. Ray, father of Indian Chemistry, philanthropist and entrepreneur who founded modern chemistry teaching and research in India." The Plaque was installed in Presidency College on 31 January, 2012. The scope of this article will be limited to the scrutiny of his education as a chemist and selected chemical researches of his school in Calcutta (Presidency College and University College of Science).

## 2. GERMINATION OF INTEREST IN CHEMISTRY

After Entrance (1879), Prafulla Chandra took admission in the First Course in Arts (FA) at Metropolitan Institution established by Pandit

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Iswarchandra Vidyasagar. Chemistry was then a compulsory subject in the FA course. Because only Presidency College had the required facilities students of other colleges also studied chemistry there. The moving force behind the chemistry department of Presidency College was a young British teacher Mr. Alexander Pedler (1849-1918) who was then the professor and head of the chemistry department. In teaching he introduced practical work by students in the science departments and his class lectures were animated with neat experimental demonstrations. He also published several research papers from Calcutta in major journals. Coming in contact with him in the FA course, Prafulla Chandra writes, "I began almost unconsciously to be attracted to this branch of science". He started going through many works on chemistry beyond the prescribed text in the course.



**Prafulla Chandra in the year of discovery of Mercurous Nitrite (1896)**

After completing FA (1881) he enrolled for Bachelor of Arts (BA) in Metropolitan Institution and continued further studies of chemistry at Presidency College. But only halfway through with the BA studies, he won the *Gilchrist scholarship* and proceeded (1882) to Edinburgh University - a seat of higher learning in medicine, physics and chemistry- to fulfill his dream of studying chemistry in UK. Professor Alexander

Crum Brown (1838-1922), a man of vast erudition and head of the chemistry department was the chemistry teacher in Prafulla Chandra's class. To the chemist he remains best known for introducing the now commonly used graphical structures of organic molecules. Prafulla Chandra completed his B Sc. in 1885.

### 3. GROWING UP: DOCTOR OF SCIENCE

By then he was feeling that he 'was born for chemistry' and decided to go for the doctorate degree. For this it was necessary to submit a thesis based upon original research on a chosen topic. At that time organic chemistry was marching ahead (tetrahedral carbon, carbon-carbon chains and rings etc), physical chemistry was just being born (equilibria, electrochemistry, reaction rates, activation energy etc) and inorganic chemistry was rather disorganized with little more than the periodic table as an unifier (coordination theory and geometrical ideas were years away). Although Crum Brown was there, Prafulla Chandra was not much inclined to pursue research in organic chemistry. He looked for research problems that will have a large component of laboratory work involving preparations and careful chemical analyses. This drew him to inorganic chemistry and he chose the field of double salts, double sulfates in particular, which was attracting good attention among inorganic chemists at that time.

Double sulfates of the type  $MbSO_4 \cdot Mm_2SO_4 \cdot 6H_2O$  (Mb is a bivalent Mg- or Fe-group ion and Mm is monovalent ammonium or K-group ion) have been well known. There were conflicting reports in the literature on the existence of 'double-double' sulfates where two different double sulfates with Mb and Mb' combine in definite proportions giving rise to a new composition  $x[MbSO_4 \cdot Mm_2SO_4 \cdot 6H_2O] \cdot y[Mb'SO_4 \cdot Mm_2SO_4 \cdot 6H_2O]$  where x and y are integers. Prafulla Chandra took up his investigation to settle the question about such 'double-double sulfates'. He mixed the constituent

sulfates in aqueous solution, subjected the isolated crops of crystals to quantitative metal analysis and thus derived their compositions. Doing this for many combinations he concluded that his work, 'prove the existence of 'double-double' sulphates'. In the light of later developments in crystallography it would appear that these 'double double' sulfates were actually mixed crystals of two double salts and formation of no qualitatively new lattice or phase was involved. At 26 (1887) Prafulla Chandra became DSc.

By then he had become 'passionately fond of chemistry' and was awarded the Hope Prize Scholarship and the Trustees of the Gilchrist Endowment also made an additional grant on the expiry of his scholarship. He continued his work and studies for one more year and then decided to return home. He reached Calcutta in August 1888 but could take up a position of assistant professor in Presidency College only in July 1889.

