

Specific Recoil Features of Central Metal Atoms of Zinc and Cadmium in the Solid System of Water-Soluble Metalloporphyrin Ion Associates(II. Radiochemistry)

著者	Shoji H.
journal or publication title	核理研研究報告
volume	34
page range	52-58
year	2001-11
URL	http://hdl.handle.net/10097/30996

Specific Recoil Features of Central Metal Atoms of Zinc and Cadmium in the Solid System of Water-Soluble Metalloporphyrin Ion Associates

H. Shoji*

Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305-8571

Water-soluble metalloporphyrin ion associates with central metal atoms of zinc and/or cadmium were subjected to bremsstrahlung and thermal neutron irradiation under cooling. After the bombardment samples were treated in wet chemical separation procedures using ion exchangers. Radionuclides of copper, zinc and cadmium preferentially substituted cadmium central atoms in the Cd-complex side.

§ 1. Introduction

Generally, in the study of recoil chemistry in the solid phase, bi-component systems sometimes show us the hidden predominant factor, especially the contribution of the possible individual elementary reaction process to the over-all result in the form of numerical reaction probability. As a bi-component system isomorphous mixed crystals were used in many cases, where components of isomorphous metal complexes such as metal phthalocyanines, metallocenes, hexahalogenometallates and so on were chemically combined in various mole-ratios. As for these series of mixed crystals with different compositions, it is one of great merits to obtain, by extrapolating, the tendency in the situation of infinite dilution of each component. In these cases, however, almost all isomorphous components used for mixed crystals had very similar crystalline structures to each other. Therefore their X-ray powder diffraction patterns were also much too close to prove that mixed crystals with microscopic homogeneity, "true solid solutions", were really produced. It was extremely difficult to prepare statistically homogeneous genuine mixed crystals even from the microscopic point of view.

So our interest shifted to another bi-component system of "water-soluble metalloporphyrin ion associates", which were obtained by our group rather by chance. This kind of large ion associates was expected to be statistically more homogeneous because of the necessity of electrical neutralization of the component counter ions, though the mole ratio of the component complex ions could not be changed from (1:1). So far our group investigated the recoil features in this kind of systems of various combinations of central metal atoms and ligands, for example $[M(\text{TMPyP})] [M'(\text{TCPP})]$ ($M, M' = \text{Cu}, \text{Zn}$), $[M(\text{TMPyP})] [M'(\text{TPPS})]$ ($M, M' = \text{Cu}, \text{Zn}$ and Co, Cu) where $\text{H}_2\text{TMPyP} =$ tetrakis (4-N-methylpyridyl) porphine, $\text{H}_2\text{TCPP} =$ tetra (p-carboxyphenyl) porphine, and $\text{H}_2\text{TPPS} =$ tetra (p-sulfophenyl) porphine [1-4]. This time our results on specific recoil tendencies of central atoms in the system of $[M(\text{TMPyP})] [M'(\text{TPPS})]$ ($M, M' = \text{Zn}, \text{Cd}$) are reported here, on which only the preliminary

*Present address: 3-46-3 Utsukushigaoka, Aoba-ku, Yokohama 225-0002

results were published [3, 5]. On the water-soluble metalloporphyrin ion associate systems investigated, all our previous data showed that the final fate of the recoil was determined in the very late stage of chemical reaction processes after losing its high recoil energy and/or high electric charge. However, some experimental confirmation was thought to be necessary whether the elastic billiard-ball-like dynamical process might give any contribution to the over-all final result or not. So the homologous elements with large mass difference, Zn-Cd were combined as the central metal atom in the system of $[M(\text{TMPyP})]$ $[M'(\text{TPPS})]$.

Figure 1 shows the structural formula of the water-soluble metalloporphyrin ion associate used this time.

