Synthesis of Water-Soluble Lanthanide Porphyrin Sandwich Complexes: Bis(tetrapyridylporphyrinato) Cerium(IV), [Ce(tpyp)$_2$], and Bis(tetramethylpyridylporphyrinato) Cerium(IV), [Ce(tmpyp)$_2$]

Jianzhuang JIANG, Ken-ichi MACHIDA,* and Gin-ya ADACHI*
Department of Applied Chemistry, Faculty of Engineering,
Osaka University, Suita, Osaka 565
(Received February 26, 1992)

Synopsis. A reaction of tris(acetylacetonato) cerium(III), [Ce(acac)$_3$], with tetrapyridylporphyrinato dilithium, Li$_2$tpyp, produces a water-soluble sandwich complex bis(tetrapyridylporphyrinato) cerium(IV), [Ce(tpyp)$_2$], in appreciable yield, which is followed by the same water-soluble sandwich complex bis(tetramethylpyridylporphyrinato) cerium(IV), [Ce(tmpyp)$_2$], formed by methylation of the tpyp ligand in [Ce(tpyp)$_2$].

In the past ten years, metalloporphyrin compounds, especially the sandwich lanthanide porphyrins have been intensively studied not only as a new class of prospective materials for electrical devices[1] but also as possible compounds for collection and storage of solar energy in the photosynthesis process because of their special molecular structure.[2] However, all the sandwich lanthanide porphyrins so far reported are insoluble in water or aqueous solution, and hence this property impairs their importance especially for developing the biophysical study. For this reason, we have synthesized bisporphyrinato cerium(IV), [Ce(tpyp)$_2$], as a first example of water-soluble sandwich lanthanide complex.[3] However, this complex dissolves only in acidic solutions and the synthesis yield is very low. In this paper, we describe the synthesis procedure to obtain [Ce(tpyp)$_2$) and [Ce(tmpyp)$_2$] in high yield, of which the latter complex particularly dissolves even in neutral, and basic solutions as well as the acidic one.

Experimental

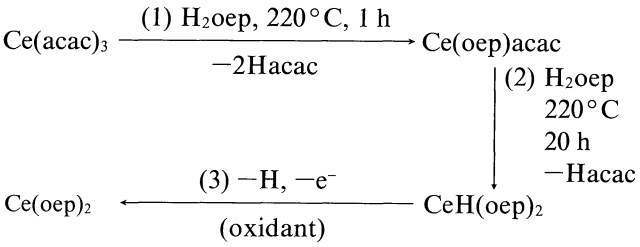
Reagents. Tetrapyridylporphyrin, H$_2$tpyp, and *n*-butyllithium, C$_4$H$_9$Li, were obtained from Aldrich, acetylacetone from Wako, and alumina (super I, neutral) from Woelm-ICN-Biomedicals. [Ce(acac)$_3$·3H$_2$O] was prepared from CeCl$_3$·*n*H$_2$O (*n*=ca. 6).[4] TCB (1,2,4-trichlorobenzene) was dried by vacuum distillation at 50°C.

[Ce(tpyp)$_2$]. 6.4 ml of a 2.0 molar hexane solution of butyllithium was added dropwise to a solution of 50 ml TCB containing 330 mg (0.533 mmol) of H$_2$tpyp under Ar. After stirring for 1 h at 20°C, 1 g (2.28 mmol) of [Ce(acac)$_3$·3H$_2$O] was added and refluxed under a rapid stream of Ar. The color of reaction mixture changed from red-violet to black-green after 2 d. The TCB was removed by evaporation at 50°C and the residue was dissolved in 100 ml of CHCl$_3$. Stirring this mixture solution for 1 day at 20°C in air led to the color change from black-green to purple. The residue obtained by filtrating most of unreacted [Ce(acac)$_3$] and evaporating CHCl$_3$ was chromatographed with alumina column (35 mmϕ×80 mm). After an orange-yellow forerun of unknown composition, the violet fraction of unreacted H$_2$tpyp was eluted with CHCl$_3$. Next, a purple fraction was obtained by the elution of CHCl$_3$/CH$_3$OH (volume ratio=100 : 1), but at the end portion it was contaminated with [Ce(acac)$_3$]. This eluate was rechromatographed in order to remove the [Ce(acac)$_3$] impurity. Finally, the blue-violet solid of [Ce(tpyp)$_2$] was obtained: 215.03 mg (60.6%). Anal. Mass spectrum: Calcd for C$_{80}$H$_{48}$N$_{16}$Ce [Ce(Tpyp)$_2$]: M=1372.3 (^{140}Ce isotope). Found: M=1373. UV-vis spectra (λ_{max}) 394, 489, 539, and 639 nm.