#### 4. A CHEMICAL RESEARCHER IN CALCUTTA

Prafulla Chandra retired from Presidency College after twenty seven years (1889-1916) and then at the invitation of vice-chancellor Asutosh Mookherjee joined the new University College of Science as Palit Professor (1916-1936). Before we proceed to outline some of his research activities, a few general observations are in order. The number of his original papers in major journals published either singly or jointly with students is well over one hundred and fifty. Of these nearly ninety were contributed from Presidency College and the rest from the College of Science. He published most of his major works up to 1923 in the *Journal of Chemical Society Transactions* and in all that amounted to more than forty percent of his research publications. From 1924 his main medium of publication became the *Journal of Indian Chemical Society* which had come into being in the same year. The decade-wise break-up of his publications follows the logical pattern peaking near the middle decade: 1894-1899(12),

1900-1909(31), 1910-1919(52), 1920-1936 (29). The peak year was 1912 with sixteen publications.

Prafulla Chandra was basically an inorganic chemist but with active interest in organic molecules and reactions. The initial cutting edge of his research activity was the chemistry of nitrites and related species and later it shifted to organic thio compounds and their metal binding. The metals of particular interest to him were mercury, and platinum metals. To illustrate his organic interest we can cite the use of thallos fluoride, TlF, as a reagent for the fluorination<sup>2</sup> of certain organic bromo compounds and the use of dry H<sub>2</sub>S/HCl gas for converting cyclic ketones like camphor to the corresponding thioketones.<sup>3</sup> A collection of his research papers is available<sup>4</sup>. In what follows some selected works of Prafulla Chandra will be sketched.

#### 5. MERCUROUS NITRITE

Around 1895 Prafulla Chandra began his work in the sparsely explored field of nitrite chemistry that turned out to be highly fertile. He and his students deftly tilled this field over years resulting in a long chain of research papers.<sup>4</sup> It all started with the unexpected discovery of mercurous nitrite which Prafulla Chandra called 'a new chapter in life'. It was known that mercury reacted with cold dilute and concentrated nitric acids affording respectively mercurous and mercuric nitrates, Hg<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> and Hg(NO<sub>3</sub>)<sub>2</sub>, both occurring in hydrated forms. Prafulla Chandra while trying to prepare mercurous nitrate using dilute nitric acid noticed in 1896 the formation of a yellow crystalline solid as well and this turned out to be the hitherto unknown mercurous nitrite, Hg<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>.<sup>5</sup> The nitrite ion probably arise via initial reduction of nitric acid by mercury.

The discovery of mercurous nitrite was immediately noticed by *Nature* magazine which wrote in the May 28 issue of 1896, "...a paper by Dr. P. C. Ray... on mercurous nitrite, that is worthy of note...". Later this unusual compound attracted

the attention of X-ray crystallographers and it has been structurally authenticated (see below). In a recent paper<sup>6</sup> dealing with the possible binding of mercury nitrites to a crown ether Prafulla Chandra's work was highlighted. Earlier in a 1966 paper formation of yellow crystals as described by Prafulla Chandra was observed and these were found to slowly decompose leaving a white solid but none of the substances were characterized<sup>7</sup>. As noted by Prafulla Chandra mercurous nitrite crystals when carefully freed from mother liquor and dried are indefinitely stable; otherwise they slowly get converted to a white basic salt, now of known structure (see below).

The structure of mercurous nitrite was determined thrice (1985, 1986, 2011)<sup>8</sup>.

As shown in Fig.1 the molecule is planar and centrosymmetric. Each Hg atom of the mercurous moiety is unsymmetrically bonded to two oxygen atoms of a nitrite ion generating a four-membered chelate ring. The Hg-Hg distance is 2.54 Å and the shorter and longer Hg-O distances are 2.20 Å and 2.61 Å respectively<sup>8</sup>.

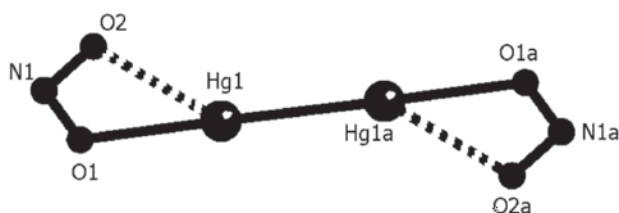


Fig. 1. Structure of  $\text{Hg}_2(\text{NO}_2)_2$

When mercurous nitrite, wet with mother liquor is left in air it slowly gets transformed into a stable white crystalline solid which is a basic salt, now of known structure<sup>8</sup>. Other aspects of the chemistry of mercurous nitrite was elaborated in a series of papers by Prafulla Chandra<sup>4</sup>. Examples are its oxidation to the nitrate,  $\text{Hg}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ , its reaction with ethyl iodide giving rise to a mixture of ethyl nitrite and nitroethane, its thermal decomposition and its molecular volume vis-à-vis those of silver and alkali metals. Such activities eventually led to the

