



A Dream and Reality to Chemical Science in India- Acharya Prafulla Chandra Rây

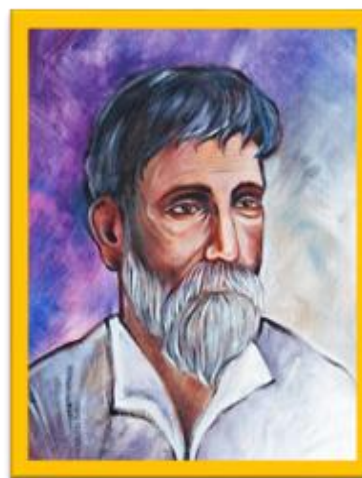
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Received: 02 March 2023; Revised: 20 March 2023; Accepted: 23 March 2023.

Article type: Coverage article.

Acharya Sir Prafulla Chandra Rây, a member of Companion of the Indian Empire (CIE, the Most Eminent Order of the Indian Empire founded by Queen Victoria), Founder Fellow of the Indian National Science Academy (FNI, Delhi which is now renamed as FNA), Fellow of the Royal Asiatic Society of Bengal (FRASB, Kolkata), Fellow of the Indian Association for the Cultivation of Science (FIAS, Kolkata), and Fellow of the Chemical Society (FCS, London), is a pathfinder and originator of India's modern chemistry – teaching and research, chemical industry, philanthropist, industrialist and educationist. He was born on August 2, 1861 in the village Raruli, Khulna, (now in Bangladesh). He learned science by attending as an external student, particularly chemistry from Prof. Alexander Peddler, Presidency College (now Presidency University, Kolkata). It was the only college, where science teaching started in pre-independent India. After receiving Gilchrist Scholarship, he joined the Edinburgh University UK in 1882 and received B. Sc. in Chemistry from Prof. Alexander Crum Brown in 1885 and D. Sc. in 1887. His research thesis entitled, *"Conjugated Sulphates of the Copper-magnesium Group: A Study of Isomorphous Mixtures and Molecular Combinations"* earned Hope Prize from the University.^[1,2] The double sulfates known in his times are a few only like Mohr's salt (*i.e.*, $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$); cyanochroite, $\text{K}_2\text{SO}_4 \cdot \text{CuSO}_4 \cdot 6\text{H}_2\text{O}$. Prafulla Chandra worked in the laboratory of organic chemist and the global research tempted to physical chemistry at that time. He found out more space in double-double sulphates, like $\text{Mm}_2\text{SO}_4 \cdot \text{MbSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{Mm}_2\text{SO}_4 \cdot \text{Mb}'\text{SO}_4 \cdot 6\text{H}_2\text{O}$ (where Mm refers to monovalent; Mb or Mb'

refers to the bivalent metal ion).^[3] However, the structure of such salts was known much later, after the discovery of single crystal X-ray diffraction measurements in early 1930's and the present form only appeared after 1960's.^[4] Rây was elected as Vice-President of the University of Edinburgh Chemical Society in 1888 and the President was Prof. Alexander Crum Brown.



^{*}The portrait is drawn by Mr. Bitihotra Roymahapatra, which is also been used in designing the cover page of this special volume.

Chemical Research in India

He returned India in 1888, joined the Presidency College in July 1889, and engaged in teaching and research in Chemistry. His first research publication entitled, *"On the Chemical Examination of Certain Indian Food Staffs, Part I, Fats & Oils"* was published in 1894 *Journal of the Asiatic Society of Bengal*.^[5] His brilliant discovery appeared in the same journal in 1896 on mercurous nitrite ($\text{Hg}_2(\text{NO}_2)_2$), a compound consisting of $\text{Hg(I)}\text{-Hg(I)}$ bond, the simplest example of two atom metal cluster.^[6] It raised huge controversy related to the oxidation state (*i.e.*, Hg(I)) and had been settled by Prof. Animesh Chakravorty by preparing the compound following the same procedure and determining its X-Ray structure.^[7] The