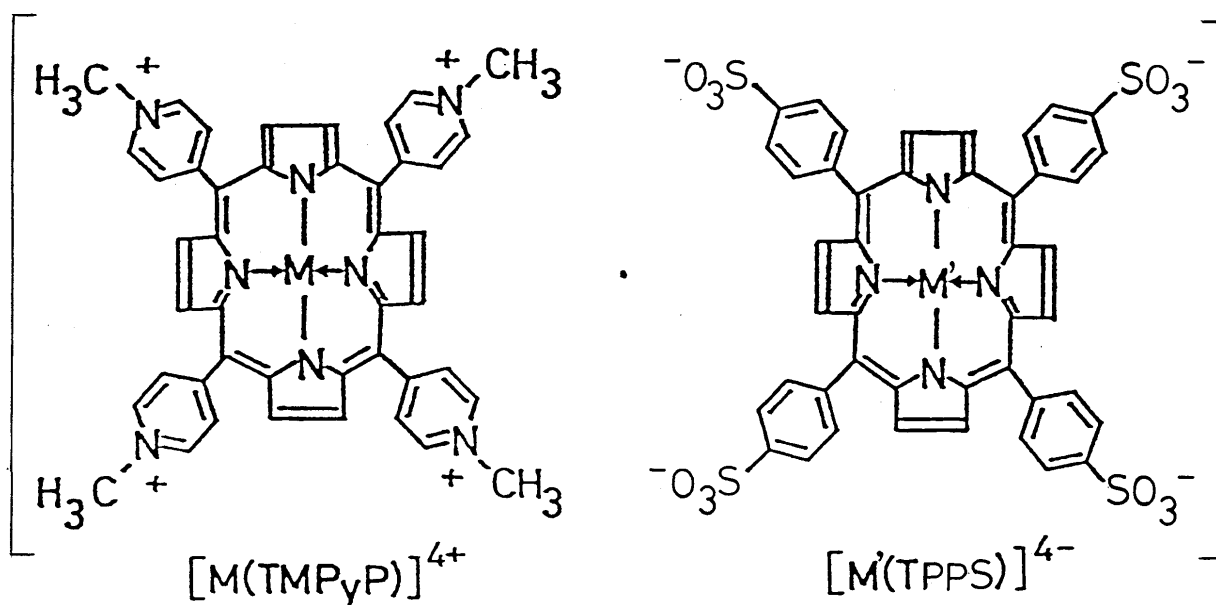


Fig.1. Structural formula of water-soluble metalloporphyrin ion associates used. $[M(\text{TMPyP})]$ $[M'(\text{TPPS})]$ ($M, M' = \text{Zn}, \text{Cd}$).

§ 2. Experimental

For the preparation of ion associate samples, first the component complex ions were synthesized, respectively. As a metal-free ligand is now commercially available, which was developed as the highly sensitive reagent for the spectrophotometric determination of trace amount of heavy metal ions, it was mixed with small excess of metal salt corresponding to a central metal in an appropriate solvent and the mixture was refluxed for a few hours or so. The metal porphyrin was obtained in the form of precipitate, which was purified by reprecipitation. Two aqueous solutions of each component complex ion were mixed in (1 : 1) mole ratio and the solution was left aside for overnight or longer. Then the complex ion associate formed as the amorphous or very fine crystalline precipitate. It was purified by repeated precipitation using the same aqueous medium as that in the dissolution of the irradiated sample. The samples were checked by elemental analysis and spectrophotometric measurement.

The purified samples were subjected to two kinds of irradiation. One was bremsstrahlung irradiation and the other was thermal neutron irradiation. The bremsstrahlung irradiation was done in the 300 MeV Electron Linear Accelerator in Tohoku University, Sendai, Japan. The irradiation was

carried out using Pt-converter under the following conditions: max energy of photons; 50 MeV, Current; 100~150 μ A, irradiation temp; $< -130^{\circ}\text{C}$, irradiation time; 8~10 hours. Unconverted electrons were removed by a sweep magnet. The thermal neutron irradiation was done in TRIGA MARK II Reactor of Rikkyo University, Yokosuka, Japan. The samples were irradiated in the in-core tube at -78°C for 2 hours, where the thermal neutron flux was 1.5×10^{12} n/cm² · sec.

Figure 2 represents the chemical separation procedures for the irradiated sample.