opening up of the-then sparsely known field of nitrites in general. It got established that as a class nitrites are far more stable than chemists had supposed so far. Many new nitrites of metallic and other cations were synthesized and their properties and reactions studied. Nearly seventy percent of Prafulla Chandra's papers from Presidency College in major journals belonged to nitrite chemistry. We sketch a few examples below.

## 6. AMMONIUM AND ALKYLAMMONIUM NITRITES AND NITROUS ACID

Ammonium nitrite,  $\text{NH}_4\text{NO}_2$ , had long been known as a crystalline hygroscopic solid that decomposed even on moderate heating to nitrogen and water ( $\text{NH}_4\text{NO}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$ ); later it was shown that a second decomposition route affording ammonium nitrate, nitric oxide, ammonia and water ( $3\text{NH}_4\text{NO}_2 \rightarrow \text{NH}_4\text{NO}_3 + 2\text{NO} + 2\text{NH}_3 + \text{H}_2\text{O}$ ) also make a small contribution. Prafulla Chandra found that on careful heating to 70°C in moderate vacuum, a part of the ammonium nitrite also sublimes unchanged evidently via vaporization:  $\text{NH}_4\text{NO}_2(\text{solid}) \rightarrow \text{NH}_4\text{NO}_2(\text{vapour})$ . This prompted him to determine the vapour density of ammonium nitrite. After applying meticulous corrections for the decomposition reactions the observed density was found to agree very well with that calculated (32) for  $\text{NH}_4\text{NO}_2$  thus demonstrating that the salt remains in undissociated molecular form (ion-pair form in today's language) in the vapour<sup>9</sup>. At that time only  $\text{NH}_4\text{Cl}$  was known to behave in this manner. Later Prafulla Chandra also determined the vapour densities of other ammonium salts. In 1912 when he visited UK he presented the ammonium nitrite work at the Chemical Society in London before a highly appreciative audience including Nobel Laureate William Ramsay. *Nature* magazine described it as, "...a further accomplishment in determining the vapour density of this very fugitive compound."

While in the midst of the ammonium nitrite work Prafulla Chandra noticed that very little had



been documented about the preparation, nature and properties of the nitrite salts of amines<sup>4</sup>. He explored the chemistry of many alkylammonium nitrites:  $\text{RNH}_3\text{NO}_2$ ,  $\text{R}_2\text{NH}_2\text{NO}_2$ ,  $\text{R}_3\text{NHNO}_2$ . These were generally prepared by a method analogous to that used for ammonium nitrite, i.e., by reacting amine hydrochlorides with silver nitrite. In most cases the parent amines required for making the hydrochlorides were not available in the country and the first task was to prepare them in pure form. The thermal stability and reactions of the compounds were examined.

Apart from his extensive involvement with nitrites, Prafulla Chandra also looked at some properties of the parent acid viz., nitrous acid – its dissociation constant and rate of decomposition<sup>10</sup>. The dissociation constant determined from electrical conductivity data was found to be  $6 \times 10^{-4}$  which corresponds to a pKa of 3.22, a value which has remained more or less unchanged to this day.

## 7. MERCURIC NITRITE

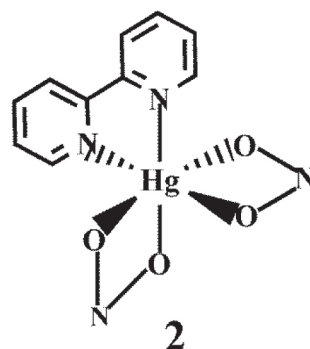
Whereas mercurous nitrite is intimately linked with his name in popular literature, Prafulla Chandra did a large amount of significant work on the mercuric analogue as well. In 1904 he succeeded in isolating pure mercuric nitrite as light yellow needles by reacting mercuric chloride with silver nitrite in aqueous media<sup>11</sup>. It was unstable even in dry atmosphere but afforded interesting stable complexes with many ligands which engaged Prafulla Chandra and his students over many years. We briefly cite below selected examples along with clarifications specially on the structural side that became available only much later.