[Ce(tmpyp)$_2$]. 10 ml of methyl iodide (purity, 95%) was added dropwise to a solution of 40 mg of [Ce(tpyp)$_2$] in 10 ml of dried CHCl$_3$. After stirring for 1 day at 20°C in air, the solid was filtrated and well washed with CHCl$_3$, followed by drying in vacuo at 50°C. 73 mg (96.3%) of green-black [Ce(tmpyp)$_2$] was obtained. Anal. Calcd for C$_{88}$H$_{72}$N$_{16}$I$_8$Ce [Ce(tmpyp)$_2$]: C, 42.13; H, 2.89; N, 8.93%. Found: C, 42.16; H, 3.15; N, 8.92%. UV-vis spectra (λ_{max}) 422, 490, 564, and 619 nm. No mass spectrum was observed on [Ce(tmpyp)$_2$] as it was not ionized.

Results and Discussion

Chemistry. The formation of sandwich porphyrinato cerium(IV), [Ce(porp)$_2$] (porp=oep, ttp; H$_2$oep=octaethylporphyrin, H$_2$ttp=tetratolylporphyrin), have been discussed by Buchler[2,5] as Scheme 1.



Scheme 1. Formation of double-decker [Ce(oep)$_2$] from [Ce(acac)$_3$] and H$_2$oep.

After the formation of the monoporphyrinato cerium(III) intermediate, [Ce(oep)acac], by refluxing the reactionts in TCB for 1—4 h, the prolonged heating (up to 20 h) provides the cerium(III) double-decker intermediate, [CeH(oep)$_2$], and at last it changes to the double-decker porphyrinate, [Ce(oep)$_2$], as an end product. However, [CeH(oep)$_2$] has not been so far isolated except the analog bis(tetratolylporphyrinato)-praseodymium(III) hydrogen, [PrH(ttp)$_2$],[6] which is obtained as the end compound of the reaction of [Pr(acac)$_3$] with H$_2$ttp.

[Ce(Tpyp)$_2$]. The Li$_2$tpyp derived from a reaction between H$_2$tpyp and butyllithium is instead used as the reactant to synthesize [Ce(tpyp)$_2$] since the reactivity of H$_2$tpyp is low. As described in the experimental section, the expected color change from the red-violet of H$_2$tpyp to the purple of [Ce(tpyp)$_2$] did not occur, but to

