Available online at www.sciencedirect.com
ScienceDirect
*Mendeleev Commun.*, 2023, **33**, 729–731

Mendeleev
Communications

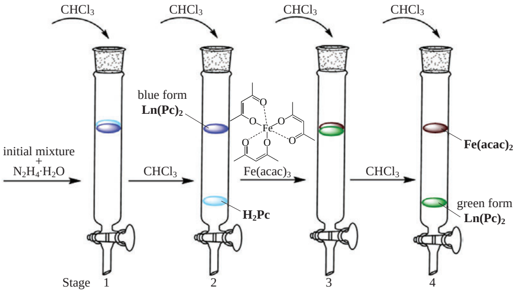
# Column chromatography separation of lanthanide(III) bisphthalocyaninate and phthalocyanine ligand

**Anna A. Botnar,* Tatyana V. Tikhomirova and Arthur S. Vashurin**

*Ivanovo State University of Chemistry and Technology, 153000 Ivanovo, Russian Federation.*
*E-mail: botnar_aa@isuct.ru*

DOI: 10.1016/j.mencom.2023.09.044

**During the synthesis of double-decker *f*-metal phthalocyanine complexes Ln(Pc)$_2$ free phthalocyanine ligands can be also formed, however, routine column chromatography is not effective for their separation. The preliminary reduction of the complexes with hydrazine hydrate affords the low mobile forms, which can be re-oxidized in the chromatography columns after the free ligand is eluted.**



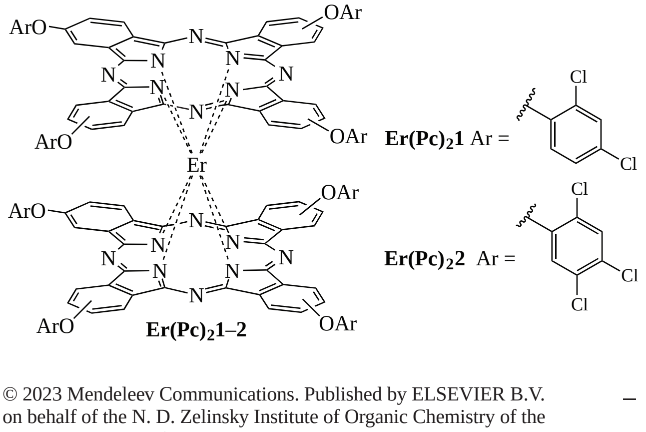
*Keywords:* phthalocyanine, ligand, double-decker complex, lanthanide, chromatography.

Currently, the chemistry of phthalocyanine macrocycles is rapidly developing.[1,2] Peripherally and non-peripherally substituted sandwich complexes of trivalent lanthanides attract special attention as sensors and molecular magnets.[3–5] During the synthesis, in addition to bisphthalocyaninates, the corresponding free phthalocyanine ligands can be formed,[6] which can manifest in the broadening of the *Q* absorption band or the appearance of a new absorption maximum bathochromically shifted relative to the native *Q* band. The ambiguous form of the electronic absorption spectrum may be related to both the peculiarity of the complex structure and the presence of the free ligand impurity.[7,8] Since the preparation of high-purity macrocycles is one of the priority tasks in the phthalocyanine chemistry, this paper describes an efficient method for separating the mixture of lanthanide bisphthalocyaninate and phthalocyanine ligand obtained in the course of the synthesis.

The electronic absorption spectra (UV–Vis) of samples **Er(Pc)$_2$1** and **Er(Pc)$_2$2** purified by column chromatography on silica gel with chloroform elution show two maxima at 697 and 726 nm, respectively (Figure 1). The appearance of extra bands in this region might be associated with aggregation or protonation processes.[9–13] However, addition of pyridine as monomerizing agent to a solution of **Er(Pc)$_2$1** sample (see Online Supplementary Materials, Figure S1) does not cause significant changes in the UV–Vis spectrum, which indicates the absence of aggregated forms in the solution. Either, keeping of **Er(Pc)$_2$1** in chloroform with potassium carbonate also does not lead to any changes in the spectrum.