Prafulla Chandra examined double nitrites like  $\text{Hg}(\text{NO}_2)_2 \cdot 2\text{MNO}_2$  ( $\text{M} = \text{Na}, \text{K}$ ) for which he strongly supported the prevalent formulation  $\text{M}_2[\text{Hg}(\text{NO}_2)_4]$ <sup>12</sup>. Later he prepared double nitrites of calcium, strontium and barium. Years later X-



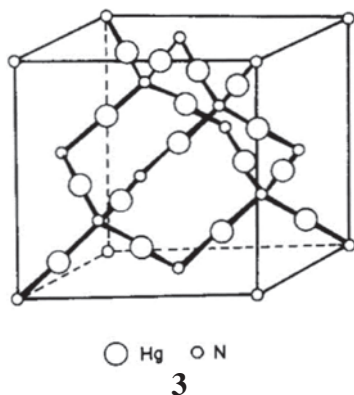
ray work authenticate the  $[\text{Hg}(\text{NO}_2)_4]^{2-}$  ion in which each nitrite group is chelated to the metal via the two oxygen atoms, the eight-coordinated anion has distorted square anti-prismatic geometry as in **1** ( $\text{Hg-O}$ , 2.34-2.58Å)<sup>13</sup>.

Numerous complexes of amines were isolated. For example ethylenediamine (en),  $\text{NH}_2(\text{CH}_2)_2\text{NH}_2$ , afforded  $[\text{Hg}(\text{en})(\text{NO}_2)_2]$ . Electrical conductivity data in aqueous solution showed it to be a 1:2 electrolyte meaning that dissociation into  $[\text{Hg}(\text{en})]^{2+}$  and nitrite occurs<sup>14</sup>. Later it was found to be non-electrolytic in nitrobenzene by others implying lack of dissociation in this solvent. The X-ray structure of  $[\text{Hg}(\text{en})(\text{NO}_2)_2]$  itself is not known but that of the bipyridine (bpy) analogue,  $[\text{Hg}(\text{bpy})(\text{NO}_2)_2]$ , is<sup>15</sup>. Both bpy and nitrite are chelated defining a distorted octahedral  $\text{HgO}_4\text{N}_2$  metal coordination sphere as in **2**. Prafulla Chandra's  $[\text{Hg}(\text{en})(\text{NO}_2)_2]$  may have a similar structure (en in place of bpy). The amine- $\text{Hg}(\text{NO}_2)_2$  work was extended later to include alkaloids like nicotine, quinine etc. as amine ligands. The nicotine complex was

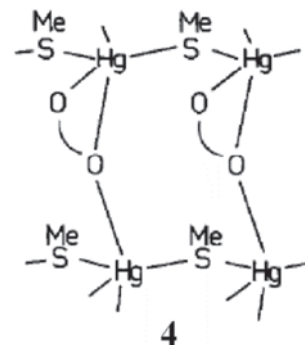


formulated as  $[\text{Hg}(\text{nicotine})(\text{NO}_2)_2]^{16}$ . Its structure is not known but the interested reader can make a guess by looking at the known structure of the chloro complex,  $[\text{Hg}(\text{nicotine})\text{Cl}_2]^{17}$ .

Preceding the amine work Prafulla Chandra had scrutinized the case of ammonia. He isolated a pale yellow salt formulated as a hemihydrate of  $\text{Hg}_2\text{N}(\text{NO}_2)$  and converted it to compounds of the general type  $\text{Hg}_2\text{N}(\text{X})$  via reaction with the acid  $\text{HX}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{NO}_3$  etc)<sup>4, 18</sup>. Several  $\text{Hg}_2\text{N}(\text{X})$  type compounds had been known for long as products of salt formation between  $\text{HX}$  and Millon's base i.e., dihydrated  $\text{Hg}_2\text{N}(\text{OH})$  which was first made in 1845 from mercuric oxide and ammonia. Prafulla Chandra's work provided a new synthetic route to  $\text{Hg}_2\text{N}(\text{X})$ . These have three dimensional framework structures constituted of connected  $\text{NHg}_4$  tetrahedra, each Hg atom being shared between two nitridic N atoms (linear  $\text{HgN}_2$  fragment)<sup>19</sup>. The anion  $\text{X}^-$  and water molecules are accommodated in the holes of the network. Weakly coordinating ions like nitrate support a cubic lattice as in **3**.