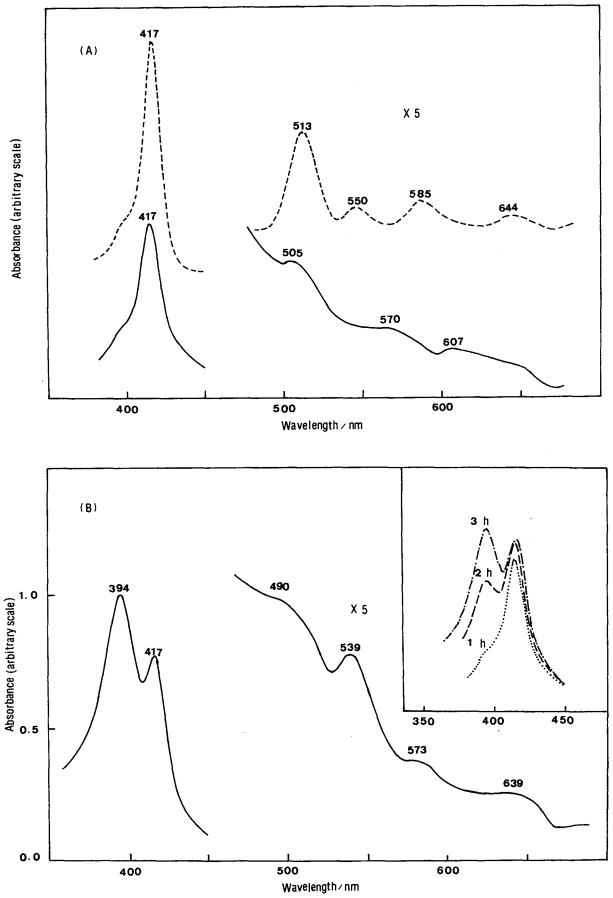
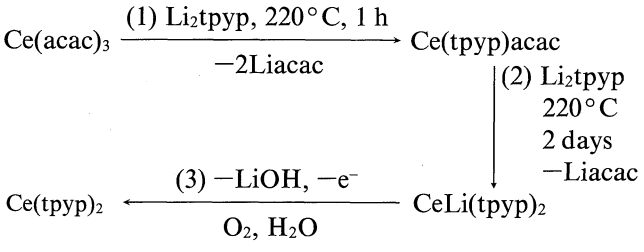


Fig. 1. UV-vis absorption spectra of the reaction mixture. (A) After refluxing in TCB under Ar for 2 d. The sample was dissolved in $CHCl_3$ and the spectra were immediately measured together with that of H_2tpyp (dash line). (B) After stirring in $CHCl_3$ under air for 1 d. The inset figure on the right hand corner shows the trangents of the Soret band over 1—3 h after dissolving the reaction mixture in $CHCl_3$.

black-green, even after refluxing the reaction mixture in TCB for 2 d. However, when this reaction mixture was diluted with $CHCl_3$ and exposed to air, its color gradually changed to purple. This process has been monitored by UV-vis absorption spectrum measurements (see Fig. 1). On the basis of the spectrum patterns, the formation process of [Ce(tpyp)$_2$] through this reaction process is explained according to Scheme 2.



Scheme 2. Formation of double-decker [Ce(tpyp)$_2$] from [Ce(acac)$_3$] and Li_2tpyp.

It is conceivable to assume that after the refluxing of the reaction mixture for initial several hours, the mono-porphyrinato cerium(III) intermediate, [Ce(tpyp)acac], is formed and then it converts into the cerium(III) double-decker intermediate, [CeLi(tpyp)$_2$], with the prolonged refluxing. The UV-vis absorption spectrum obtained from the reaction mixture after the refluxing for 2 d (Fig. 1. A) is mainly assigned to [CeLi(tpyp)$_2$] together with unreacted H_2tpyp from two reasons as follows: Firstly, [CeLi(tpyp)$_2$] seems to give no absorption peak in the Soret band region in a similar manner as the analog [PrH(ttp)$_2$] (the peak at 416 nm belongs to the Soret band of unreacted H_2tpyp).[6] Secondly, the absorption peak at 450—500 nm in the Q band region due to the porphyrin-to-cerium(IV) charge-transfer transition is not observed as on [Ce^{IV}(oep)$_2$], [Ce^{IV}(ttp)$_2$], and [Ce^{IV}(tpyp)$_2$]. Therefore, the cerium ion is trivalent and is reasonable to exist as [CeLi(tpyp)$_2$].

By stirring the $CHCl_3$ solution of the reaction mixture in air, [CeLi(tpyp)$_2$] is gradually oxidized to the end product [Ce(tpyp)$_2$]. The intensity of Soret band at 394 nm increases with time and the Q band due to the porphyrin-to-Cerium(IV) charge-transfer transition also appears gradually at about 490 nm (see Fig. 1. B)

[Ce(tmpyp)$_2$]. Another bisporphyrinate, [Ce(tmpyp)$_2$], was synthesized as follows: At first, it was unsuccessful to obtain [Ce(tmpyp)$_2$] by the reaction between [Ce(acac)$_3$] and H_2tmpyp or Li_2tmpyp because of the limited solubility of H_2tmpyp for TCB. Then, the direct reaction of [Ce(tpyp)$_2$] with methyl iodide (the methylation of pyridyl groups in the tpyp ligand) was carried out and the green-black solid of [Ce(tmpyp)$_2$] was isolated. This complex dissolves in acidic, neutral, and basic solutions (except strong acidic solution) without the demetalation of cerium ion.

