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Development of modern solution chemistry: a search of new fields

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Contents

Abstract

In order to investigate new fields and how one can approach a new field of chemistry, studies carried out by Nobel laureates are surveyed from the historical point of view and are classified into five categories. A brief discussion shows how they created new fields of chemistry and how one can open a gate to a new world. A short history of the development

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of solution chemistry is reviewed in connection with a view for the development of theories and methodologies used for investigations in solution chemistry. New fields and new methodologies have often been discovered by extension and combination of existing theories and methodologies with a new vision recognising existing chemistry from another side of the traditional face of chemistry. A recently developed method to determine the structure of short-lived reaction intermediates in solution, which has not been determinable by traditional analytical methods, is shown as an example. This is a method combining a stopped-flow technique and the EXAFS method. Some results obtained for metal substitution reactions of porphyrin complexes are given, and emphasis is placed on an effective combination of different methodologies to create a new method of investigation.

Keywords: EXAFS; Nobel laureates; Solution chemistry; Stoped-flow; Reaction intermediates

1. Introduction

It is a dream of scientists to create a new field of science. A review of the research carried out by eminent scientists may provide a means by which one can approach a new field.

When we survey the work of Nobel laureates in chemistry from 1901 to 1997, their research may be classified into five categories as shown in Table 1.

Although it may not be easy for solution chemists to discover new elements, we may be able to produce new materials. Introduction of new concepts and new theories may be possible for solution chemists. To develop a new methodology or a new technique may also be possible for us if we are lucky. The two-dimensional NMR and double-beam Raman spectroscopies may be examples of new methodologies which are extended from existing methods. The synthesis of new compounds and new methods of synthesis are the principal subjects of many organic and inorganic chemists.

The work of Richards who received the Nobel prize for chemistry in 1914, devoted his life work to accurate determination of the atomic weights of elements. Of course, he had to improve various analytical methods for determining atomic weights more accurately than before and probably he had to develop new analytical methods to achieve his work. However, we can imagine that his work might not attract very much scientific attention in the beginning, but his work would be highly valued after much data had been accumulated. Such kinds of laborious work can be done by even average scientists.

2. Development of modern solution chemistry

In order to provide a “bird’s-eye view” of the work carried out in modern solution chemistry, we trace back the history of solution chemistry.

It is not easy to say who is the originator of solution chemistry. Someone might say Michael Faraday (1791–1867). Some others might say that C. M.

Guldberg (1863–1902) and P. Waage (1833–1900) of Norway are the fathers of modern solution chemistry. They reported their studies on affinities [1], which was later known as the law of mass action. Some physical chemists might prefer to say

Table 1
A classification of works by Nobel laureates in chemistry

Category	Case[a]	Example
Discovery of new elements and new materials	6	Marie Curie (1911): discovery of the elements radium and polonium E.M. McMillan and G.T. Seaborg (1951): discoveries in the chemistry of the transuranium elements R.F. Curl, H.W. Kroto and R. Smalley (1996): discovery of fullerenes
Introduction of new concepts and new theories	20	S. Arrhenius (1903): advancement of chemistry by his electrolyte theory of dissociation A. Werner (1913): new light on earlier investigations and opened up new fields of research especially on inorganic chemistry K. Fukui and R. Hoffmann (1981): theories concerning the course of chemical reactions H. Taube (1983): Mechanisms of electron transfer reaction in metal complexes.
Development of new methodologies and new techniques	32	A.W.K. Tiselius (1948): electrophoresis and adsorption analysis of serum proteins J. Heyrovsky (1959): discovery and development of polarography. M. Eigen, R.G.W. Norrish and G. Porter (1967): Studies of extremely fast chemical reactions R.R. Ernst (1991): development of high resolution NMR
Synthesis of new compounds, new methods of synthesis and new findings in molecular structure	30	F. Haber (1918): synthesis of ammonia from its elements F. Joliot and I. Joliot-Curie (1953): synthesis of new radioactive elements F. Sanger (1958): structure of proteins, especially insulin D.C. Cram, Jean-Marie Lehn, and C.J. Pedersen (1987): development and use of molecules with structure-specific interactions of high selectivity
Others	1	Th. W. Richards (1914): accurate determination of atomic weight of elements
Total[b]	89	

[a] Number of Nobel prizes awarded in this general catagory.
[b] Total number of Nobel prizes in chemistry.

that the work of W. Henry (1774–1836) and F. M. Raoult (1830–1901) provided the origin of physicochemical solution chemistry.

The author prefers to say that the originator of modern solution chemistry is Arrhenius (1859–1927), who established the Theory of Dissociation of Electrolytes [2]. He also found the Arrhenius' plot for determining activation energies of chemical reactions [3]. The electroconductivity was the method employed by Arrhenius, the method also being used by Clausius, Hittorf, Kohlrausch and Ostwald at that time. The osmotic pressure measurement of solutions, which was extensively used by van't Hoff (1852–1911) and others, was another important physicochemical method used in studies of solutions of the late 19th to the early 20th century. Arrhenius derived his dissociation theory from the comparison of the results obtained by measurements of electroconductivities and osmotic pressures of dilute electrolyte solutions.

The period of the late 1800's to early 1900's can thus be classified as the first golden period of 'solution chemistry', although the term of solution chemistry had not yet been created. In this period, the equation *Physical Chemistry = Thermodynamics = Solution Chemistry* was approximately held.

Studies by van't Hoff, who introduced laws holding for gases to solutions by replacing pressure to osmotic pressure, provided part of the basis of Arrrhenius' work, and the theory of dissociation proposed by Arrhenius contributed to the work of Ostwald (1853–1932). In modern science in Europe, the knowledge obtained by some investigators was efficiently transferred to their successors to develop another new field, and the accumulation and effective transfer of information provided remarkable achievement for modern science in Europe from the end of the 19th to the beginning of the 20th century; such information transfer continues even at present days.

The second golden era for solution chemistry was started by the pioneering works of Nernst (1864–1941) and Lewis (1875–1946). In addition the work by Debye (1884–1966) and Hückel (1896–1980) published in 1923 [4] should be noted. This work was immediately followed by Bjerrum (1879–1958) [5], whose idea of ion–pair formation was induced by the Debye–Hückel Theory. Here again we see the transfer of knowledge from Debye–Hückel to Bjerrum, as we have seen in the case of van't Hoff–Arrhenius–Ostwald in the past. In their treatments Debye–Hückel and Bjerrum accepted the existence of ions with finite sizes but they ignored the molecular and liquid structures of solvents by regarding the solvent as a homogeneous continuum. We have to wait for the middle 20th century when the molecular aspects of solution were developed.

In the late 1950's to early 1960's the concept of the molecular and liquid structures of solvents, as well as solutes, were well accepted by solution chemists in their theories and explanations of experimental results, and solution chemistry entered the third golden period. This period was sometimes called the 'renaissance of solution chemistry'. The contributions of American physical chemists, such as Kirkwood, Hildebrand, Eyring, Pitzer, Guggenheim and Gurney to thermodynamics and statistical thermodynamics of solution should also be mentioned.

The structures of water and other liquids, solvated ions and molecules in solutions were discussed in various ways on a molecular basis. Theoretical consideration and analyses of experimental results were supported by high-speed electronic computers. A new methodology called Computer Simulations appeared in this period to provide a *computational microscope* by which we could *see* dynamic behavior and the instantaneous distributions of ions and molecules in solution, as well as their statistically averaged behavior which could be observed by the usual experimental methods.