With simple aliphatic thiols  $\text{RSH}$ , Prafulla Chandra isolated crystalline nitrites of type  $\text{RSHgNO}_2$  which constituted a new thiolato family of mercury akin to the known thiolatomercuric halides  $\text{RSHgX}^{20,21}$ . The latter are now known to be generally polymeric. Thus in the acetate complex  $\text{MeSHg}(\text{O}_2\text{CMe})$  each metal atom of the  $(-\text{Hg}-\text{SMe}-)_n$  chain is chelated to one acetate ligand which additionally interlinks the chains as



depicted in **4**<sup>22</sup>. Since the four-membered O, O-chelation by acetate is similar to that by nitrite, one may suspect that  $\text{MeSHgNO}_2$  has a similar structure.

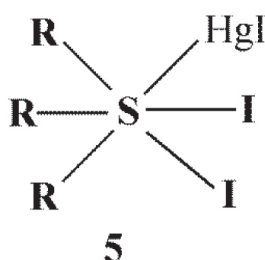
## 8. SULFUR LIGANDS AND THEIR COMPLEXES: GENERAL COMMENTS

Around 1914 Prafulla Chandra initiated work on organic thio compounds (note the  $\text{RSHgNO}_2$  system described above) like thiols, thioethers and related species and their binding to metals. This endeavour flourished when he moved to College of Science but it was riddled with difficulties of purification and elemental analysis that sometimes lead to erroneous chemical compositions and misleading conclusions. Another problem was the inherent complexity of the structures of the species (macrocycles, polynuclear species etc.) he often attempted to synthesize. This problem had no ready solutions in those days, certainly not with the facilities available to him.

A problematic case is well illustrated by triethylene trisulfide or 1,4,7-trithianonane,  $(\text{C}_2\text{H}_4)_3\text{S}_3$ . In 1920 he claimed its syntheses by the reaction of ethylene dibromide with potassium hydrogen sulfide<sup>23</sup>. Later he reported its reactions with mercury and platinum salt as well as with oxidizing agents. But what he had actually made<sup>24</sup> was the well known 1,4-dithiacyclohexane,  $(\text{C}_2\text{H}_4)_2\text{S}_2$  and the reported metal complexes and oxidation products were those derived from it. In the next two sections we describe cases where lasting progress was achieved by Prafulla Chandra.

### 9. TRIALKYL SULFONIUM SALTS OF TRIIODOMERCURY(II)

The reaction of  $\text{RSHgNO}_2$  with alkyl iodides (RI) afforded a mixture of nitroalkane and alkyl nitrite and a yellow crystalline solid to which Prafulla Chandra initially assigned the composition  $[\text{R}_2\text{S}_2, \text{HgI}_2, \text{RI}]$  that was later corrected to  $[\text{R}_2\text{S}, \text{HgI}_2, \text{RI}]$ <sup>25</sup>. But this family of compounds had been known for some years as a product of the reaction among  $\text{R}_2\text{S}$ , RI and  $\text{HgI}_2$  and Smiles had suggested<sup>26</sup> the monosulfonium constitution **5** based on hexavalent sulfur. Prafulla



Chandra's electrical conductivity data in acetone however showed that the compounds are univalent electrolytes<sup>27</sup>. This prompted him to reject the hexavalent sulfur model of Smiles and to conclude that the  $[\text{R}_2\text{S}, \text{HgI}_2, \text{RI}]$  species are actually trialkyl sulfonium salts of triiodomercury(II),  $[\text{R}_3\text{S}][\text{HgI}_3]$ . Subsequently others confirmed this.

When the X-ray crystal structure of  $[\text{Me}_3\text{S}][\text{HgI}_3]$  was solved many years later (1963, 1995, 2013)<sup>28</sup> The structure consists of pyramidal  $[\text{Me}_3\text{S}]^+$  and  $[\text{HgI}_3]^-$  (Fig.2). The anion is nearly planar, the Hg atom being displaced by only 0.12 Å from the plane of the iodine atoms (Hg-I, 2.69 - 2.74 Å). In leading text books of inorganic

