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Synthesis and Spectroscopic Properties of Water-Soluble Cerium(III) or Praseodymium(III) Mono[tetra(4-pyridyl)-porphyrinate] and Cerium(IV) Bis[tetra(4-pyridyl)-porphyrinate]

Jianzhuang JIANG, Ken-ichi MACHIDA,* Eiji YAMAMOTO, and Gin-ya ADACHI*
Department of Applied Chemistry, Faculty of Engineering,
Osaka University, Osaka 565

Water-soluble lanthanoid mono- and bisporphyrins, Ln(TPyP)acac (Ln=Ce, Pr) and $Ln(TPyP)_2$ (Ln=Ce) [TPyP=tetra(4-pyridyl)-porphyrin, acac=acetylacetone] were synthesized by refluxing $Ln(acac)_3 \cdot nH_2O$ (Ln=Ce, Pr) and H_2TPyP in 1,2,4-trichlorobenzene. The complexes were characterized based on UV/vis absorption and ^1H-NMR spectra, respectively.

Metalloporphyrins have been providing an active research field since the beginning of this century because of their involvement in various chemical and biological processes. It is also known that the lanthanoid porphyrins have a possibility of prominent uses as prospective materials (e.g. molecular metals)$^{1)}$ or as magnetic and spectroscopic probes for the study of biological systems (e.g. NMR shift reagents).$^{2)}$ Throughout 1970s, the lanthanoid monotetraphenylporphyrinates have been intensively studied by Horrocks et al.$^{3)}$ In 1983, $Ce(TTP)_2$ and $PrH(TTP)_2$ [TTP=tetra(4-tolyl)-porphyrin] were synthesized as first samples with a sandwich-like structure by Buchler et al.$^{4)}$ After that, the studies on lanthanoid porphyrins were mainly focused on the lanthanoid octaethylporphyrins$^{5,6)}$ because of the high reactivity of octaethylporphyrin with lanthanoid ions and the high solubility of the resulting porphyrinates in organic solvents. This paper describes the synthesis and some spectroscopic properties of water-soluble lanthanoid mono- and bistetrapyridylporphyrinates, Ln(TPyP)acac (Ln=Ce, Pr) and $Ln(TPyP)_2$ (Ln=Ce).

The synthetic procedure employed was the modified one reported by Buchler et al.$^{4)}$ for the preparation of a variety of lanthanoid porphyrinates. A solution of 50 ml 1,2,4-trichlorobezene (TCB) containing 0.330 g (0.52 mmol) tetra(4-pyridyl)-porphyrin and 1 g (ca. 2.20 mmol) $Ln(acac)_3 \cdot nH_2O$ (Ln=Ce, Pr; n=3) was refluxed under a slow stream of nitrogen (99.99%, O_2<50 ppm) for 3 days. The color of the solution gradually changed from blue to blue-brown. The solvent was evaporated at 323 K and the residue was repeatedly washed with warm toluene to remove the unreacted H_2TPyP. The resulting solid was dissolved in CH_2Cl_2, followed by filtrating and evaporating. Then, the sample was chromatographed on a silicagel column (Kieselgel 60, 35110 mm). A black-green first fraction was eluted with methanol, followed by a brown second fraction with chloroform/methanol (25:1). The first fraction contained the unreacted H_2TPyP and some unknown materials. The porphyrinates Ln(TPyP)acac (Ln=Ce,Pr) [and a small amount of Ce$(TPyP)_2$ when Ln=Ce] were obtained mainly as the second fraction. The latter fraction of Ce was then eluted with $CHCl_3$ by using a liquid chromatograph equipment with a polystylene gel column (JAIGEL-2H, 20 X 600 mm): The initial fraction with red-brown color and the second fraction with brown color were collected and, after evaporating $CHCl_3$, Ce(TPyP)acac (131 mg, 29%) and Ce$(TPyP)_2$ (12 mg, 1.6%) were obtained from these fractions, respectively (Table 1).

Table 1. Elemental analysis and yield of Ln(TPyP)acac (Ln=Ce,Pr) and Ln$(TPyP)_2$ (Ln=Ce)

Complex		C	H	N	Yield/%
Ce(TPyP)acac	Calcd	61.01	3.53	12.65	29
	Found	61.41	3.45	13.21	
Pr(TPyP)acac	Calcd	60.95	3.53	12.64	26
	Found	61.47	3.53	12.56	
Ce$(TPyP)_2$	Calcd	69.96	3.52	16.32	1.6
	Found	66.84	3.89	14.33	

Figure 1 shows the UV/vis absorption spectra of the monoporphyrinate Ln(TPyP)acac (Ln=Ce,Pr). They resemble those of monotetraphenalporphyrinates, Ce(TTP)acac and Pr(TTP)acac reported previously,$^{3)}$ which give the spectroscopic evidence of the formation of the lanthanoid monoporphyrins.