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discovery of mercurous nitrite was reported by *Nature* magazine immediately after its publication and wrote “*The Journal of the Asiatic Society Bengal can scarcely be said to have a place in our chemical libraries; the current number, however, contains a paper by Dr. P. C. Ray, of the Presidency College, Calcutta on Mercurous Nitrite, that is worthy to note-----*”.[8]

The preparation, stability and vapor density measurement of NH_4NO_2 [9] and its demonstration in Royal Society of Chemistry (RSC), London meeting earned congratulation from the Nobel Laureate, Prof. William Ramsay. *Nature* magazine published the news “...success in preparing ammonium nitrite in a tangible form, a further accomplishment in determining the vapour density of this very fugitive compound”.[10] During this time, Rây and his group isolated different double nitrites of type $2\text{MNO}_2 \cdot \text{Hg}(\text{NO}_2)_2$ (two different metals M & Hg, form mixed nitrites); however, the conductance and chemical characteristics of these compounds are believed to be a complex type of $\text{M}_2[\text{Hg}(\text{NO}_2)_4]$. [11] A series of nitrito $\text{Hg}(\text{II})$ additive compounds of ethylenediamine (en) was characterized by Rây by measuring the conductance as 1:2 electrolyte, $[\text{Hg}(\text{en})_2](\text{NO}_2)_2$. [12] In 1912, his group published sixteen research papers in three different journals of Royal Society of Chemistry. He was rightly named the fame of ‘*Master of Nitrites*’ by Professor W. E. Armstrong. [13]

Since 1916 onwards, Rây started to work on chemistry of thiols with mercury. He was probably interested to explore Hg-S chemistry from its relevance in Ancient Indian Culture where *Makardhwaj* (mixture of Hg, Au, Ag, S) was used as medicine for the treatment of many diseases. [14] Aliphatic thiols (RSH) reacted with $\text{Na}_2[\text{Hg}(\text{NO}_2)_4]$ to isolate compounds like $\text{Hg}(\text{RS})\text{NO}_2$. PCR worked on the reaction of thiourea with $\text{Hg}(\text{II})$ salts and thione-thiol tautomerism was recommended. In later period, the structures of the compounds in many cases were proved by X-Ray diffraction measurements. Although the concept and realization of ionic liquids appeared currently, however, Ray noticed this character long back in 1916 when he worked on mercury mercaptide nitrites and alkyl iodide. He proposed composition $[\text{R}_2\text{S} \cdot \text{RI} \cdot \text{HgI}_2]$ and the conductivity measurement confirmed the ionic structure, which has been proven by X-Ray structure

as $[\text{Me}_3\text{S}][\text{HgI}_3]$. [15,16] Ray contributed substantially to the Au(I,III)-S chemistry. Au(III)- R_2S chemistry, $[\text{AuCl}_3(\text{R}_2\text{S})]$, and its reduced product $[\text{AuCl}(\text{R}_2\text{S})]$ were credited the first time to P. C. Rây. [17]

In coordination chemistry, he established the complexes of heavier transition series like Hg, Au, Ir, Pt along with the chemistry of many metals, metalloids including alkali and alkaline earth metals, Cu, Ag, Fe, Mn, Zn, Cd, P, As and Sb. His research is collected in a book published in Kolkata. [18] In the early third decades of twentieth century, Rây started to develop platinum group metal chemistry of sulfur compounds. In 1923, with the reaction of Et_2S with chloroplatinic acid (H_2PtCl_6) in ethanol for two or three days, he isolated yellow crystalline complex of composition $[\text{PtCl}_2(\text{Et}_2\text{S})_2]$ and also $[\text{PtCl}_2(\text{Et}_2\text{S})_2]$. He reported the mixed-valent Pt(II,IV) (not trivalent) complex also. Both yellow and white compounds $[\text{PtCl}_2(\text{Et}_2\text{S})_2]$ were characterized as *cis* and *trans* structure, respectively following Werner’s coordination theory. PCR also examined the substitution reaction using bases like NH_3 , EtNH_2 , pyridine (py) of $[\text{PtCl}_2(\text{Et}_2\text{S})_2]$. [19,20]