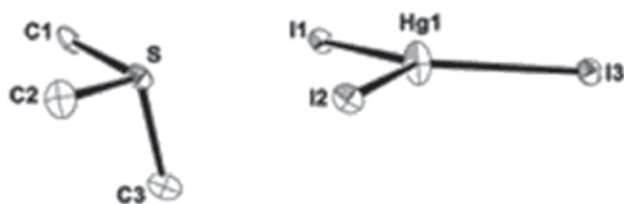


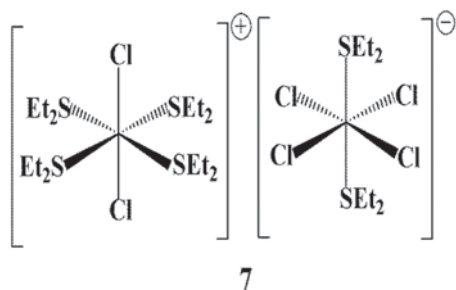
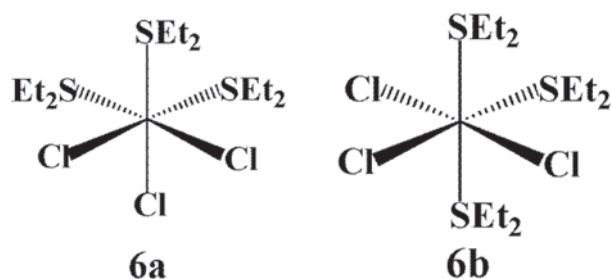
Fig. 2. Structure of  $[\text{Me}_3\text{S}][\text{HgI}_3]$

chemistry one example of the relatively rare phenomenon of tricoordination among transition metal complexes of simple ligands is almost invariably cited *viz.*, the triiodomercury(II) anion as in the trimethyl sulfonium salt,  $[\text{Me}_3\text{S}][\text{HgI}_3]$ , in the crystalline state. It is hardly remembered that this formulation is originally due to Prafulla Chandra<sup>25</sup>.

### 10. THIOETHER COMPLEXES OF TRIVALENT IRIDIUM

The chemistry of this family illustrates well Prafulla Chandra's early contributions towards the advancement of platinum metal chemistry of sulfur ligands. Upon treating iridium tetrachloride ( $\text{IrCl}_4$ ) with dialkyl sulfides ( $\text{R}_2\text{S}$ ) in ethanol he found the metal to be reduced to the trivalent state affording a compound of composition  $[\text{IrCl}_3, 3\text{R}_2\text{S}]$  isolated in two isomeric forms differing in colour and in solubility in organic solvents<sup>29,30</sup>. The more soluble isomer was orange (more appropriately yellow as found by others later) in colour while the less soluble isomer was coloured red. Detailed studies were limited to the  $\text{R} = \text{Et}$  species. On the basis of composition, stability and nonelectrolytic nature of the yellow isomer in acetone solution Prafulla Chandra promptly concluded that it is a hexacoordinated coordination compound of type  $[\text{IrCl}_3(\text{Et}_2\text{S})_3]$  and suggested that the red isomer is also similarly constituted. He assigned *cis (fac)* and *trans (mer)* geometries **6a** and **6b** to the yellow and red isomers respectively<sup>29,30</sup>. This he did on the basis of the colours of other geometrically isomeric iridium compounds as described by Delepine. He also studied the successful partial/complete replacement of  $\text{Et}_2\text{S}$  in yellow  $[\text{IrCl}_3(\text{Et}_2\text{S})_3]$  by ammonia, pyridine and ethylamine.

Later nmr spectral and other physical data convincingly demonstrated that yellow  $[\text{IrCl}_3(\text{Et}_2\text{S})_3]$  had the *mer* geometry **6b** the red form was a dimerization isomer in the form of the 1:1 electrolytic salt  $[\text{IrCl}_2(\text{Et}_2\text{S})_4][\text{IrCl}_4(\text{Et}_2\text{S})_2]$ , **7**,



where both the cation and the anion have *trans* geometry<sup>31, 32</sup>. In conclusion we note that Prafulla Chandra's original proposals on isomer geometry of the iridium thioether species did not survive. The true nature of the yellow isomer which he thought to be *fac* actually turned out to be *mer* and the red isomer thought to be *mer* was actually the dimerization isomer 7. But it is Prafulla Chandra's original synthetic work that brought the interesting compounds to light very early and started the ball rolling. Eventually this generated much interest and work in major laboratories with the help of modern physical tools revealing their true nature. In the history of the now-well-known  $[MX_3(R_2S)_3]$  family where M is a heavier transition element like Ru, Os, Rh or Ir and X is usually Cl or Br, Prafulla Chandra with his iridium work remains an original torch bearer<sup>33</sup>.