Besides the physicochemical studies on solution chemistry, investigations of chemical reactions in solution were extensively developed in the latter half of the 20th century. Studies on inorganic chemical reactions in solution originated from Werner's synthetic work on coordination compounds.

Coordination chemistry and solution chemistry were rapidly developed in this period especially in the USA under the leadership of Bailar Jr., who educated eminent American coordination chemists such as Basolo who studied reaction mechanisms in solution and Kirschner who was the permanent secretary of the society of coordination chemists in the world. In the UK Nyholm also significantly contributed to the chemistry of reaction mechanisms.

The Irving–Williams series for the stability constants of divalent transition metal complexes developed in 1948 by Irving and Williams [6] was initally unexplainable and was seriously criticized by Pauling, at that time [7]. The order was later interpreted well in terms of the ligand field stabilization energies.

One of the most important results of solution coordination chemistry is the work on electron transfer reaction mechanisms [8] and the inner and outer sphere reaction mechanism concept introduced by Taube.

The work on fast reactions by Eigen in Germany is another landmark in modern solution chemistry. He developed the method for determining fast reaction rate constants [9] and he and his coworkers determined rate constants of water exchange reactions of many hydrated ions [10].

Ionic hydration is a fundamental subject of solution chemistry. After the work by Frank–Wen [11] and Samoilov [12] in 1957, a number of studies have been carried out to determine the hydration structure around ions.

NMR is one of the most effective methods for studying ionic hydration and the hydration numbers of most ions were determined by this method. However, for some ions such as Zn^{2+}, alkali metal ions and most anions, which have large water exchange rate constants, the NMR results were sometimes erroneous.

X-Ray diffraction (XD) studies on the hydration structure of ions had already been examined in the 1920s to early 1930s. At that time the results were not well accepted by most physical chemists and coordination chemists because the workers did not take into consideration sufficiently the chemical reactions taking place in the solutions. However, the methodology is accepted by chemists nowadays as one of the most important tools in studying the structures of liquids and solutions.

Neutron diffraction (ND) and EXAFS studies arrived much later than XD and they have provided information on the static and dynamic structures of the hydration shells of ions. Molecular dynamics (MD) simulations gave us information on the instantaneous and dynamic view of hydrated water molecules and ions. XD, ND and XAFS (EXAFS and XANES) studies and MD simulations are complementary methodologies which support each others results. However, the subject of ionic solvation remained as an attractve but incompletely solved problem for solution chemists.

The introduction of new concepts in science is highly appreciated as we categorized in Table 1. If we could summarize known facts in a proper way, we might create new concepts and new theories. A typical example is the Periodic Table proposed by Mendeleev (1834–1907) in 1869. The 'hard and soft acids and bases (HSAB)' concept originally proposed by Ahrland–Chatt–Davies [13] and then improved by Pearson [14] and the 'donor–acceptor' concept together with empirical parameters proposed by Gutmann and his colleagues [15,16], as well as other work on solvent and reaction parameters, are important concepts which summarize the chemical properties of solutes and solvents in semi-quantitative ways. They are very useful for the more complete understanding of chemical reactions in various solvents.

3. The history of solution chemistry in Japan

The development of solution chemistry in Japan clearly shows two distinct trends originating from physical and coordination chemistry.

Solution chemistry in Japan was started by Sakurai (1858–1936), who was a professor of the Imperial University of Tokyo and a leading scientist in the entire field of chemistry in Japan. Since he was a physical chemist, the equation 'physical chemistry = thermodynamics = solution chemistry' also applied in Japan at that time. Both Ikeda (1864–1936) of the Imperial University of Tokyo who discovered sodium glutamate ("Aji-no-moto") which turned his interest to organic chemistry from physical chemistry and Ohsaka (1867–1950) of Kyoto Imperial University studied physical chemistry in Ostwald's laboratory in Germany. Katayama (1877–1961) contributed to the development of solution chemistry in the field of thermodynamics and thermochemistry. However, in this period most chemistry in Japan was imported by Japanese pioneering scientists from Europe as copies of European studies. In contrast to these, Hirobe (1883–1914), who was a lecturer at the Imperial University of Tokyo, made a calorimeter of his own design and measured the heats of mixing of liquids in 1913 [17]. His work was published in 1926 after his death. He can be recognized as the pioneer of solution thermochemistry in Japan.

In the early 1900's solution chemistry seemed to be one of the most modern, fashionable and active branches or even the main area of physical chemistry. On the other hand solution chemistry as a branch of inorganic chemistry grew by using the spectroscopic method after Shibata (1882–1980) returned from the laboratory of Werner in Switzerland in 1913. His method, developed for the determination of the composition of metal complexes formed in solution [18], was created prior than Job's work [19], although this is now mostly referred to as Job's method. The first spectrometer was brought into Japan by Shibata from Switzerland in 1913 when he returned. Yuji Shibata is recognized as the pioneer of spectrochemistry and geochemistry in Japan, as well as inorganic synthetic chemistry which spread to many schools in various universities in Japan after him. The spectroscopic method used in the visible region was one of the most advanced and important methods in inorganic chemistry and analytical chemistry in Japan in 1930's–1940's. The spectrochemical series of absorption curves of cobalt(III) complexes proposed by Tsuchida (1903–1962) (who was one of Shibata's pupils) and his colleagues [20] is one of the most remarkable achievements of coordination and solution chemistry in Japan before World War II. The series was later explained in terms of the ligand field theory.

Polarograhy, a new method discovered in 1929 by Heyrovsky (1890–1967) of Czechoslovakia was introduced by Shikata (1895–1964), who was a coworker of Heyrovsky, to Japan and the method immediately attracted many Japanese analytical chemists and electrochemists. The method was applied to study the redox reactions of various metal complexes in solution. Studies on ion-pair formation were carried out by the method, as well as by the conductivity method.

4. The development of methodologies in solution chemistry

The introduction of the definition of pH [21] by Sϕrensen (1868–1939) connected concentrations to electromotive forces through the logarithmic operation. Production of glass electrodes accelerated the emf measurements of electrolyte solutions, especially acidic solution. The method is called pH-metry, and was widely employed for the determination of dissociation constants of acids and stability constants of various metal complexes by employing the methodologies developed by Bjerrum of Denmark, Sillén of Sweden, Schwarzenbach of Switzerland, and Marthell of USA around 1960–1970. There are many students and 'grandstudents' of those scientists in Japan.

Equilibrium constants give us the corresponding values for the Gibbs free energies of the reactions. The enthalpies of reaction can be determined by calorimetric measurements. Then, the entropies of reaction can be derived from measurements of equilibrium constants and enthalpies. Therefore, the two methods are complementary to each other.

The spectrometric method was remarkably improved by the introduction of photosensitive detectors, which extended the measurable region from the visible range to the ultraviolet and to the infrared regions. Infrared and Raman spectroscopies and circular dichroism spectroscopy have been widely used in studies of solutions from physicochemical and inorganic chemical points of view.

Nuclear magnetic resonance spectroscopy is extremely useful for investigating various systems, and nowadays NMR is an indispensable tool for studying structure and static and dynamic behavior of molecules in solution.

Structural studies of molecules and molecular ensembles were carried out mainly by spectrophotometric methods, and structural information was usually obtained from the results of X-ray crystallography. However, direct structural analysis of species in solution could be achieved by XD and ND methods, although the latter method only became usable when intensive neutron sources became available from reactors and synchrotron radiation facilities. In contrast to the ND studies, the solution X-ray diffraction method (SXD) for the structural studies of molecules and molecular arrangements in solution was already examined immediately after the work by Laue and Bragg in 1912–1913. The first important paper by Bragg (1862–1942) and Bragg (1890–1971) for XD of crystals was published in 1913 [22], and a shadow pattern caused by diffraction of X-rays from amorphous substances was observed by Debye and Scherrer in 1916 [23]. Subsequently the method has been used for water and other liquids, molten salts, alloys and electrolyte and nonelectrolyte solutions.