Towards the end of his research in the University College of Science, University of Calcutta, Rây and his associates started to work on Ir and Rh chemistry of thiolato compounds. They reacted $\text{Ir}^{\text{IV}}\text{Cl}_4$ with Et_2S in hot ethanol and isolated orange-yellow crystals of composition $[\text{IrCl}_3.3\text{Et}_2\text{S}]$. The reaction was so specific that could not be arrested by adding a strong oxidizing agent like aqua regia. From different physicochemical measurements and his chemical intuition, he concluded that it is a hexacoordinated compound of type $[\text{IrCl}_3(\text{Et}_2\text{S})_3]$, which can have two geometrically isomeric forms, i.e., the *facial* (abbreviated *fac*; also called *cis*) and *meridional* (*mer*) isomer, which is also called the *trans* isomer. [21]

Rây also designed few reagents to carry out organic transformation. The use of acidified H_2S as thiolating agent was recommended for the first time to synthesize thioketones and Ray reported in *Nature* the preparation of thiocamphor. [22] P. C. Rây reported the use of thallium fluoride (TlF) for preparing fluoroorganics and also other fluorinating agents like AgF , ZnF_2 for the preparation of fluoroformate esters. [23,24] His broad areas of scientific research include (i) chemistry of nitrogen oxyacids and their metal derivatives, (ii) organic

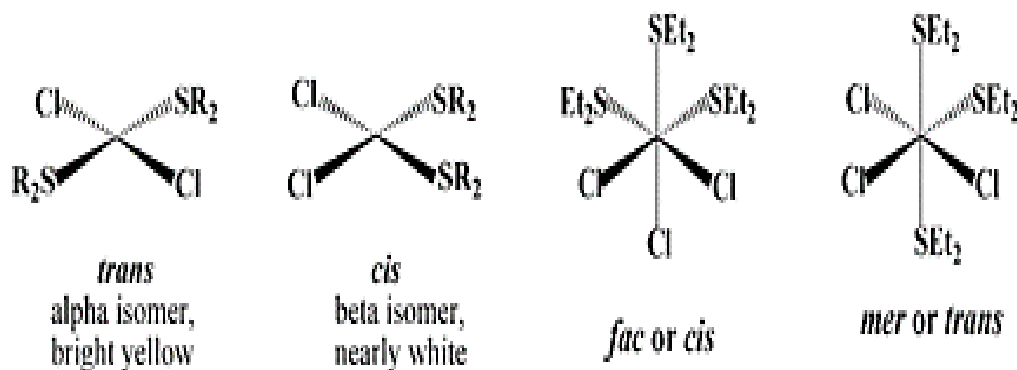


Fig. 1 Isomeric square planar, $[\text{PtCl}_2(\text{Et}_2\text{S})_2]$, and octahedral, $[\text{IrCl}_3.3\text{Et}_2\text{S}]$, complexes.

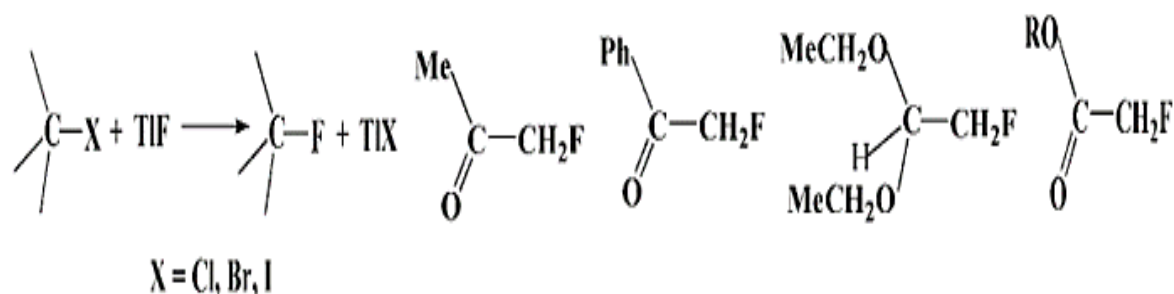


Fig. 2 Fluorinating agent, TIF in C-H activation reaction and synthesis of organo-fluoro compounds.

