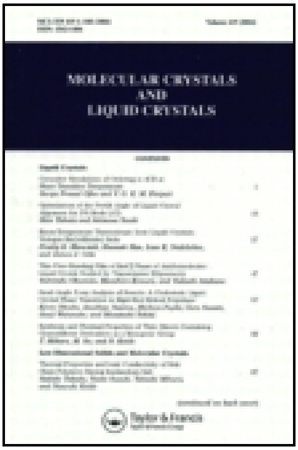

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Synthesis, Spectroscopic, and Electrochemical Properties of Homoleptic Bis(Substituted-Phthalocyaninato) Cerium(IV) Complexes

Jianzhuang Jiang [a] , Jinglei Xie [a] , Dennis K. P. Ng [b] & Yan Yan [b]

[a] Department of Chemistry, Shandong University, Jinan, 250100, P. R. China

[b] Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong, P. R. China

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Synthesis, Spectroscopic, and Electrochemical Properties of Homoleptic Bis(Substituted-Phthalocyaninato) Cerium(IV) Complexes

JIANZHUANG JIANG [a], JINGLEI XIE[a], DENNIS K.P.NG[b] and YAN YAN[b]

[a]*Department of Chemistry, Shandong University, Jinan 250100 P. R. China and* [b]*Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong, P. R. China*

The homoleptic bis(phthalocyaninato) cerium(IV) sandwiches $Ce(Pc^*)_2$ [$Pc^* = Pc(C_7H_{15})_8$, $Pc(OC_5H_{11})_8$, Pc] have been prepared and characterized by UV-vis, near IR, IR, mass spectrometries, CV and differential-pulse voltammetry (DP).

Keywords: Sandwich Complex; Phthalocyanine; Cerium

1 INTRODUCTION

Recently, the sandwich-type double-decker homoleptic phthalocyaninato rare earth complexes in which long alkyl or crown ether substitutents are introduced onto the Pc rings started to arouse research interest as novel forms of mesogenic liquid crystals or potential iono-electronic materials.[1,2] As Ce has a low lying redox couple Ce^{3+}/Ce^{4+}, it gives specific affection to the interaction between the two Pc ring in the molecules of double-decker. However, no report has been so far given to our knowledge on the substituted bisphthalocyaninato cerium double-decker complexes. In the present paper, we describe the synthesis, spectroscopic characterization and electrochemistry of the cerium(IV) sandwich complexes of octasubstituted phthalocyanines.

2. EXPERIMENTAL

A mixture of $Ce(acac)_3$ H_2O (22mg, 0.05mmol), DBU (40mg, 0.26mmol) and corresponding dicyanobenzene (0.6 mmol) was refluxed in amyl alcohol (2 ml) under a slow stream of N_2 for 12h. The mixture was cooled to room temperature and filtered to remove the metal free phthalocyanine and washed with a little amount of amyl alcohol. The combined filtrates were concentrated under reduced pressure and chromatographed on a silica gel column with $CHCl_3$ hexane(2:3) as eluent. The target double-decker $Ce(Pc^*)_2$ was developed after metal free $H_2(Pc^*)$. The crude product was further purified by the same chromatographic procedure followed by recrystallization from a mixture of $CHCl_3$ and MeOH. Another method to prepare the unsubstituted $Ce(Pc)_2$ is condensation of $Li_2(Pc)$. A mixture of $Li_2(Pc)$ and $Ce(acac)_3 \cdot H_2O$ in anhydrous TCB was refluxed for 12h under nitrogen, and the reaction solution was treated in a similar way discribed above.

3. RESULTS AND DISCUSSION

The complexes $Ce(Pc^*)_2$ [$Pc^* = Pc(C_7H_{15})_8$, $Pc(OC_5H_{11})_8$, Pc] (1, 2, 3) were prepared by the method utilized to prepare the analogous Eu, Gd, and Y complexes.[3,4] Complex 3 was prepared in two methods discribed above. While the substituted cerium bisphthalocyaninato compounds $Ce(Pc')_2$ [$Pc' = Pc(C_7H_{15})_8$, $Pc(OC_5H_{11})_8$] could only be obtained by treatment of $Ce(acac)_3 \cdot H_2O$ with the corresponding dicyanobenzene and DBU in amyl alcohol in moderate yields(Table 1). The by-product metal free phthalocyanines could be easily removed by filtration and column chromatography. It must be pointed out that attempts to treat $Li(Pc^*)_2$ prepared *in situ* with $Ce(acac)_3$ H_2O in refluxing TCB or amyl alcohol failed to provide target sandwich compounds, instead, a significant amount of metal free phthalocyanine was produced.

As described earlier, very satisfactory elemental analysis results can not be obtained for the double-decker complexes containing substituted phthalocyanine.[3-5] However, these compourds gave satisfactory LSI mass spectra showing intense molecular ion signals for $Ce(Pc')_2$ (Table 1).

Table 1. Yield of synthesis and Mass spectroscopic data for $Ce(Pc')_2$

Compound	Yield(%)	Mass (m/z)	
		Calculated[a]	Measured
$Ce[Pc(C_7H_{15})_8]_2$ (1)	50.4	2736.14	2736
$Ce[Pc(OC_5H_{11})_8]_2$ (2)	48.8	2543.56	2544
$Ce(Pc)_2$ (3)	36	1165.20	1164.3

[a] Mass corresponding to the average molecular weight of the compound.