The early SXD studies around the 1930's on the structure of complexes in solution are not very reliable. The method became more reliable owing to the development of equipment after 1950, but the explanations of results are sometimes rather curious from the view point of solution chemistry. Johansson, who was a member of Sillén's school in Stockholm, Sweden and had a lot of experience in the solution equilibria of complex formation reactions, presented sound analyses of his diffraction data.

The structural investigation of water by SXD was carried out in 1930–1931 [24–26] and provided experimental evidence for the theoretical considerations of Bernal and Fowler in 1933 [27]. The diffraction work on water was followed by Morgan and Warren (1938) [28], and then, Levy and Narten [29]. Introduction of the ND method was much later [30].

The structural studies of metal complexes in solution by X-ray diffraction, and then, neutron diffraction and XAFS methods were developed in Europe and the USA in the 1950's, and were introduced to Japan around the 1960's in studies of liquid metals, molten salts, and then, ionic aqueous and non-aqueous solutions. From a historical point of view, the first study on the structure of metal complexes in solution in Japan was demonstrated for the tetraiodocadmate complex in 1974 [31]. The method was then employed for studies on the hydration structure of various ions, and the results summarized in reviews [32,33]. The structures of hydrated ions are fundamental to solution chemistry, and thus, we have to have reliable information about the structural as well as the dynamical behavior of hydrated ions. The structure of a single ion may not be very attractive to most solution chemists. However, if the hydration structure of all ions in the periodic table could be determined, this would make a remarkable contribution to solution chemistry.

Results of the structural studies on ionic hydration by diffraction methods were combined with those derived by computer simulations.

I wish to quote an interesting sentence written in Marcus' review [32]: 'The diffraction measurements and the computer simulations are applied to electrolyte solutions in only a relatively small number of laboratories. The same names reappeared in the publications. The most active groups are located in Italy, Germany, England, Hungary, Sweden and Japan, while several additional groups have also made important contributions. Remarkable, however, is the constant cooperation between many groups, co-workers from one being temporary guests with another, so that many of the papers bear the addresses of several laboratories. A community of researchers with interest in this field appears to have built up with worldwide connections, a very commendable development'. Such cooperation among different laboratories of various countries is common in European and USA communities as seen in the case of vant' Hoff–Arrhenius–Ostwald, and nowadays we see such cooperation everywhere, but in the 1970's it was very rare to have a worldwide multilateral cooperation in the field of chemistry in Japan, although bilateral cooperation was common.

5. Search for ways to new fields

A scientist who can show flashes of genius may have a good chance to create a new field. How about scientists with an average talent? Do we need super-human efforts to accumulate knowledge? Should we expect a luck?

Ostwald created a new field (at least, a new term) of physical chemistry by the combination of physics and chemistry. An interdisciplinary field can be created at a boundary of two or three different fields. Bioinorganic chemistry is an interdisciplinary chemistry among inorganic chemistry, biochemistry and solution chemistry. The combination of different knowledge is thus one of the ways to create a new field. The combination of different methods may also create a new method. One of the typical examples is the work by Michael Smith of Canada who received the Nobel prize of chemistry in 1993 due to his significant contribution to the synthesis of proteins.

As we discussed in previous sections, the extension of existing methods can result in a new field. One of the typical examples is the work of Richard R. Ernst of Switzerland who developed the methodology of high resolution NMR spectroscopy. He received the Nobel prize for chemistry in 1991.

Thus, we may have an opportunity to make a new pathway to approach a gate of a new field by combining or extending existing theories and methods.

In the following section a newly developed methodology will be shown as an example which has been explored by our group for the determination of the structure of reaction intermediates to elucidate mechanisms of complex formation reactions in solution from the structural point of view. The method is to combine the stopped-flow technique and the EXAFS method.

6. The stopped-flow EXAFS method

It may be a natural trend that one who is investigating reaction mechanisms in solution wishes to see the structure of reaction intermediates. One who is using EXAFS apparatus may wish to try the method to the determination of structure of reaction intermediates, because the EXAFS method is very convenient for the structural determination of metal complexes in solution. However, no one has succeeded in achieving this objective with sufficient reliability until recently.

The time resolved structural analysis of species in solution by EXAFS was reported by Thiel et al. [34]. for the $[Pt_2(P_2O_5H_2)_4]^-$ complex by using laser flash for exciting the complex and an synchrotron radiation (SR) facility, but the result is not very reliable because the quantities of excited species formed was small (only 18%). They measured Pt–P and Pt–O bond lengths and the nonbonding Pt···Pt distance in the excited species of the binuclear complex. The measurement was rather difficult because the excited species coexists with the reactant and product which are the major components in the solution.

We could not find in the literature the stopped-flow EXAFS (SF-EXAFS) method for the structural determination of reaction intermediates when we undertook exploration of the method. We were looking for financial support for constructing an SF-EXAFS apparatus for the study of the structure of short-lived reaction intermediates in complex formation reactions in solution. However, it was difficult to find a suitable reaction system for study. At that time people in the Photon Factory of the National Laboratory of High Energy Physics in Tsukuba, Japan conceived the same idea and they examined the use of their SF-EXAFS apparatus for the structural analysis of reaction intermediates in a reducing reaction of Fe(III) ions with hydroquinone by constructing an SF-EXAFS apparatus with SR. Unfortunately for them and fortunately for us, they did not succeed in the structural determination of the intermediate of the reduction reaction. They only traced changes in the EXAFS spectrum of the Fe(III)–Fe(II) ions by the stopped-flow method [35], because the reaction rate was too fast to use the method for the structural determination of a reaction intermediate. Then, they abandoned further investigation of this subject.

In 1991 we obtained funding from the Ministry of Education, Science and Culture of Japan and found a suitable system for the use of the SF-EXAFS method to determine the structure of reaction intermediates in solution. We modified a laboratory scale EXAFS apparatus which we had in our laboratory since 1985. The metal substitution reaction of the mercury(II) porphyrin complex with divalent transition metal ions [36,37] was selected as the system to be studied. Copper(II) and cobalt(II) ions are suitable ions to be examined by our table-top EXAFS apparatus with a rotating anode emitting the characteristic X-rays of the Mo–K_α and K_β lines, which interfere with the EXAFS measurements of transition metals other than Cu and Co due to the overlap of the lines with the energies at their absorption edges. Moreover, the rate constants of the reaction are reasonable for the structural determination of the reaction intermediate with this method. By choosing appropriate experimental conditions, almost 100% of the reaction intermediate is formed in the solution for a certain time range. A relatively simple reaction mechanism is also convenient for analysis of the EXAFS spectra obtained. Thus, we adopted this system as the first test case for the structural determination of reaction intermediates in solution by the newly explored SF-EXAFS method [38–40].