nitro compounds and nitrates, (iii) organic thio compounds and their metal derivatives, (iv) chemistry of platinum group metals, (v) mercury alkyl/aryl compounds, (vi) fluorination of organic compounds, (vii) isomorphism and chemical homology, and (viii) classical physical chemistry like catalysis, thermal decomposition, measurement vapor densities and ionic conductance. So, Acharya Rây is all along a chemist, who travelled all unknown paths of organic, inorganic, analytical and pharmaceutical chemistry.

Quanta of Research

In India, Acharya P. C. Rây started the first model Research laboratory both in academia (Presidency College & later Science College, Kolkata) and in industry (Bengal Chemical & Pharmaceutical Works Ltd.). Among his more than 150 research publications, 8 publications appear in *Nature* magazine; and 86 articles appear in the journals of the Royal Society. In the *Journal of the Indian Chemical Society* (1924-1936), he published 37 research papers (he was the founder and first President of the Indian Chemical Society started in 1924) and in German language, there are 11 publications. Out of 150 publications, there are 71 articles published as a single name (P. C. Rây); two-author articles are 68. One can imagine how much intellectual and physical labor he had invested against many odds to establish an experimental laboratory. Along with purchasing chemicals and glass wares, he had invested his own earnings, no financial support was given by British Raj to a person whose laboratory was the centre of the *Swadeshi Movement*! His brilliant research in the laboratory and inspiring class demonstration attracted enthusiastic young men to join in the modern chemical research, what he started in India.

In his long and distinguished career as a research worker, he had evoked a true spirit of scientific enquiry among his many disciples, which has resulted in the creation of the flourishing school of chemistry who had shown their ability not only in India but also in other parts of the world. He recognized the first modern Indian research school in chemistry and was regarded as the Father of Chemistry in India. The Indian Chemical Society, a premier Scientific Society and the oldest such society in India, was founded on 9th May 1924, and Acharya Prafulla Chandra Rây was the First President along with his disciples J. N. Mukherjee, J.C. Ghosh and S.S. Bhatnagar. To begin with, Indian Chemical Society

started the publication of The Journal of the Indian Chemical Society.

Last Recognition: International Chemical Landmark Plaque

The International Year of Chemistry was celebrated in 2011 by the United Nations. The Royal Society of Chemistry (RSC, UK) used this platform to honor his life and work at his 150th Birth Anniversary by establishing an International Chemical Landmark Plaque in the Presidency College (now Presidency University, Kolkata), the place where the dream of research and teaching in chemistry was blossomed.

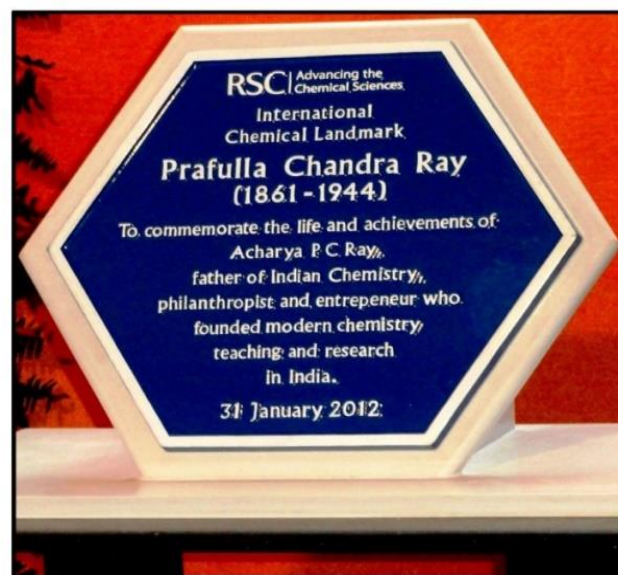


Fig. 3 Photo Courtesy (own collection of Prof. Chittaranjan Sinha).