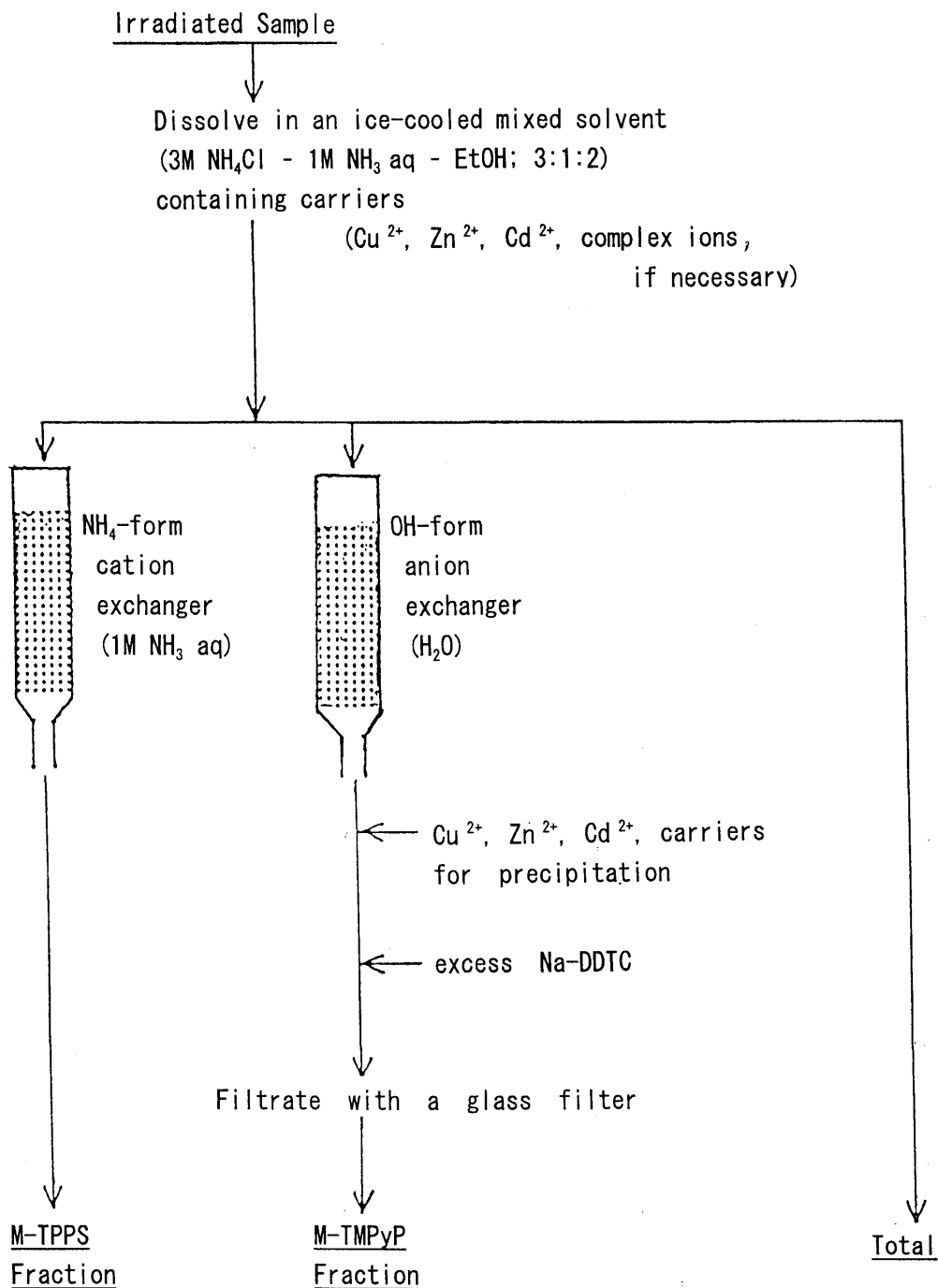


Fig.2. Chemical separation procedures.

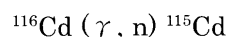
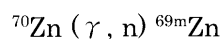
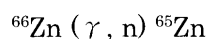
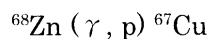
Irradiated samples were dissolved in ice-cooled mixed solvents of 3M NH₄Cl, 1M ammonia water and ethanol (the volume ratio, 3:1:2) containing the necessary carriers (Cu²⁺, Zn²⁺, Cd²⁺, Cu-complexes ions, if necessary, and M-complex ions whose central metal atoms were reverse to the target sample in the case of different central metal atoms in the associate). An aliquot of a sample solution was passed through cation and anion exchanger columns. In the effluent from the anion exchanger column, the coexisting bare metal ions were removed in a form of the precipitate of metal carbamates by adding carriers for precipitation and sodium diethyldithiocarbamate. Three counting samples were prepared from one irradiated sample.

The γ -spectra of these samples were measured using a Ge (Li) or HPGe detector and they were analysed by the connected computer system.

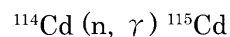
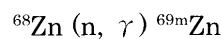
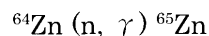
§ 3. Results and Discussion

The nuclear reactions concerned in the both irradiation are listed below.