6.1. Apparatus

The SF-EXAFS apparatus [41] consists of two parts; a stopped-flow cell and a

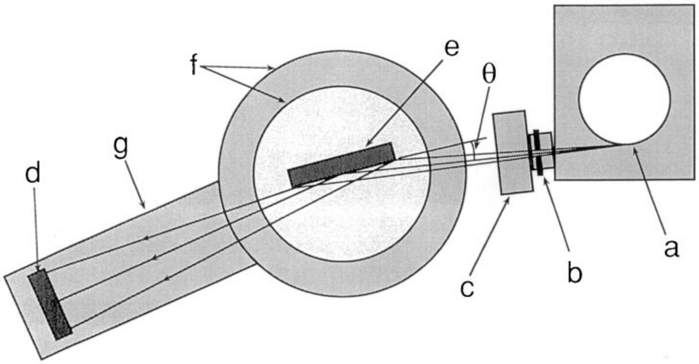


Fig. 1. Schematic diagram of SF-EXAFS apparatus: (a) rotating anode; (b) slit; (c) stopped-flow unit; (d) photodiode detector; (e) monochromator; (f) goniometer; (g) detector arm.

table-top EXAFS apparatus. The detector used is a photodiode-array detector (Fig. 1). A computer-controlled system is employed for data collection and opening and closing a shutter to extract a suitable EXAFS spectrum of a mixture under investigation within a certain time range after mixing the two solutions, one being a solution containing divalent metal ions and the other the mercury(II) porphyrin complex. A polychromatic X-ray flux generated from a rotating anode X-ray generator (RU-300, RIGAKU Co. Lt., Tokyo, Japan) with a voltage of 12 kV and the current of 160 mA is transmitted through an observation cell in the stopped-flow unit. The transmitted X-rays are reflected at the surface of a flat LiF(200) monochromator crystal, and their intensities are measured by a position sensitive self-scanning photodiode array (S3904-1024Q, Hamamatsu Photonics K.K., Shizuoka, Japan). The incident angle of the X-ray flux on the monochromator crystal is changed continuously along the crystal surface.

The goniometer is equipped with two rotary disks (f in Fig. 1) with the same rotation center. The monochromator crystal is placed on one disk, and the incident angle θ of the X-ray flux on the monochromator center is varied by rotation of the disk. The detector is mounted on the other disk. The distance between the monochromator and the detector can be varied from 15 to 45 cm.

The block diagram of the stopped-flow assembly and the observation cell are shown in Fig. 2. Two solutions A and B are contained in each piston cylinder (Fig. 2i) from reservoirs (r), and then pushed out toward the mixing chamber (d). The cell is shown in Fig. 2ii.

The background intensity of transmitted X-rays (I_b) is measured when the observation cell in the stopped-flow unit is filled with a medium solution. When the cell is filled with solutions which are mixed in the cell, the intensity of transmitted X-rays through the cell with the sample solution is measured (I_s) for a given time (we call it ‘gate time’). Then, the value, $\ln(I_b/I_s)$, corresponds to the absorbance. The 150 μm thick window of the stopped-flow cell is made of boron nitride pyrolytically prepared.

6.2. Reaction system

5,10,15,20-Tetrakis(4-sulfonatophenyl)porphine (H_2tpps^{4-}; see Fig. 3) forms a binuclear complex with the mercury(II) ion $[\mathrm{Hg}_2^{\mathrm{II}}(\mathrm{tpps})]^{2-}$ which is in equilibrium with the mononuclear mercury(II) complex $[\mathrm{Hg}^{\mathrm{II}}(\mathrm{tpps})]^{4-}$ and the hydrated mercury(II) ion in water at pH 5.8 and at 25°C (Eq. (1)). The rate of dissociation of $[\mathrm{Hg}_2(\mathrm{tpps})]^{2-}$ depends on pH.

$$[\mathrm{Hg}_2^{\mathrm{II}}(\mathrm{tpps})]^{2-} \underset{k_{-1}}{\overset{k_1}{\leftrightarrows}} [\mathrm{Hg}^{\mathrm{II}}(\mathrm{tpps})]^{4-} + \mathrm{Hg}^{2+} \tag{1}$$

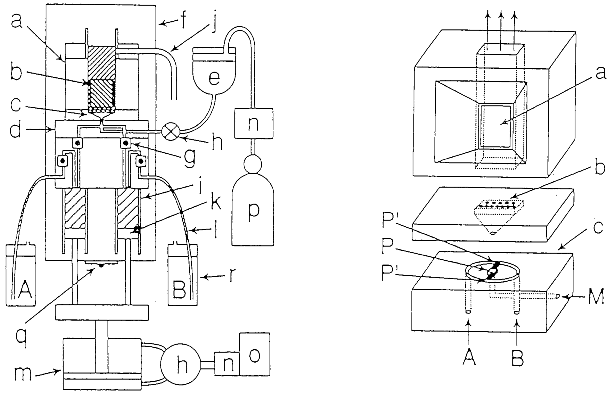
A divalent metal ion M^{2+} attacks the mononuclear species to form a heterobinuclear complex $[\mathrm{Hg}^{\mathrm{II}}(\mathrm{tpps})\mathrm{M}^{\mathrm{II}}]^{2-}$ as a reaction intermediate. The intermediate decomposes to the complex with the divalent metal ion and the hydrated mercury(II) ion (Eq. (2)).

$$[\mathrm{Hg}^{\mathrm{II}}(\mathrm{tpps})]^{4-} + \mathrm{M}^{2+} \overset{k_2}{\rightarrow} [\mathrm{Hg}^{\mathrm{II}}(\mathrm{tpps})\mathrm{M}^{\mathrm{II}}]^{2-} \overset{k_3}{\rightarrow} [\mathrm{M}^{\mathrm{II}}(\mathrm{tpps})]^{4-} + \mathrm{Hg}^{2+} \tag{2}$$

In the case of the cobalt(II) ion the reaction proceeds further to $[\mathrm{Co}^{\mathrm{III}}(\mathrm{tpps})]^{3-}$ by oxidation with dissolved oxygen in water.

$$[\mathrm{Co}^{\mathrm{II}}(\mathrm{tpps})]^{4-} \underset{\mathrm{slow}}{\overset{\mathrm{O_2}}{\rightarrow}} [\mathrm{Co}^{\mathrm{III}}(\mathrm{tpps})]^{3-} \tag{3}$$

Since the rate determining step is the leaving step of the mercury(II) ion from the $[\mathrm{Hg}^{\mathrm{II}}(\mathrm{tpps})\mathrm{M}^{\mathrm{II}}]^{2-}$ complex, the rate constants, k_1, k_2/k_{-1} and k_3 should be indepen-



(i) (ii)

Fig. 2. (i) Block diagram of stopped-flow assembly: (a) observation cell; (b) window; (c) nozzle; (d) mixing chamber; (e) medium solution vessel; (f) thermostated block; (g) ruby ball; (h) electromagnetic two-way valve; (i) piston cylinder; (j) drain; (k) piston head; (l) Teflon tube; (m) gas cylinder, (n) pressure regulator; (o) air compressor; (p) nitrogen gas cylinder; (q) microswitch; (r) reservoir. A and B are a medium solution containing the mercury–porphyrin complex with an acetate buffer of ca. pH 5.8 and a solution containing divalent metal ions, respectively. (ii) Block diagram of observation cell and mixing chamber: (a) window made of boron nitride; (b) nozzle; (c) mixing chamber. A and B are the two solutions given in (i). P and P′ are three point outlets of solutions in the mixing chamber.

