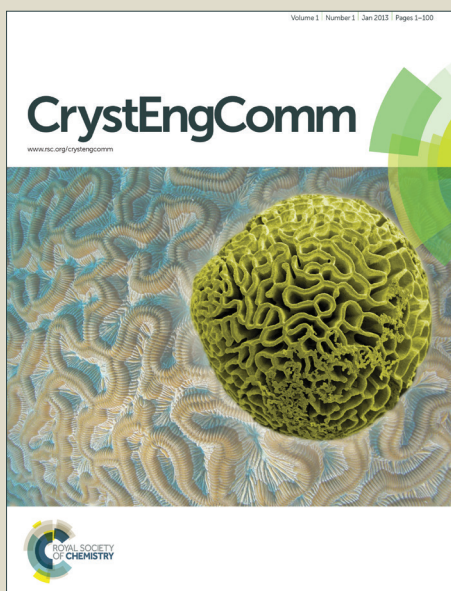


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ARTICLE TYPE

Coordination complex of boron subphthalocyanine (BSubPc) with fluorenone pinacolate. Effective π - π interaction of concave BSubPc macrocycle with fullerene C₆₀

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Coordination assembly of dimeric fluorenone ketyl (pinacolate, C₂₆H₁₆O₂²⁻) with boron subphthalocyanine (BSubPc) was obtained in the complex with fullerene, $\{(BSubPc)_2(C_{26}H_{16}O_2)\} \cdot C_{60}$, featuring an effective π - π interaction between concave-shaped BSubPc macrocycle and spherical C₆₀ molecules.

Coordination chemistry of metal macroheterocycles is rapidly developed allowing the preparation of coordination assemblies with variety of ligands.¹ Metal macroheterocycles including boron subphthalocyanine (BSubPc) have tendency to coordinate oxygen-containing ligands such as phenols and bisphenols, bridged oxygen atoms yielding monomeric and dimeric assemblies.^{1a, 2} Some of these assemblies can be interesting for preparation of solar cells and photovoltaic devices as well as optically active systems.^{1a, 2} Paramagnetic ketyls which have $S = 1/2$ spin state³ are of particular interest as ligands for the development of magnetic supramolecular assemblies since they can introduce magnetic moments into the systems. Potentially, ketyls can also form supramolecular assemblies with boron subphthalocyanines but such assemblies have not been obtained so far.

In this work we prepared coordination assembly of BSubPc with dimerized fluorenone ketyl (pinacolate). Previously we even showed that fullerenes can be co-crystallized effectively with neutral and anionic metal phthalocyanines.⁴ Therefore, fullerenes are suitable to crystallize the coordination assembly of BSubPc which has concave shape of the macrocycle. As a result, the formation of complex $\{(BSubPc)_2(C_{26}H_{16}O_2)\} \cdot C_{60} \cdot 2C_6H_4Cl_2$ (**1**) allowed one to study the molecular structure, optical and magnetic properties of the $(BSubPc)_2(C_{26}H_{16}O_2)$ assembly. In spite of that the assembly is diamagnetic due to the dimerization of ketyl radical anions, it is the first example of metal macroheterocycle coordination complex with ketyl (pinacolate) type ligand. Up to now such complexes were obtained with some low-valent lanthanides and alkali metals only.⁵

The structure of **1** was solved at 100 K.⁶ Fluorenone ketyl substitutes chloride in BSubPcCl and coordinates to boron atoms of BSubPc to form the B-O bonds of 1.426(4) and 1.436(5) Å length (Fig. 1a). Two ketyl units dimerize over the carbonyl carbons to form a single C-C bond of 1.569(5) Å length (Fig. 1a). This σ -bond links two $\{B^{III}SubPc(2-)\}(C_{13}H_8O^{\cdot-})$ units in dimeric $\{B^{III}SubPc(2-)\}_2(C_{26}H_{16}O_2^{2-})$ assembly (Fig. 1a). The

(Na⁺)(C₁₃H₈O^{•-}) salt is very weakly soluble in *o*-dichlorobenzene so that ketyl-pinacolate transformation is not possible in solution. Probably, the formation of the coordination $\{B^{III}SubPc(2-)\}(C_{13}H_8O^{\cdot-})$ units allows their dissolution followed by dimerization. The substitution of Cl⁻ by the pinacolate ligand in **1** noticeably elongates the average B-N(SubPc) bonds (1.503(5) Å, in comparison with the length of these bonds in BSubPcCl (1.466(5) Å)⁷. The single C-C bond in **1** of 1.569(5) Å is shorter than that in the pinacolate-samarium complex (1.613(9) Å)⁴ and even closer to the length of intercage C-C bonds in the σ -bonded fullerene (C₆₀)₂ dimers (1.58-1.60 Å)⁸. The length of carbon-oxygen bond in fluorenone ketyl of 1.27-1.32 Å⁵ is intermediate between the length of double C=O bond in fluorenone (1.220(4) Å⁹ and single C-O bond in fluorenone pinacolate (1.401(7) Å)^{5a}.