## 11. DOUBLE SALTS

Prafulla Chandra did his doctoral work on double salts (Section 3). There are a few instances where he looked at this class of compound in Calcutta. For example, he prepared crystalline trialkyl sulfonium ( $R_3S^+$ ) and tetraalkyl

phosphonium ( $R_4P^+$ ) analogues of  $M^{II}SO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$  with the difference that the number of water molecules came out different such as  $M^{II}SO_4 \cdot (Me_3S)_2SO_4 \cdot 8H_2O$  (M = Fe, Mg etc);  $M^{II}SO_4 \cdot (Et_3S)_2SO_4 \cdot 10H_2O$  and  $M^{II}SO_4 \cdot (Et_4P)_2SO_4 \cdot 8H_2O$ .

The work on new double salts based on homology of ions composed of elements belonging to widely different groups of the periodic table was more interesting. In the 1920's good progress was being made by physicists and chemists in defining the principles that determine the structure of ionic crystals. It emerged that different complex ions having the same number of atoms may be expected to give rise to isomorphous salts provided their sizes are similar and they have the same number of valence electrons (also meaning that they have the same net charge).

In Prafulla Chandra's laboratory this principle was very successfully employed in the case of the anion triad  $BeF_4^{2-}$ ,  $PO_3F^{2-}$  and  $SO_4^{2-}$ . All three have five atoms and thirty two valence electrons. And Goldschmidt's ionic radii data suggested that the size of the above anions were about the same. It was checked that the salts  $K_2BeF_4$ ,  $K_2PO_3F$  and  $K_2SO_4$  have very similar molecular volumes. This prompted attempts to isolate double salts. And indeed crystalline salts like  $MSO_4 \cdot K_2BeF_4 \cdot 6H_2O$  (M = Fe and Mg group element);  $MSO_4 \cdot (NH_4)_2BeF_4 \cdot 6H_2O$ ;  $MSO_4 \cdot (NH_4)_2PO_3F \cdot 6H_2O$ ;  $NiBeF_4 \cdot (NH_4)_2BeF_4 \cdot 6H_2O$  and  $NiPO_3F \cdot (NH_4)_2PO_3F \cdot 6H_2O$  salts, all isomorphous with the well known double sulfates (Section 3) were successfully synthesized. And so were the salts  $Al_2(SO_4)_3 \cdot (NH_4)_2BeF_4 \cdot 24H_2O$ ;  $Al_2(SO_4)_3 \cdot (NH_4)_2PO_3F \cdot 24H_2O$  and  $Al_2(PO_3F)_3 \cdot (NH_4)_2PO_3F \cdot 24H_2O$  which were isomorphous with common alum<sup>34, 35</sup>.

## 12. CONCLUSION

A galaxy of young students were attracted to Prafulla Chandra who later wrote, "bonds



existing between them and me was subtle as those of chemical affinity.” An outcome of this was the emergence of the first school of chemistry in this country. It has been said, “His laboratory is the nursery from which issue forth the young chemists of new India”. Only some of the ‘young men’ noted above did their doctoral work with Prafulla Chandra, others worked with him on one or two projects and then proceeded elsewhere, often abroad for higher studies, and yet others which included some bright physicists were simply deeply influenced by his ways and adhered to him. Many of them later played major roles in post-independence Indian science. Included among them were the likes of N. R. Dhar, J. C. Ghosh, J. N. Mukherjee, P. Ray, S. N. Bose and M. N. Saha. S. S. Bhatnagar considered himself to be a grandpupil as he was taught chemistry in Lahore by A. C. Ghosh, a pupil of Prafulla Chandra. On his passing away (June 16, 1944) *Nature* wrote, “Sir Prafulla was more than anyone else responsible for the great development of scientific research in India during the past fifty years.”

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#### ABBREVIATIONS

*CC* - *Chemical Communications*

*IC* - *Inorganic Chemistry*

*ICA* - *Inorganica Chimica Acta*

*IJC* - *Indian Journal of Chemistry*

*JASB* - *Journal of the Asiatic Society of Bengal*

*JCST* - *Journal of the Chemical Society, Transactions*

*JICS* - *Journal of the Indian Chemical Society*

*NAT* - *Nature*

*PRSE* - *Proceedings of the Royal Society of Edinburgh*

*SA* - *Spectrochimica Acta*

*ZN* - *Zeitschrift für Naturforschung*

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