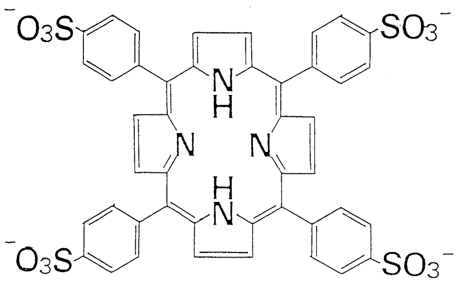


Fig. 3. 5,10,15,20-Tetrakis(4-sulfonatophenyl)porphine.

dent of the entering divalent metal ions (for Cu^{2+}; $k_1 = 1.95 \times 10^8$ mol^{-1} dm^3 s^{-1}, $k_2/k_{-1} = 7.14$, and $k_3 = 1.00 \times 10^{-2}$ s^{-1} [37] and for Zn^{2+}; $k_1 = 1.56 \times 10^8$ mol^{-1} dm^3 s^{-1} $k_2/k_{-1} = 0.14$, and $k_3 = 1.09 \times 10^{-2}$ s^{-1} [36] at 25°C). Although no rate constant was determined for the cobalt(II) ions, the values of the constants should be practically the same as those for copper(II) and zinc(II) ions.

From the rate constants and results from some additional experiments, we found that the reaction intermediates of the metal substitution reactions of the mercury(II) ion with copper(II) and cobalt(II) ions form approximately 100% after 1 s of mixing the two solutions and they exist in the solution for several seconds without significant decomposition. We repeated the measurements several hundred times (we call ‘accumulation’) until we obtain an EXAFS spectrum with reasonably smooth modulations (Scheme 1).

The reaction between H_2tpps^{4-} and Co^{2+} is slow and the product $[Co^{II}(tpps)]^{4-}$ is slowly oxidized to $[Co^{III}(tpps)]^{3-}$. The rate of oxidation is faster than the rate of formation of the cobalt(II)–porphyrin complex, and thus, the structure of the $[Co^{II}(tpps)]^{4-}$ complex is hardly determinable by the normal SXD method or the usual EXAFS method. Since a small amount of mercury(II) ions catalyzes the metallation reaction through the reaction scheme shown in Eqs. (1) and (2), we can determine the structure of $[Co^{II}(tpps)]^{4-}$, as well as $[Hg^{II}(tpps)Co^{II}]^{2-}$ and $[Co^{III}(tpps)]^{3-}$, by the SF-EXAFS method. The structure of the final product $[Co^{III}(tpps)]^{3-}$ is also determinable by the usual SXD and EXAFS methods.

The EXAFS spectra of solutions of copper(II) perchlorate, cobalt(II) perchlorate, and hexaamminecobalt(III) chloride are measured in the same way as reference. Some additional EXAFS measurements including structural determinations of the hydrated mercury(II) ion and $[Hg_2^{II}(tpps)]^{2-}$ were carried out by the EXAFS method at the Photon Factory in Tsukuba, Japan. The composition of the solutions used and the experimental conditions employed in the present work are shown in Table 2.

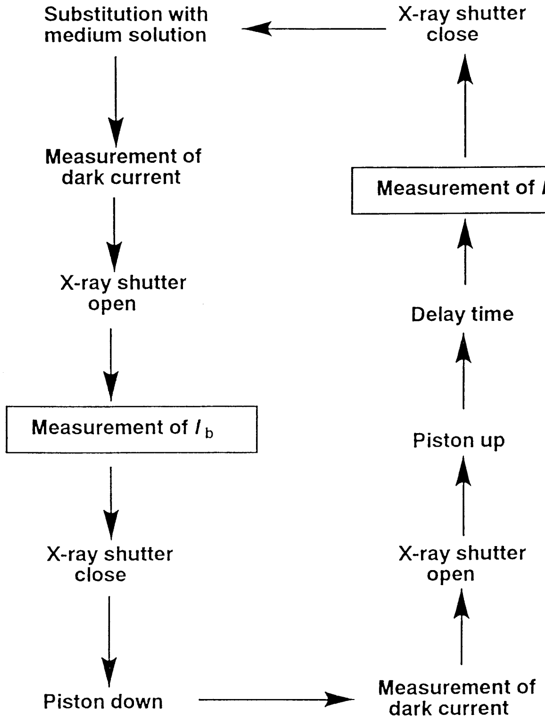
6.3. Analysis of SF-EXAFS data

After accumulation of SF-EXAFS data by repeating the measurements several hundred times, the smooth modulation spectrum was analyzed by the method usually employed for EXAFS analyses.

Background absorption other than that of K-shell absorption is estimated by the least-squares fitting Victoreen formula to the pre-edge data, and then subtracted from the total absorption in the post-edge region by extrapolation. The smooth K-shell absorption μ_b is evaluated by fitting a smooth curve to the observed absorption spectrum using an eighth-order polynomial function. The EXAFS pattern $\chi(k)$ is then extracted and normalized as

$$\chi(k) = \{\mu_s(k) - \mu_b(k)\}/\mu_b(k) \tag{4}$$

where k is the photoelectron wave vector and given as $2\pi\{2m(E-E_0)\}^{1/2}/h$. The parameter E represents the energy of the incident X-rays. The threshold energy of a K-shell electron E_0 is selected as the position of the inflection point of the edge jump in each sample. Other notations are of usual meaning. The $\chi(k)$ values weighted by k^3 are converted to the radial structure function $F(r)$ as



Scheme 1.

Table 2
Compositions of sample solutions and experimental conditions for the SF-EXAFS measurements at the metal substitution reaction of the mercury(II)–porphyrin complex with Cu^{2+} and Co^{2+}

Solution	Cu^{2+} system					Co^{2+} system				
	Solute content	Concentration (mol kg^{-1})	Gate time (s)	Accumulation (times)	Total time (s)	Solute content	Concentration (mol kg^{-1})	Gate time (s)	Accumulation (times)	Total time (s)
A	$Cu(CH_3COO)_2$	0.20				$Cu(CH_3COO)_2$	0.20			
	CH_3COONa	2.58	25	48	1200	CH_3COONa	1.58			
	CH_3COOH	0.2				CH_3COOH	0.20	30^b	100	3000
	pH 5.67					pH 5.67				
B	$Cu(CH_3COO)_2$	0.10				$Cu(CH_3COO)_2$	0.20			
	H_6tpps	0.10				H_6tpps	0.20			
	CH_3COONa	0.50	25	36	900	CH_3COONa	1.61			
	CH_3COOH	0.20				CH_3COOH	0.20			
	NaOH	0 66				NaOH	1.01			
	pH 5.70					pH 5.70				
C	$Hg(CH_3COO)_2$	0.20				$Hg(CH_3COO)_2$	0.0021			
	H6tpps	0.20				H6tpps	0.20			
	CH_3COONa	1.61				CH_3COONa	1.61			
	CH_3COOH	0.20				CH_3COOH	0.20			
	NaOH	1.01				NaOH	1.01			
	pH 5.80					pH 5.80				

Table 2 (Continued)
Compositions of sample solutions and experimental conditions for the SF-EXAFS measurements at the metal substitution reaction of the mercury(II)–porphyrin complex with Cu^{2+} and Co^{2+}

Solution	Cu^{2+} system					Co^{2+} system				
	Solute content	Concentration (mol kg^{-1})	Gate time (s)	Accumulation (times)	Total time (s)	Solute content	Concentration (mol kg^{-1})	Gate time (s)	Accumulation (times)	Total time (s)
D	A+C pH 5.43 after mixing		10	180	1800	A+B pH ca. 5.5 after mixing		10[c]	266[c]	2660[c]
						A+C pH ac.5.5 after mixing		30[d]	90[d]	2700[d]
E[a]	$CuSO_4$	0.20	5	750	3800	$Co(ClO_4)_2$	0.10	30[b]	80	2400
F[a]						$[Co(NH_3)_6]Cl_3$	0.10	30[b]	100	3000
G[e]						$[Co^{III}(tpps)] \cdot (CH_3COO)_3$	0.10	30[b]	111	3330

[a] Standard solution.