The UV-Vis data of the homoleptic $Ce(Pc^*)_2$ in $CHCl_3$ are recorded and organized in Table 2. Figure 1 shows the UV-vis spectrum of $Ce[Pc(C_7H_{15})_8]_2$. The profound splitting of the Q band indicates the composition of $Ce^{IV}(Pc^*)_2$ instead of $HCe^{III}(Pc^*)_2$ as the large size of trivalent cerium in $HCe^{III}(Pc^*)_2$ could not induce strong π-π interaction in the double-decker molecule and relative profound splitting of its Q band.[6] It can be seen from Table 2 that all the absorptions are red-shifted when electron-donating groups are introduced onto the Pc rings. This is consistent with results reported for analogous Eu, Gd and Y complexes. However, the splitting of B band in other $RE^{III}(Pc^*)_2$ (RE =

Y, Eu, Gd) containing substituted phthalocyanine was not observed in these $Ce(Pc^*)_2$ complexes.[3,4] No absorption was observed in the near IR region.

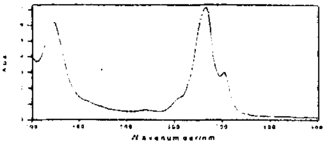


Figure 1. UV-vis absorption spectrum of $Ce[Pc(C_7H_{15})_8]_2$ in $CHCl_3$

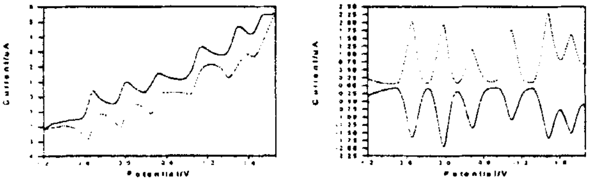
Table 2. UV-vis data for $Ce(Pc')_2$ in $CHCl_3$

Compound	λ_{max} (nm) (log ε)			
1	344 (5.63)		667 (5.69)	705 (5.63)
2	355 (5.38))	490 (4.81)	648 (5.40)	690 (sh)
3	329 (5.33)		639 (5.36)	679 (5.07)

In the IR spectra for compounds **1** and **3** a strong peak at 1330 cm^{-1} and 1328 cm^{-1} is assigned to the Pc^{2-} and $[Pc(C_7H_{15})_8]^{2-}$ respectively.[7-10] But for 2, the characteristic IR band appears at 1383 cm^{-1}.[11] The IR spectra of **1** and **2** also exhibited three peaks from medium to strong in the region of 2852-2971 cm^{-1} which are due to the C-H stretching vibrations of CH_2 and CH_3 in the phthalocyanine side chains. Complex **2** also shows the C-O-C stretch bands at about 1271 and 1050 cm^{-1} respectively. A medium to strong band derived from the phthalocyanine isoindole stretch appears at about 1458 cm^{-1}.

These three $Ce(Pc^*)_2$ do not give any NMR signals for the aromatic atom as reported by Kadish et.al.[7] for the phthalocyaninato complexes of tetravalent metal, only the atoms in the substitutents show signals with expected integration. This result suggests some paramagnetic nature for the double-decker center, which is probably due to the existence of part of $HCe^{III}(Pc^*)_2$.[12]

The electrochemistry of $Ce(Pc^*)_2$ was examined by CV and DP and the data were organized in Table 3. Figure 2 gives the CV and DP diagrams of $Ce[Pc(C_7H_{15})_8]_2$, two reversible oxidation processes and four reversible reduction processes have been observed. The two current peaks in the cathodic range are related to the successive oxidation processes of Pc ligands and the first current peak(-0.462v) in the aniodic region is metal centered reduction process, the other three current peaks corresponds to three successive single electron reduction processes of Pc rings. These results are well consistent with those of $[RE^{III}(Pc)_2]$,[14] but not in good correspondence with that of Homborg for $(nBu_4N)[Ce^{III}(Pc^*)_2]$.[12] Similar experimental results have been observed for the complexes **2** and **3**. Noteworthy is that due to the low solubility and strong adsorption,[13b,14] the redox peaks in both the CV and DP diagrams for compound **3** are not as well resolved as its analogues **1** and **2**. As expected, when the electron donating groups of OC_5H_{11} and C_7H_{15} are introduced to the Pc ring, the compounds are more easily to be oxidized and more difficult to be reduced, which corresponds well with the results for $RE(Pc')_2$ [RE = Eu, Gd; Pc' = $Pc(OC_5H_{11})_8$, $Pc(C_7H_{15})_8$].[3]



(a) (b)

Figure 2. (a) CV and (b) DP diagrams of $Ce[Pc(C_7H_{15})_8]_2$ in CH_2Cl_2

Table 3. Redox potentials (V) for $Ce(Pc')_2$ vs SCE

Compound	E_{oxd}(III)	E_{oxd}(II)	E_{oxd}(I)	E_{red}(I)	E_{red}(II)	E_{red}(III)	E_{red}(IV)
1		0.517	0.033	-0.462	-1.038	-1.594	-1.981
2	1.327	0.463	0.006	-0.452	-0.854	-1.620	
3	1.630	0.680	0.230	-0.205	-1.044	-1.418	-1.724

Recorded with $(nBu_4N)(PF_6)$ as electrolyte in CH_2Cl_2 (0.1 mol dm^{-3}) at room temperature. Scan rate = 100mV s^{-1}.

Acknowledgments

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