This is the first ever landmark plaque, which was placed outside Europe. The name of Acharya Rây was nominated as the first Indian for Fellow of Royal Society on 16th December 1912 by William A. Tilden, Herold Baily Dixon, Henry E. Roscoe, Victor H. Veley, Alexander Crum Brown, Martin O. Forster, James Walker, Arthur W. Crossley, William Henry Perkin, Hugo Müller, Thomas H. Holland, James E. Reynolds, Herbert B. Baker, Percy F. Frankland, Alexander Pedler, William J. Pope and Alexander Scott. However, for some reasons, it was not realised. Everybody believed that an Author of "India: Before and After The Mutiny", an essay published

by Rây in 1885 as a participant in Essay Competition of Edinburgh University where he criticised the British imperialism and a Gandhian, could not be successful.

Acknowledgements

Special thanks to Mr. Bitihotra Roymahapatra, Student of Class X, Vivekananda Mission School, Haldia Township, Haldia 721657, India, for drawing the beautiful portrait of Acharya P. C. Ray, which is also been used in the cover page of this special volume.

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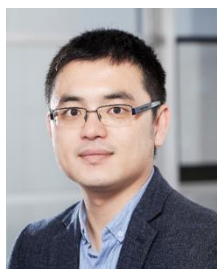
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Dr. Chittaranjan Sinha M. Sc., Ph. D., Professor & Former Head, Department of Chemistry, Jadavpur University, Kolkata-700 032, India is working on the design of chemosensors and detection of ions/molecules. Environmentally important ions/molecules like Zn^{2+} , Al^{3+} , Cr^{3+} , Cu^{2+} , Pd^{2+} , Phosphates, F^- , CN^- , ATP, Cytosine etc. are analyzed at nM concentration by using spectrofluorometric techniques. His research encompasses photochromism, electrochemistry, Coordination Polymers/Metal Organic Frameworks, functionalization and exploration of known antibiotics (sulfonamides) etc. So far, he has published 470+ internationally cited articles with 8250 citations. More than 15 Book Chapters are also published by Prof. Sinha. Dr. Sinha participated more than 150 national and international chemical; science conferences/seminars/workshops. His name

is enlisted in top 2% scientists of the world in the list prepared by Stanford University and Elsevier on 2020, 2021, 2022 and 2023. Dr. Sinha received International Lecturer Award from Padova University, Italy in 2011. He was awarded Best Chemistry Teacher in Post-Graduate level by Tata Chemicals in Association with Association of Chemistry Teachers and Confederation of Indian Industries in 2012. Prof. Sinha was also awarded William Ramsay Distinguished Researcher Award 2022 in Inorganic Chemistry by International Multidisciplinary Research Foundation (IMRF), Institute of Higher Education and Research. He is Elected Fellow of West Bengal Academy of Science & Technology (FAScT) since 2018. He served as Secretary of World Science Congress and arranged Student's competition and State level and National/International conferences. He is a life-time Fellow of Indian Chemical Society (FICS) and served the society as Hon. Secretary for two terms (2017-19 and 2020-22). Indian Chemical Society is the oldest Chemical Society in India established by Father of Indian Chemistry, Acharya Prafulla Chandra Ray in 1924. Prof. Sinha has supervised 52 Ph. D. Scholars; more than 70 Master's Thesis and conducted 21 Govt. Research Projects. He served as Editor (Inorganic Chemistry Section) of the Journal of the Indian Chemical Society published by the Indian Chemical Society; currently Senior Editor of Current Organocatalysis and Current Microwave Chemistry published by Bentham Science Publishers. He is also engaged in the science popularization, support to financially challenging meritorious students for higher studies and has conducted a school (up to VIIIth Standard) blessed by Ramakrishna Mission at his native place. For his outstanding research contribution in the field of Metal Organic Framework (MOF), he has been admitted as a Fellow of The Royal Society of Chemistry (FRSC) in August 2023.

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