[b] Upper limit of the gate time due to the saturation of the diode array used.

[c] For the determination of the intermediate $[Hg^{II}(tpps)Co^{II}]^{2-}$.

[d] For the determination of $[Co^{III}(tpps)]^{4-}$ after mixing for 300 s

[e] $[Co^{III}(tpps)](CH_3COO)_3$ was prepared by mixing cobalt(III) acetate with H_6tpps which had been neutralized with a stoiciometric amount of NaOH in water, and then, by heating the resultant solution on a water bath for several hours.

$$F(r) = (1/2\pi)^{1/2}\int_{k_{\min}}^{k_{\max}} k^3\chi(k)W(k)\exp(-2ikr)\mathrm{d}k \tag{5}$$

where $W(k)$ is the window function of the Hanning type [42].

The structure parameters are optimized in the k-space by comparing the observed EXAFS spectrum with the model function $\chi(k)_{\mathrm{calcd}}$ given by the single-electron and single-scattering theory[43–46] as

$$\chi(k)_{\mathrm{calcd}} = \sum\{n_j/kr_j^2\}\exp(-2\sigma_j^2k^2 - 2r_j/\lambda)F_j(\pi, k)\sin(2kr_j + \alpha_j(k)) \tag{6}$$

where $F_j(\pi, k)$ is the backscattering amplitude from each of n_j scatters j at distance r_j from the X-ray absorbing atom. σ_j is the Debye–Waller factor and λ is the mean free path of photoelectrons. $\alpha_j(k)$ is the total scattering phase shift experienced by the photoelectrons.

The values of $F_j(\pi, k)$ and $\alpha_j(k)$ in Eq. (6) are quoted from the literature [47,48]. By comparing the Fourier filtered $k^3\chi(k)$ curve with the model function to minimize the error-square sum $\Sigma k^6(\chi(k)_{\mathrm{obsd}} - \chi(k)_{\mathrm{calcd}})^2$, the parameters E_0 and λ are evaluated from EXAFS spectra of standard samples. The parameters are then used as constants in the course of the subsequent structure analysis of unknown samples, while the r, σ and n values are optimized as variables.

6.4. Structure of reaction intermediate $[\mathrm{Hg^{II}(tpps)M^{II}}]^{2-}$

The EXAFS spectra extracted for solutions A, B, D, and E given in Table 2 are shown in Fig. 4i. The Fourier transforms of the EXAFS data are depicted in Fig. 4ii. It is obvious that the peak of the curve of solution D containing the reaction intermediate $[\mathrm{Hg^{II}(tpps)M^{II}}]^{2-}$ shifts towards the longer side of the Cu–ligand distance than that of solution B, which contains the final product $[\mathrm{Cu(tpps)}]^{4-}$. Theoretical curves calculated from the structural parameters finally obtained (Table 3) fit well to the experimental curves which are inversely Fourier transformed ones of the peaks in Fig. 4ii after treatment of the peak region by employing a window function.

The structural parameters of the $[\mathrm{Hg^{II}(tpps)M^{II}}]^{2-}$ complex, together with other complexes used as reference are summarized in Table 3. By using the bond lengths obtained for the reaction intermediate, we can draw a scheme of the bond-length variation between the copper(II) ion and ligand atoms (oxygen and nitrogen atoms) in the course of the metal substitution reaction of $[\mathrm{Hg_2^{II}(tpps)}]^{2-}$ with $\mathrm{Cu^{2+}}$as seen in Fig. 5.

The copper(II) ion in the heterobinuclear reaction intermediate is six coordinate with two nitrogen atoms in the porphyrin ring and four oxygen atoms which may be water molecules and acetate ions. The Cu–N distance is longer by about 4 pm than the Cu–N distance in the stable final product of $[\mathrm{Cu(tpps)}]^{4-}$. If we simply assume that the porphyrin ring was planar, the copper(II) ion should be off from the plane by 40 pm. Since the porphyrin plane is expected to be distorted, the deviation of the copper(II) ion from the center of the ring should be much larger.

Table 3

Structural parameters around the copper(II) and cobalt(II)/(III) ions and those around the mercury(II) ion in solutions used for the studies on the metal substitution reaction of mercury(II)–porphyrin complexes with Cu^{2+} and Co^{2+} ions

Cu^{2+} system					Co^{2+} system				
Solution and complex to be determined	Atom pair	Interatomic distance r (pm)	Debye–Waller factor, σ (pm)	Number of scatters, n	Solution and complex to be determined	Atom pair	Interatomic distance r (pm)	Debye–Waller factor, σ (pm)	Number of scatters, n
A	Cu–O_{eq}	196(1)	5.5(0.3)	4[e]	A	Co^{II}–O	212(1)	8.4(0.1)	6.4(0.1)
$[Cu(CH_3COO)_p]^{(2-p)+}$	Cu–O_{ax}	225(3)	8.9(0.7)	2[e]	$[Co^{II}(CH_3COO)_p]^{(2-p)+}$				
A[a,b]	Cu–O_{eq}	197(1)	7.4(0.1)	4.4(0.1)	E	Co^{II}–O	210(1)	6.9(0.3)	6[e]
$[Cu(CH_3COO)_p]^{(2-p)+}$	Cu–O_{ax}	225(1)	10.1(0.5)	2.1(0.2)	$[Co(H_2O)_6]^{2+}$				
A[a,c]	Cu–O_{eq}	197(1)	5.8(0.4)	4[e]	D	Co^{II}–N	212(2)	1.3(0.2)	2[e]
$[Co(H_2O)_6]^{2+}$	Cu–O_{ax}	226(2)	11.9(0.9)	2[e]	$[Hg^{II}(tpps)Co^{II}]^{2-}$	Co^{II}–O	221(2)	1.3(0.2)	3.6(0.3)
B[a,d]	Cu–N	200(1)	8.0(0.6)	3.8(0.2)	D[f]	Co^{II}–N	203(1)	2.7(0.4)	4[e]
$[Cu(tpps)]^{4-}$					$[Co^{III}(tpps)]^{4-}$	Co^{II}–O	215(1)	2.7(0.4)	2.3(0.1)
B[a,d]	Cu–N	200(1)	4.8(0.1)	3.5(0.1)	G[g]	Co^{III}–N	189(1)	1.0(5.7)	4[e]
$[Cu(tpps)]^{4-}$					$[Co^{III}(tpps)](CH_3Coo)_3$	Co^{III}–O	187(2)	1.0(5.7)	1.8(0.1)
C[a]	Hg–N	223(1)	8.9(0.5)	2.2(0.3)	F	Co^{III}–N	194(1)	5.6(0.2)	6[e]
$[Hg_2(tpps)]^{4-}$	Hg–O	260(3)	11.0(3.0)	0.7(0.5)	$[Co(NH_3)_6]^{3+}$				
D	Cu–N	294(1)	8.0[e]	2[e]					

Table 3 (Continued)
Structural parameters around the copper(II) and cobalt(II)/(III) ions and those around the mercury(II) ion in solutions used for the studies on the metal substitution reaction of mercury(II)–porphyrin complexes with Cu^{2+} and Co^{2+} ions

Cu^{2+} system					Co^{2+} system				
Solution and complex to be determined	Atom pair	Interatomic distance r (pm)	Debye–Waller factor, σ (pm)	Number of scatters, n	Solution and complex to be determined	Atom pair	Interatomic distance r (pm)	Debye–Waller factor, σ (pm)	Number of scatters, n
$[Hg(tpps)Cu]^{2-}$	$Cu–O_{eq}$	195(1)	8.1^{e}	2^{e}					
	$Cu–O_{ax}$	229(3)	11.8(0.4)	2^{e}					
E	$Cu–O_{eq}$	196(1)	8.1(0.2)	4^{e}					
$[Cu(H_2O)_6]^{2-}$	$Cu–O_{ax}$	229(3)	11.8(0.4)	2^{e}					

[a] The structural parameters obtained by the analysis of EXAFS data measured by SR.