Bremsstrahlung Irradiation Case:



Thermal Neutron Irradiation Case:



In the recoil process in the solid system of water-soluble metalloporphyrin ion associates, which accompanies nuclear reactions such as photonuclear reactions and thermal neutron capture listed above, some part of the radionuclide formed is found to be located at the center of the component complex, making a labelled complex. The complex yield of the nuclide in the complex fraction depends on many factors, such as the combination of central metals and ligands in the complex ion associate, nuclear reactions, irradiation temperatures and so on.

Table 1 represents the complex yields obtained experimentally, where fluctuations mean the statistical standard deviation in the repeated experiments. It shows that all the recoiling nuclides concerned (*M, including ¹¹⁵Cd) were preferentially stabilized in the Cd-complex side, not in the Zn-complex side, in all the cases in the both irradiation, which indicates that cadmium central metal atoms were very easy to be substituted by the recoiling *M because of its lower stability due to its much larger ion radius than those of the other metals. The complex yields of ⁶⁷Cu and *Zn in the Cd-complex side directly show the substitution reaction probability of cadmium central atoms by the *M, where those of ⁶⁷Cu were much higher than those of *Zn, which implies the larger difference of stability between the Cu- and Cd-complex than between the Zn- and Cd-complex. All the *Zn complex yields in Cd (TPPS) side showed almost similar numerical values and those in Cd (TMPyP) side had the almost similar tendency with one exception (⁶⁵Zn complex yield in the Cd (TMPyP) side: as low as 6%), which

Table 1. Complex Yields (%) in [M(TMPyP)] [M'(TPPS)] (M, M' = Zn, Cd)

Sample Fraction	[Zn (TMPyP)]	[Cd (TPPS)]	[Cd (TMPyP)]	[Zn (TPPS)]
	M (TMPyP)	M (TPPS)	M (TMPyP)	M (TPPS)
⁶⁷ Cu	7 ± 2	80 ± 2	29 ± 5	14 ± 3
⁶⁵ Zn	2.1 ± 1.7	17 ± 3	6 ± 3	2 ± 1
	1.13 ± 0.07	16.8 ± 0.5	20.8 ± 0.9	3.0 ± 0.4
^{69m} Zn	1.9 ± 0.9	22 ± 3	13 ± 2	2.0 ± 1.5
	3.50 ± 0.06	16.8 ± 0.2	21.9 ± 0.3	6.5 ± 0.1
¹¹⁵ Cd	0.10 ± 0.04	10.1 ± 0.4	2.5 ± 0.2	0.8 ± 0.1
	0.07 ± 0.01	11.32 ± 0.08	4.13 ± 0.04	0.83 ± 0.02

Sample Fraction	[Zn (TMPyP)]	[Zn (TPPS)]	[Cd (TMPyP)]	[Cd (TPPS)]
	M (TMPyP)	M (TPPS)	M (TMPyP)	M (TPPS)
⁶⁷ Cu	20 ± 2	37 ± 1	—	—
⁶⁵ Zn	2.0 ± 0.2	3.5 ± 0.8	—	—
	2.4 ± 0.9	6 ± 3	—	—
^{69m} Zn	1.9 ± 0.5	5 ± 1	—	—
	7 ± 2	14 ± 5	—	—
¹¹⁵ Cd	—	—	4 ± 2	5 ± 2
	—	—	5 ± 4	9 ± 3

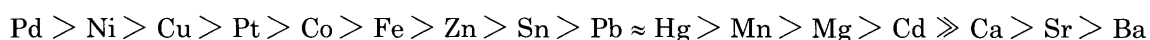
Upper value: Bremsstrahlung irradiation.

Lower value: Thermal neutron irradiation.