The UV/vis absorption spectrum of Ce$(TPyP)_2$ shown in Fig. 2 is also similar to those of bisoctaethylporphyinates, Ce$(TTP)_2$ and Ce$(OEP)_2$. The two strong Soret and Q bands locate at 394 and 539 nm, respectively. The Soret band is hypsochronically shifted as compared with that of monoporphyrinate Ce(TPyP)acac at 407 nm, just as the situation happened between the Ln$(OEP)_2$ and the Ln(OEP)acac.$^{7)}$ This demonstrates the formation of Ce$(TPyP)_2$ with sandwich-like structure since this typical hypsochronic shift only appears at such kind of bisporphyrinates in which two porphyrin

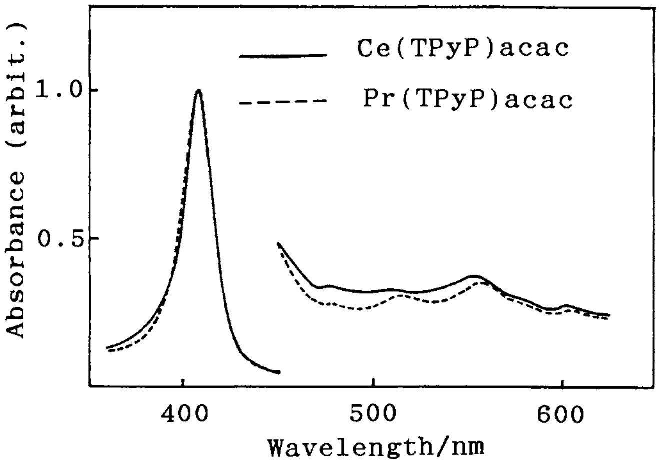

Fig. 1. UV/vis absorption spectra of (a) Ce(TPyP)acac and (b) Pr(TPyP)acac (in $CHCl_3$, room temperature).

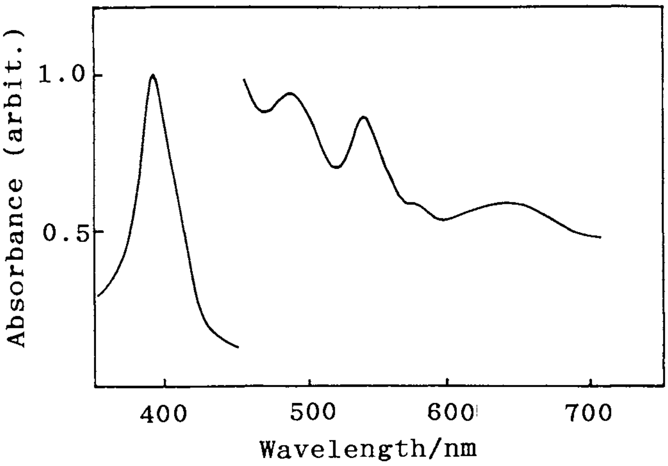

Fig. 2. UV/vis absorption spectrum of $Ce(TPyP)_2$ (in $CHCl_3$, room temperature).

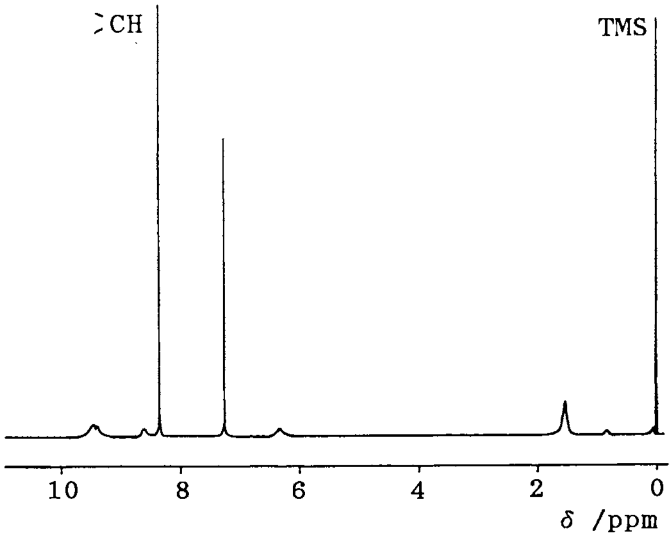

Fig. 3. NMR spectrum of lanthanoid tetra(4-pyridyl)-porphyrin $Ce(TPyP)_2$ in $CDCl_3$. The additional peaks are due to TMS and minor impurities.

rings are brought together in a face-to-face arrangement.[8,9] Another extra band appeared at 489 nm, in a similar manner as a band of Ce(TTP)$_2$ at 485 nm, is due to a charge transition between the porphyrin ring and the cerium(IV) ion, which is observed on cerium(IV) acetylacetonate, Ce(acac)$_4$, at 400-500 nm.

The sandwich property of Ce(TPyP)$_2$ as observed on Ce(TTP)$_2$ and Ce(OEP)$_2$ with the double-decker structure was unambiguously derived from its NMR spectrum. The signal from methine proton appears at an unusual high field (8.33 ppm) as compared with other porphyrin complexes of octacoordinate tetravalent metals.[10] This is a typical evidence for two porphyrin ligands linked together.[11]

Summarizing the above, one kind of sandwich-like complex, Ce(TPyP)$_2$ and two kinds of monoporphyrinates Pr(TPyP)acac and Ce(TPyP)acac were synthesized. The sandwich-like structure of Ce(TPyP)$_2$ was deduced from its UV/vis and NMR spectroscopic properties. Since they are soluble in acidic aqueous solutions, it is expected that they have a possibility of potential uses such as the NMR shift reagent for the biological study.

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