[b] $[Cu(CH_3COO)_2] = 0.10$ mol dm^{-3}; $[CH_3COONa] = 0.50$ mol dm^{-3}; $[CH_3COOH] = 0.20$ mol dm^{-3} in water.

[c] $[Cu(NO_3)_2] = 1.0$ mol dm^{-3} in water.

[d] $[Cu(tpps)]_4 = 0\ 01$ mol dm^{-3}; $[CH_3COONa] = 0.50$ mol dm^{-3}; $[CH_3COOH] = 0.20$ mol dm^{-3} in water.

[e] The value was fixed during the least-squares calculation.

[f] Measured 300 s after mixing solutions A and B.

[g] $[Co^{III}(tpps)](CH_3COO)_3$ was prepared by mixing cobalt(II) acetate and H_6tpps which had been neutralized with a stoichiometric amount of NaOH in water, and then, by heating the resultant solution on a water bath for several hours.

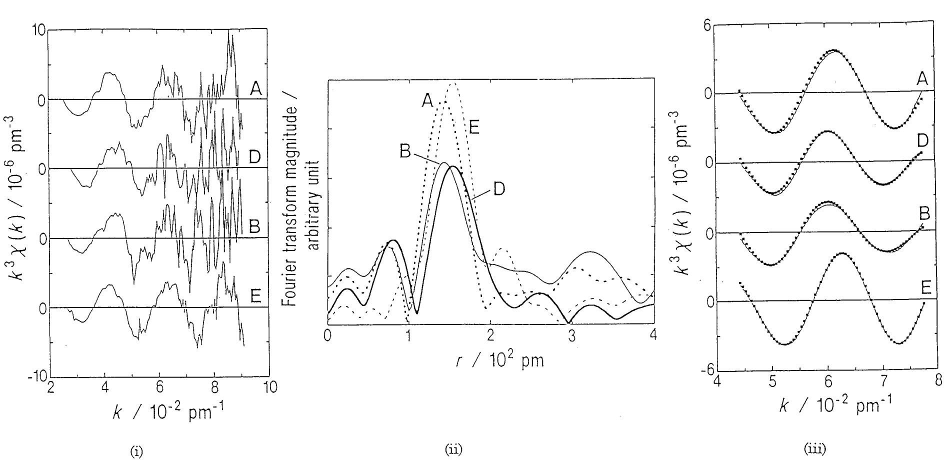


Fig. 4. (i) EXAFS spectra, (ii) their Fourier transforms, and (iii) Fourier filtered $k^3\chi(k)$ curves (experimental, dotted lines; calculated, solid lines) of solutions A, B. D and E (see Table 2) of the copper(II)–mercury(II) porphyrin system.

The same procedures have been applied to the cobalt(II) system, as seen in Fig. 6, to analyze the structure of the reaction intermediate $[Hg^{II}(tpps)Co^{II}]^{2-}$, as well as $[Co^{II}(tpps)]^{4-}$ and $[Co^{III}(tpps)]^{3-}$. The bond lengths and other structural parameters of the complexes examined are summarized in Table 3.

The reaction scheme of the metal substitution reaction of the binuclear mercury(II) complex of tpps^{6-} and bond-length variations in the course of the reaction are depicted in Fig. 7.

The Co^{2+}–N bond in the intermediate is ca. 9 pm longer in this case than the corresponding bond in the final product $[Co^{II}(tpps)]^{4-}$. The Co^{3+}–N bond in $[Co^{III}(tpps)]^{3-}$ is shorter than the Co^{2+}–N bond in $[Co^{II}(tpps)]^{4-}$ because of the smaller ionic size of Co^{3+} than Co^{2+}. The Co^{2+}–N (212 pm) and Co^{2+}–O (221 pm) distances in $[Hg^{II}(tpps)Co^{II}]^{4-}$ are longer than the corresponding bond lengths in $[Co^{II}(tpps)]^{4-}$ (203 pm and 215 pm, respectively), and the elongation of the bonds may be responsible for the instability of the reaction intermediate.

7. Concluding remarks

This is the first case that one could determine the structure of a reaction intermediate in solution with sufficient reliability without quenching the solution. This is also the first case of a successful application of the newly developed SF-EXAFS method. Although the examples shown here are rather limited, we can quote another study for a chromium complex [49].

The SF-EXAFS is a good method for determining structures of reaction intermediates provided that the life time of the reaction intermediates is around seconds to milliseconds. The application of the EXAFS method for reaction intermediates with much shorter life times may be possible if one uses other methods for producing reaction intermediates by means, for example, of flash photolysis and relaxation processes. If the maximum concentration of the intermediate is small and the solution contains significant amounts of reactants and products together with an intermediate, the spectra of the reactants and products have to be removed from