also implies that the predominant stage in determining the final fate of ^{*}Zn was the very late chemical one and that it was independent of the initial recoil energy or the kind of nuclear reactions. Although the rather high complex yields of ⁶⁷Cu in the sample of [Zn(TMPyP)] [Zn(TPPS)] are thought to be the combined result through the primary retention (the complex yield of the nuclide concerned without bond rupture and in very prompt recombination to the original site) and the substitution of stable zinc central atoms by ⁶⁷Cu recoils, numerically they have to express the latter substitution reaction probability, considering the large initial recoil energy (in 100 keV order) in the photonuclear reaction which only leads to ~0% primary retention. The complex yield of ⁶⁷Cu, as a whole, implies the higher affinity of ^{*}Cu with a TPPS ligand than with a TMPyP ligand. All the retention (the complex yield of the nuclide formed in the same chemical form as the initial target complex) is the combined result of the primary retention and the reaction retention (the retention by the substitution of the central atoms of the same metal as M by ^{*}M) and each retention value (probability) can be theoretically obtained separately by solving simultaneous equations formed using complex yields in both kinds of associates of the same and the different central metal atoms. However, no meaningful chemically consistent numerical reaction probabilities were obtained from the calculations, probably because the surrounding atmosphere of ^{*}M was different in the associate of different central metal atoms and of same central metal atoms. Comparing retention values of ^{*}Zn (that is, complex yields of ^{*}Zn in Zn-complex sides) in the case of thermal neutron irradiation, the retention of ^{69m}Zn was always higher than that of ⁶⁵Zn, which indicates the clear effect of the difference of average initial recoil energy between ⁶⁵Zn and ^{69m}Zn (446 eV and 166 eV, respectively [6]). In this initial recoil energy range of the order of 100

eV primary retention must depend on the initial recoil energy [7], and the higher initial recoil energy is, the less primary retention is.

As the expression of the stability of metalloporphyrins, two criteria were proposed. One is called "stability class" which was based on the necessary strength of the acid for demetallization of the complex [8, 9] and the other is named "stability index" which was derived from the theoretical calculation using the Pauling's electronegativity, the effective ion radius and the charge of the metal ion [10]. Although at a few point these two criteria show inconsistency, they are consistent with each other in almost all the cases. According to the former criterion, the stability order of the metalloporphyrins concerned is as follows; $\text{Cu}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+}$. The latter "stability index" shows the general stability order of metalloporphyrins whose central metal is divalent one as in the following:



where the Cd-complex is located at far weaker position. These stability orders agree with the strong substitution tendency of Cd by *Cu, *Zn and *Cd in Cd-complex side in the system of $[\text{M}(\text{TMPyP})] [\text{M}'(\text{TPPS})]$ ($\text{M}, \text{M}' = \text{Zn}, \text{Cd}$).

Although the information of the structure of each ion associate is essential for further discussion, unfortunately the degree of crystallization of this kind of ion associates has been very poor in the sample preparation yet. The X-ray powder diffraction pattern of the purified associate sample showed that the majority part of samples was in the amorphous state mixed with very fine crystals.

The elastic dynamical process can be excluded from the important factors for the final result, considering the present data without any mass difference effects.

The author expresses his hearty thanks to Professor Tsutomu Ohtsuki and all the members of LINAC machine group of this Institute for their great efforts in bremsstrahlung irradiation. The author is also very grateful to Professor Tsutomu Sekine of Department of Chemistry, Graduate School of Science, Tohoku University for his very valuable and kind cooperation. The author is also very thankful to Emeritus Professor Kenji Tomura of Rikkyo University and all the members of Institute for Atomic Energy, Rikkyo University for their very kind cooperation in thermal neutron irradiation.

References

- [1] K. Ogawa, H. Shoji and N. Ikeda: Res. Rep. of Lab. Nucl. Sci., Tohoku Univ. **19** (1986) 63.
- [2] K. Ogawa, H. Shoji and N. Ikeda: *Proc. 13th Int. Hot Atom Chemistry Symp. Mt. Fuji, 1987*, p. 22.
- [3] H. Shoji: Res. Rep. of Lab. Nucl. Sci., Tohoku Univ. **29** (1996) 57.
- [4] H. Shoji: J. Radioanal. Nucl. Chem. **239** (1999) 191.
- [5] H. Shoji: Res. Rep. of Lab. Nucl. Sci., Tohoku Univ. **25** (1992) 59.
- [6] Y. Oki: Thesis, Univ. Tsukuba, 1988.
- [7] M. H. Yang, H. Kudo and K. Yoshihara: Radiochim. Acta **15** (1971) 17.
- [8] J. W. Buchler, L. Puppe, K. Rohbock and H. H. Schneehagee: Ann. N. Y. Acad. Sci. **206** (1973) 116.
- [9] J. W. Buchler: *Habilitationschrift* (Technische Hochschule, Aachen, 1971).

- [10] K. M. Smith: *Porphyrins and Metalloporphyrins* (Elsevier Scientific Publishing Co., 1975), p. 196.