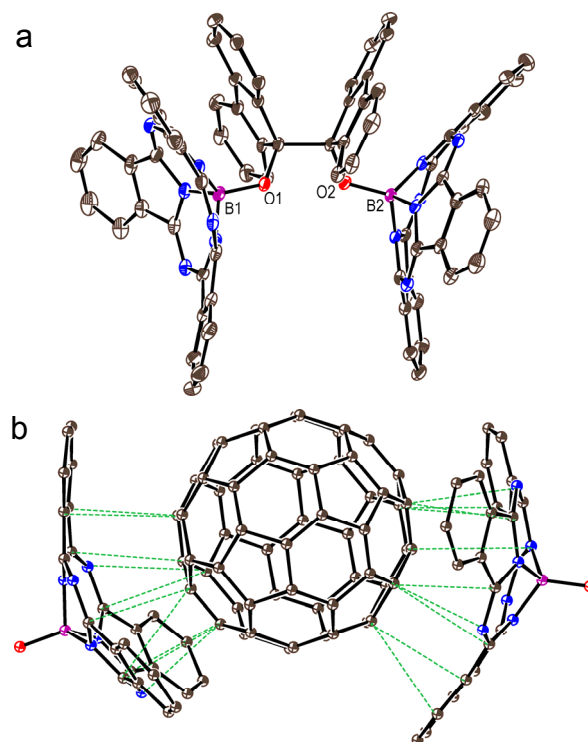


Fig. 1 (a) Molecular structure of the $(BSubPc)_2(C_{26}H_{16}O_2)$ assembly (ellipsoid probability is 30%); (b) van der Waals contacts between the BSubPc fragments and C₆₀. C₆₀ molecule is shown in major orientation.

The average length of the carbon-oxygen bonds in **1** of 1.430(4) Å justifies the formation of pinacolate structure. Dimerization of fluorenone ketyl distorts an initially planar fluorenone fragment since carbonyl carbon atom involved in σ -bond displaces out of the fluorenone plane by 0.130 Å. Oxygen atom also displaces out of this plane towards BSubPc by 0.870 Å.

Each C_{60} molecule is surrounded in **1** by two BSubPc units which form multiple short van der Waals (vdW) C...C contacts with fullerene (these contacts are shown by green dashed lines in Fig. 1b). In spite of that fullerenes are disordered between two orientations. Fullerene in major orientation is positioned in such a way that concave fragment formed by two hexagons and one pentagon of C_{60} is located oppositely to the concave fragment of BSubPc also having two hexagons and one pentagon. Planes of hexagons and pentagon from the opposite units are arranged nearly parallel to each other (the angles between them are 9.9–13.6°) and the C₆₀(BSubPc)...C(C₆₀) distances are 3.3–3.8 Å. Thus, good sterical correspondence is achieved between nearly spherical C_{60} molecule and concave-shaped BSubPc macrocycle. C_{60} molecules are packed in zigzag chains with a short center-to-center interfullerene distance of 9.87 Å and a vdW C...C contact of 3.160 Å (Fig. 2, green dashed lines).

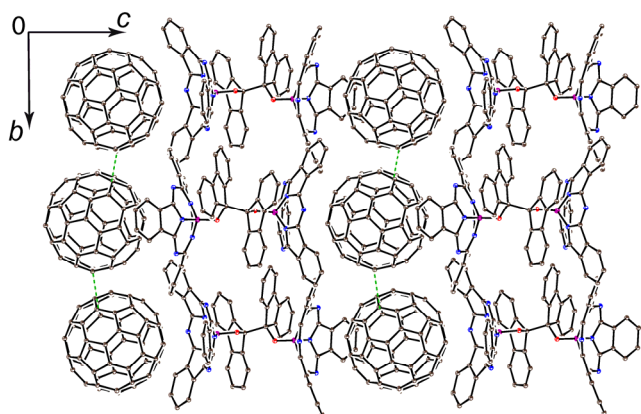


Fig. 2 View on crystal structure of **1** along the *a* axis, zigzag chains of the C_{60} molecules are arranged in the *b* direction. C_{60} is shown in major orientation. Solvent $C_6H_4Cl_2$ molecules are not shown.

Spectrum of **1** in the UV-visible-NIR range is shown in Fig. 3a. Absorption bands at 260 and 330 nm were attributed to C_{60} , and bands at 530 and 576 nm were attributed to BSubPc. The main band at 576 nm is only slightly shifted in the spectrum of **1** relative to BSubPcCl (583 nm, Fig. 3b). An additional broad band at about 750 nm (shoulder for the band at 576 nm, Fig. 3a) can be ascribed to charge transfer between BSubPc and C_{60} which realizes at the absorption of a light quantum. That can be the evidence of effective π - π interaction between BSubPc and C_{60} in **1**. Nevertheless, the energy of the charge transfer band is too large to realize charge transfer from BSubPc to C_{60} in the ground state. Absorption bands of the $C_{60}^{\cdot-}$ radical anions located in the spectra of the salts at 930–950 and 1060–1080 nm¹⁰ are absent in the spectrum of **1** indicating neutral state of fullerene. The spectrum of sodium fluorenone ketyl shows a band at 450 nm (Fig. 3c). This band is not observed in the spectrum of **1** (Fig. 3a) indicating that fluorenone pinacolate does not have noticeable absorption in the visible range. The formation of pinacolate from