However, in the UV–Vis spectrum of **Er(Pc)$_2$2** [Figure S2(*a*)] the appearance of a broadening at 696 nm may be associated with the contribution of the ligand band at 699 nm to the total spectrum, that is, the solution may consist of the ligand and bisphthalocyaninate. This assumption is also confirmed by the mass spectrum, in which the peaks for molecular ions of the ligand and the sandwich type complex were detected [see Figure S2(*b*)]. Since column chromatography on silica gel eluting with chloroform was not efficient for purification of **Er(Pc)$_2$2**, gel permeation chromatography was attempted using Bio-Beads and the chloroform/ethanol (10 : 1, v/v) mixture as the eluent. However, based on UV–Vis of **Er(Pc)$_2$2** in chloroform (Figure S3), it was found that ligand **H$_2$Pc2** and bisphthalocyanine **Er(Pc)$_2$2** mixture was not effectively separated even by repeated gel permeation chromatography.

In published paper,[14] to separate one-electron neutral form [Pc$^{2-}$(Gd$^{III}$)Pc$^{\cdot -}$] from the neutrally protonated [Pc$^{2-}$(Gd$^{III}$)PcH],



**Er(Pc)$_2$1–2**

**Er(Pc)$_2$1** Ar =

**Er(Pc)$_2$2** Ar =

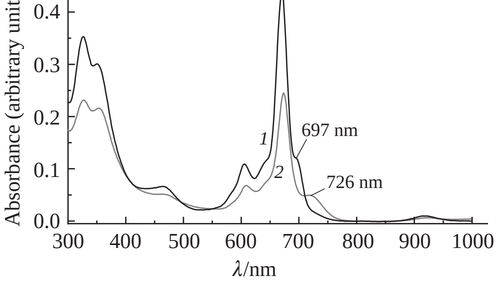
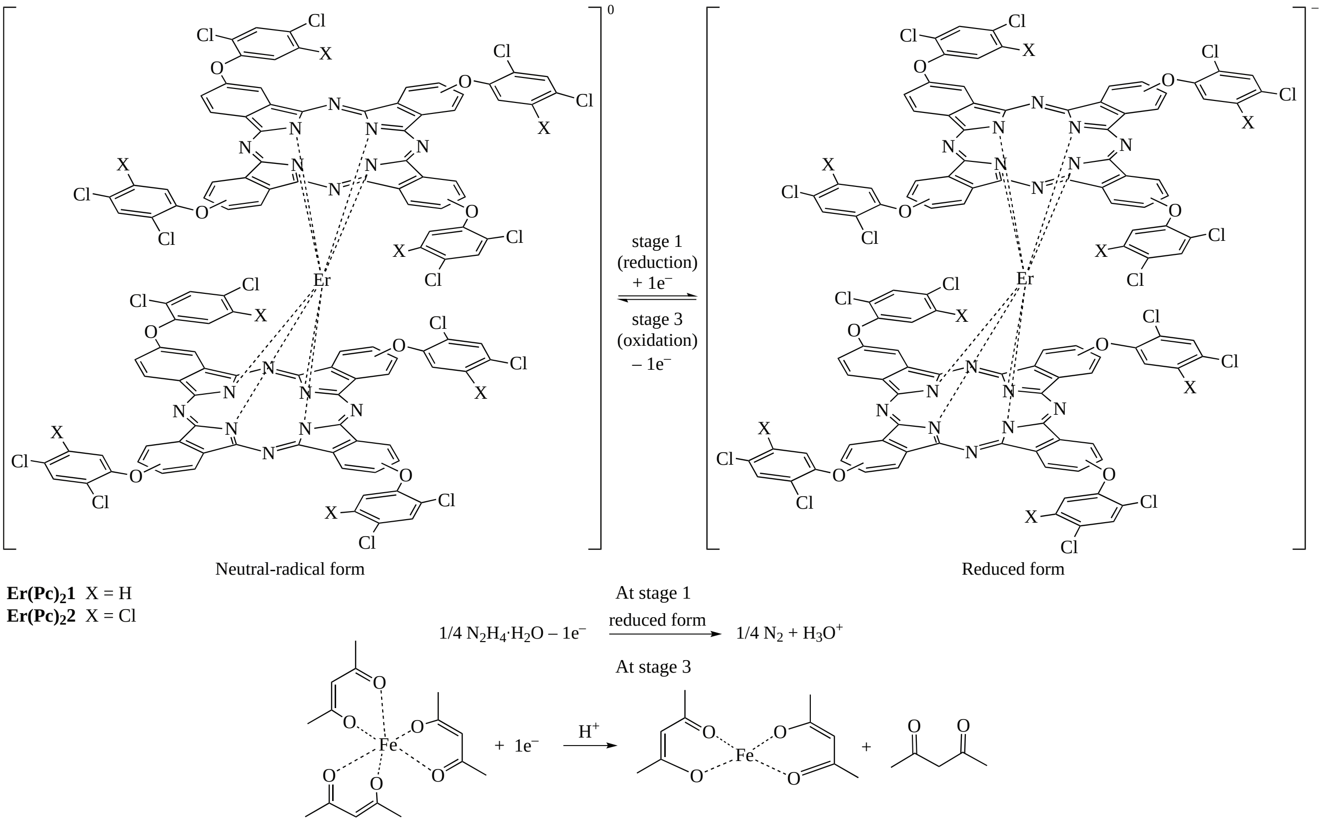