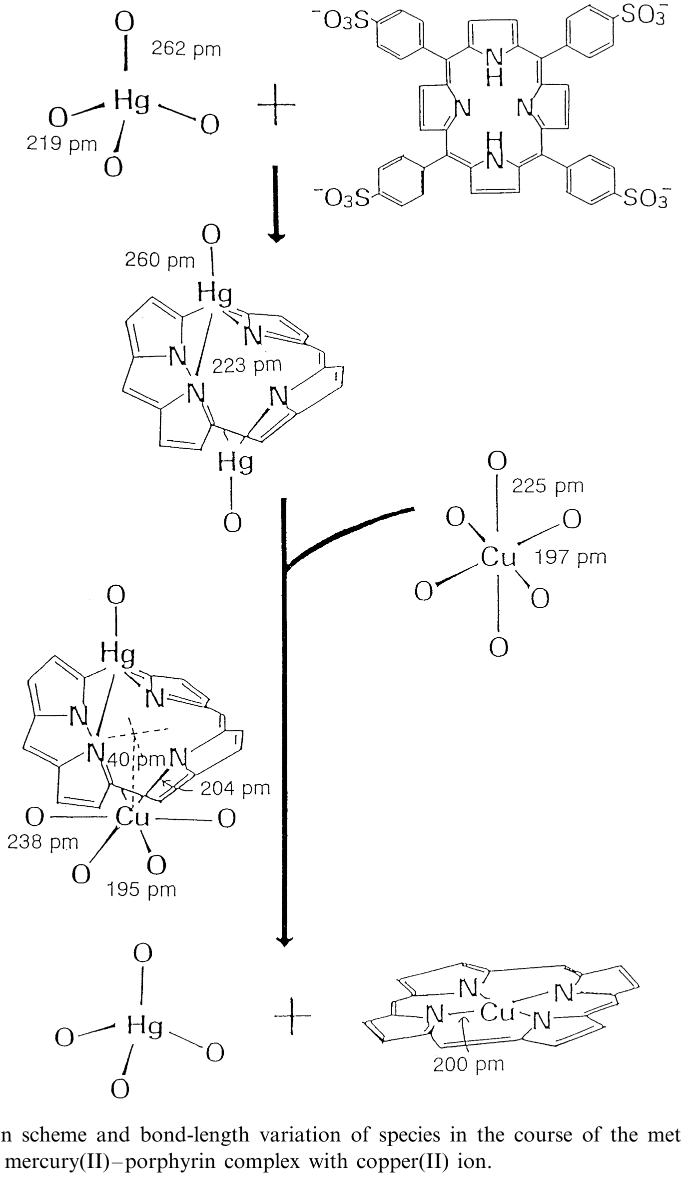
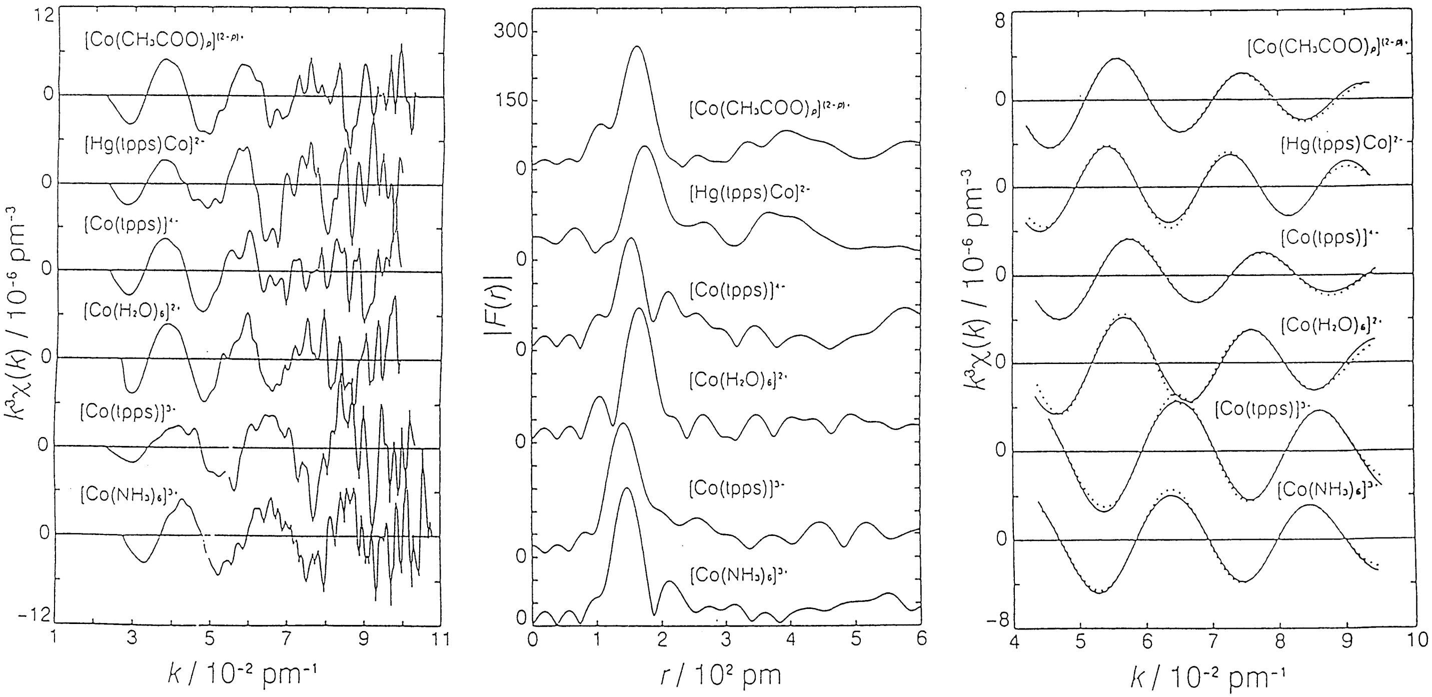


Fig. 5. Reaction scheme and bond-length variation of species in the course of the metal substitution reaction of the mercury(II)–porphyrin complex with copper(II) ion.



(i) (ii) (iii)

Fig. 6. (i) EXAFS spectra, (ii) their Fourier transforms, and (iii) Fourier filtered $k^3\chi(k)$ curves (experimental, dotted lines; calculated, solid lines) of solutions containing species indicated in the figure (see Table 2) of the cobalt(II)–mercury(II) porphyrin system.

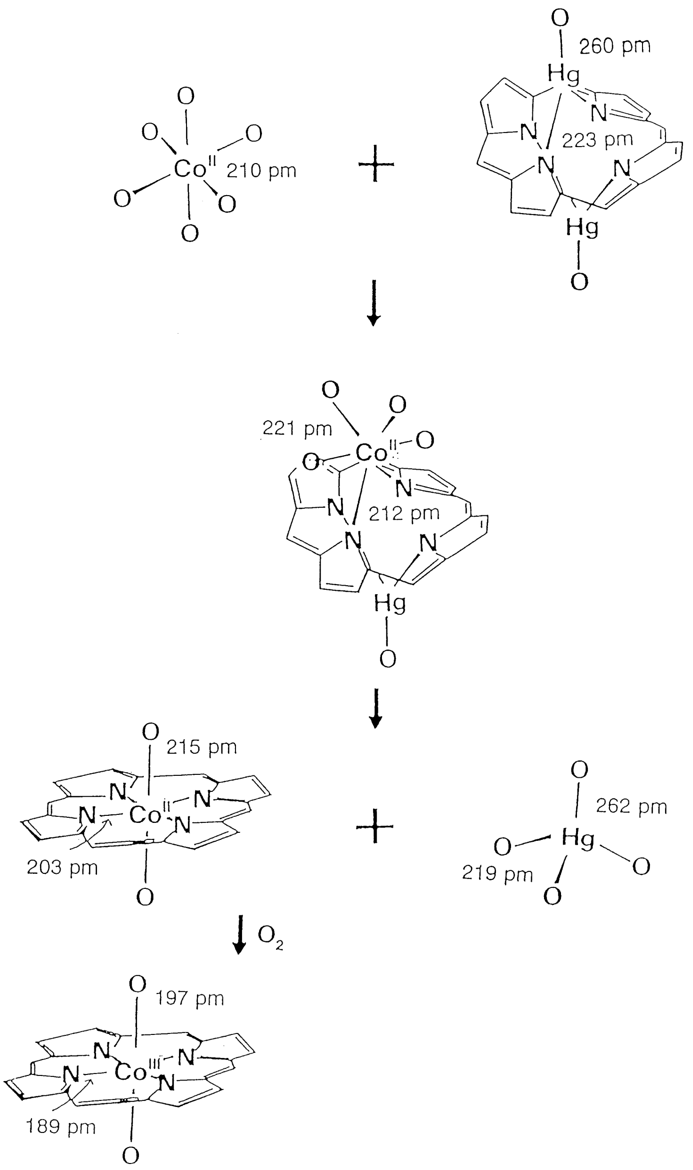


Fig. 7. Reaction scheme and bond-length variation of species in the course of the metal substitution reaction of the mercury(II)–porphyrin complex with cobalt(II) ion.

the total spectrum during the analysis of the EXAFS spectrum of the reaction intermediate. Although the spectra of reactants and products could be determined by separate experiments by using the normal EXAFS or diffraction method, this procedure certainly reduces the reliability of the extracted EXAFS data for the intermediate. In order to obtain highly reliable results in such a study, one should obtain structural data of the other species in solution with as high accuracy as possible. However, once we obtain structural data for reaction intermediates, we can draw a much clearer picture of the relevant reaction process rather than that discussed exclusively from rate laws.

The SF-EXAFS method is the one combining the stopped-flow technique and the EXAFS method, both being familiar for most chemists. Nevertheless, the combination of the existing methods creates a new method which provides a new pathway for shedding more light on chemical reaction processes.

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