Figure 2 shows the UV-vis absorption spectrum of [Ce(tmpyp)$_2$] in water. On first glance, [Ce(tmpyp)$_2$] provides the normal UV-vis absorption spectrum characteristics as would be expected for a sandwich lanthanide porphyrinate.[5] There are strong Soret and Q bands at 422, 564, and 619 nm, respectively (see Fig. 2). The peak position of Soret band is nearer to that of [Sm^{III}(tmpyp)·10H_2O] (430 nm)[7] rather than that of [Ce(tpyp)$_2$].[3] Another extra peak due to the porphyrin-to-cerium(IV) charge-transfer transition appears as a shoulder at 490 nm. However, a particularly noteworthy aspect in the UV-vis absorption spectra of the

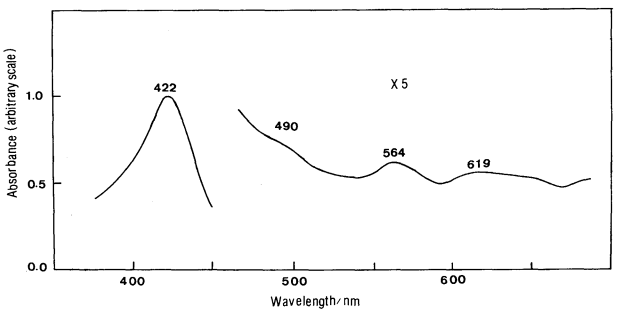


Fig. 2. UV-vis absorption spectrum of Ce(tmpyp)$_2$ in H_2O (pH=7.0).

double-decker [Ce(tmpyp)$_2$] is that both of the Soret band and Q band are significantly red shifted compared with the analogs [Ce(tpyp)$_2$] and [Ce(ttp)$_2$]. This indicates the different excitonic interaction between the B and Q excited states of the porphyrin macrocycles such as tpyp and tmpyp.[8]

Conclusion

The sandwich complex, [Ce(tpyp)$_2$], is obtained in high yield by the reaction between [Ce(acac)$_3$] and Li$_2$tpyp. In addition, [Ce(tmpyp)$_2$] is provided by the methylation of tpyp ligand in [Ce(tpyp)$_2$]. Both of these complexes are water-soluble double-decker lanthanide porphyrins, and particularly the latter complex can dissolve in aqueous solution over the whole range of pH.

References

1) J. W. Buchler, J. Huttermann, and J. Loffler, *Bull. Chem. Soc. Jpn.*, **61**, 71 (1988).
2) J. W. Buchler and M. Knoff, "Optical Properties and Structure of Tetrapyrroles," ed by G. Blauer and H. Sund, Walter de Gruyter & Co., Berlin (1985), pp. 91—105.
3) J. Z. Jiang, K. Machida, E. Yamamoto, and G. Adachi, *Chem. Lett.*, **1991**, 2035.
4) J. G. Stites, C. N. McCarty, and L. L. Quill, *Notes,* **70**, 3142 (1948).
5) J. W. Buchler, A. D. Cian, J. Fischer, M. K. Botulinski, H. Paulus, and R. Weiss, *J. Am. Chem. Soc.*, **108**, 3652 (1986).
6) J. W. Buchler, H. G. Kapellmann, M. Knoff, K. L. Lay, and S. Pfeifer, *Z. Naturforsch., B,* **38**, 1339 (1983).
7) S. Radzki, P. Krausz, S. Gaspard, and C. Giannotti, *Inorg. Chim. Acta,* **138**, 139 (1987).
8) R. J. Donohoe, J. K. Duchowski, and D. F. Bocian, *J. Am. Chem. Soc.*, **110**, 6119 (1987).