**Figure 1** UV–Vis spectra for mixtures in CHCl$_3$: (*1*) **Er(Pc)$_2$2–H$_2$Pc2** and (*2*) **Er(Pc)$_2$1–H$_2$Pc1**.



**Scheme 1**

addition of hydrazine hydrate was proposed to reduce bisphthalocyanine lanthanide complex. The final oxidation of this reduced form with $Fe(ClO_4)_3$ would produce individual $[Pc^{2-}(Gd^{III})Pc^{\bullet-}]$. That procedure made it possible to exclude the protonated $[Pc^{2-}(Gd^{III})PcH]$ component.

In this study, we extended that approach to column chromatography, which allowed us to separate the resulting mixture of complexes **Er(Pc)$_2$1/Er(Pc)$_2$2** from the ligands **H$_2$Pc1/H$_2$Pc2**. Right before the separation using silica gel column (chloroform as eluent), hydrazine hydrate was added to the solution of ligand and sandwich macrocycle mixture. This led to the transition of the neutral-radical green form of complexes **Er(Pc)$_2$1** and **Er(Pc)$_2$2** to the reduced blue ones (Scheme 1).[15,16] The resulting blue solution was placed onto the chromatographic column (Figure 2, stage 1), and the free ligand was eluted with chloroform (stage 2), while the reduced form of the sandwich complex remained at the start. Next, iron(III) acetylacetonate in chloroform was added onto the top of the column (stage 3). The usage of acetylacetonate as an anion allows iron(III) acetylacetonate to be dissolved in chloroform and to react with the sandwich macrocycle **Er(Pc)$_2$** forming a neutral-radical green form (see Scheme 1).

The neutral-radical form turned out to be quite mobile when eluted with chloroform (see Figure 2, stage 4). These manipulations make it possible to separate sandwich complexes **Er(Pc)$_2$** and their corresponding phthalocyanine ligands **H$_2$Pc**. The amounts of purified fractions related to the original analyte mass in the separated mixture are as follows: for **Er(Pc)$_2$1** 97%, for **H$_2$Pc1** 3%, for **Er(Pc)$_2$2** 92%, for **H$_2$Pc2** 8%, which is confirmed by absorption spectroscopy data (Figures 3 and S4), mass spectrometry (Figure S5), IR spectroscopy (Figure S7) and $^1$H NMR spectroscopy (Figures S8, S9). According to the proposed method, a mixture of peripheral cyclohexylphenoxy-substituted bisphthalocyaninate **Nd(Pc)$_2$3** and phthalocyanine ligand **H$_2$Pc3** (Figures S10–S14) were also separated.

In conclusion, a mixture of peripheral substituted free phthalocyanine ligands and erbium or neodimum bisphthalocyaninate mixtures were successfully separated by preliminary reduction of the complexes thus significantly lowering their chromatographic mobilities. After elution of the free ligand, the adsorbed reduced forms were re-oxidized with

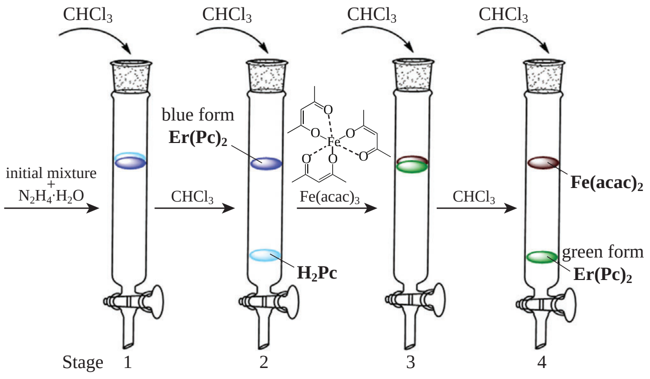


**Figure 2** Column chromatography process for separating **Er(Pc)$_2$** sandwich complex from the corresponding phthalocyanine ligand **H$_2$Pc**.

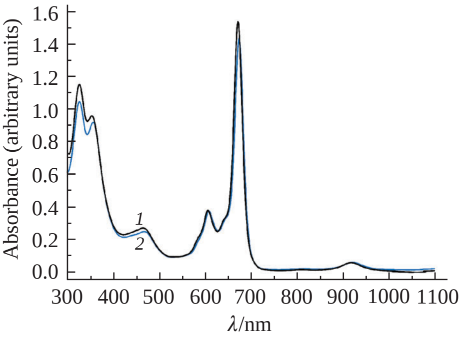


**Figure 3** UV–Vis spectra for purified (*1*) **Er(Pc)$_2$1** and (*2*) **Er(Pc)$_2$2** in chloroform.

$Fe(acac)_3$ and readily eluted with chloroform. The separation method claims to be the universal for peripherally substituted bisphthalocyanine and ligand, since the technique is based on the redox nature of phthalocyanine ring of the sandwich complex formed by trivalent lanthanide.

This work was supported by the Russian Science Foundation (grant no. 17-73-20017). The study was carried out using the resources of the Center for Shared Use of Scientific Equipment of the ISUCT (with the support of the Ministry of Science and Higher Education of Russia, grant no. 075-15-2021-671).

*Online Supplementary Materials*

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2023.09.044.

## References

1 L. A. Lebedev, M. I. Chebanenko, E. V. Dzhevaga, K. D. Martinson and V. I. Popkov, *Mendeleev Commun.*, 2022, **32**, 317.

2 D. Klyamer, R. Shutilov and T. Basova, *Sensors*, 2022, **22**, 895.

3 Y. Chen, F. Ma, X. Chen, Y. Zhang, H. Wang, K. Wang, D. Qi, H.-L. Sun and J. Jiang, *Inorg. Chem.*, 2019, **58**, 2422.

4 Y. Horii, Y. Horie, K. Katoh, B. K. Breedlove and M. Yamashita, *Inorg. Chem.*, 2018, **57**, 565.

5 A. A. Botnar, A. N. Bychkova, N. P. Domareva, T. V. Tikhomirova and A. S. Vashurin, *J. Inclusion Phenom. Macrocyclic Chem.*, 2022, **102**, 303.

6 L. G. Tomilova, V. E. Pushkarev, T. V. Dubinina and A. Yu. Tolbin, *Dostizheniya v sinteze i issledovanii svoistv ftalotsianinov i ikh analogov (Advances in the Synthesis and Study of the Properties of Phthalocyanines and Their Analogues)*, ed. L. G. Tomilova, Izdatel’stvo Moskovskogo universiteta, Moscow, 2019 (in Russian).

7 A. I. Koptyaev, N. E. Galanin and G. P. Shaposhnikov, *Russ. J. Gen. Chem.*, 2019, **89**, 271 (*Zh. Obshch. Khim*., 2019, **89**, 277).

8 C. Bozoğlu, M. Arici, A. L. Uğur, A. Erdoğmuş and A. Koca, *Synth. Met.*, 2014, **190**, 56.

9 E. A. Safonova, A. G. Martynov, S. E. Nefedov, G. A. Kirakosyan, Yu. G. Gorbunova and A. Yu. Tsivadze, *Inorg. Chem.*, 2016, **55**, 2450.

10 E. Tokunaga, S. Mori, Y. Sumii and N. Shibata, *ACS Omega*, 2018, **3**, 10912.

11 F. Würthner, T. E. Kaiser and C. R. Saha-Möller, *Angew. Chem., Int. Ed.*, 2011, **50**, 3376.

12 A. Botnar, T. Tikhomirova, K. Nalimova, D. Erzunov, M. Razumov and A. Vashurin, *J. Mol. Struct.*, 2020, **1205**, 127626.

13 A. A. Botnar, N. P. Domareva, K. Yu. Kazarian, T. V. Tikhomirova, M. B. Abramova and A. S. Vashurin, *Russ. Chem. Bull.*, 2022, **71**, 953.

14 T.-H. Tran-Thi, T. A. Mattioli, D. Chabach, A. De Cian and R. Weiss, *J. Phys. Chem.*, 1994, **98**, 8279.

15 W. Yang, L. Ma, C. Liu, T. Sun and J. Jiang, *Eur. J. Inorg. Chem.*, 2021, 3512.

16 E. O. Moiseeva, A. D. Kosov, N. E. Borisova, B. N. Tarasevich, T. V. Dubinina and L. G. Tomilova, *Inorg. Chim. Acta*, 2022, **535**, 120855.

*Received: 14th December 2022; Com. 22/7069*