fluorenone ketyl in the samarium complex also results in the colour change from purple-brown to light yellow.^{5a} IR-spectra of **1** and starting components are shown in Supporting information (Table S1, Fig. S1-S3). The band of C_{60} at 1429 cm^{-1} is sensitive to charge state of the molecule.¹⁰ This band remains unshifted in the spectrum of **1** (1431 cm^{-1}). Neutral state of C_{60} in **1** indicates that fluorenone pinacolate cannot reduce fullerene, whereas monomeric fluorenone ketyl is a strong reducing agent producing the C_{60}^{2-} dianions in solution.¹¹ Monomeric fluorenone ketyl manifests bands of the C-O bond vibrations at 1651, 1675 and 1714 cm^{-1} . In the spectrum of **1** only a single broad band at 1630 cm^{-1} is manifested. Blue shift of this band can be due to the elongation of the C-O bond in pinacolate.

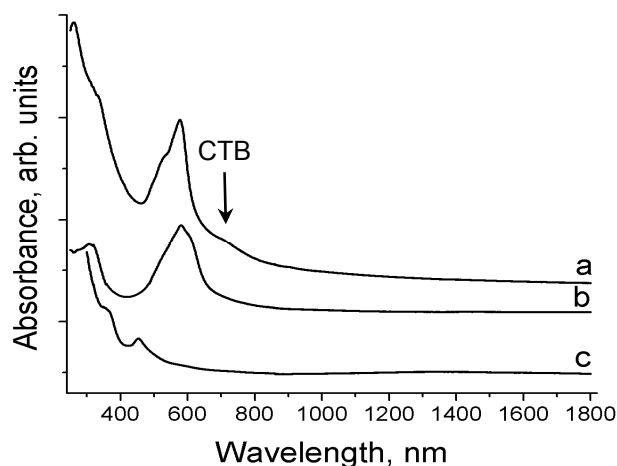


Fig. 3 UV-visible-NIR spectra of **1** (a), BSubPcCl (b) and sodium fluorenone ketyl (c). KBr pellets were prepared in anaerobic conditions. Charge transfer band (CTB) is marked by arrow.

Complex **1** is EPR silent at RT and below. That can be explained by the formation of a single C-C bond between initially paramagnetic ketyls yielding diamagnetic pinacolate which is stable up to room temperature. This behaviour is very similar to the dimerization of fullerene radical anions.⁸ For them, the formation of a single C-C bond between initially paramagnetic $C_{60}^{\cdot-}$ radical anions yields diamagnetic and EPR silent singly-bonded ($C_{60}^{\cdot-}$)₂ dimers. However, as in case of σ -bonded ($C_{60}^{\cdot-}$)₂ dimers, the reversible dissociation of the C-C bonds can be possible in **1**, for example, under heating or light excitation. In solution the pinacolate/ketyl transformation is realized simply by changing polarity of the solvent.^{5a}

Experimental

Synthesis

Synthesis and all manipulations with the crystals of **1** were made in the glove box with controlled atmosphere and water and oxygen content less than 1 ppm. The crystals of $\{(B^{III}SubPc)_2(C_{26}H_{16}O_2)\} \cdot C_{60} \cdot 2C_6H_4Cl_2$ (**1**) were obtained as follows: 18 mg (0.042 mmol) of $B^{III}SubPcCl$ reacted in the 16 mL *o*-dichlorobenzene with excess of sodium fluorenone ketyl¹² (20 mg, 0.098 mmol) for two hours at 100°C. The reaction solution changed color from violet to bright pink. The solution was cooled down to room temperature and filtered into the flask containing fullerene C_{60} (30 mg, 0.042 mmol). Fullerene was

dissolved during 2 hours at 80°C. Bright pink solution was cooled down to room temperature and filtered to a 50 mL glass tube of 1.8 cm diameter with a ground glass plug, and 30 mL of hexane was layered over the solution. Slow mixing of the obtained dichlorobenzene solution with hexane during 1 month produced dark red-pink crystals of **1**. Then the solvent was decanted from the crystals and they were washed with hexane (the yield is 52%). Composition of the complex was determined from X-ray diffraction of single crystal. Several crystals tested from the synthesis by X-ray diffraction showed the presence of only one crystal phase. Composition of **1** was justified by elemental analysis: Anal. Calcd for C₁₄₆H₄₈B₂Cl₄N₁₂O₂: C 80.98, H 2.22, B 1.01; N 7.76; Cl 6.55; O 1.48 Found: C 80.47, H 2.04, N 7.34.

Conclusions

We showed that fluorenone ketyl coordinates by oxygen atom to BSubPc forming {B^{III}SubPc(2-)}(C₁₃H₈O^{•-}) assemblies which due to the dimerization of ketyls form the {B^{III}SubPc(2-)}₂(C₂₆H₁₆O₂²⁻) dimers. Concave shape of BSubPc fits well to the spherical shape of C₆₀ allowing the cocrystallization with fullerene and effective π-π interaction between the two components. Thus, together with other concave-shaped molecules¹³ including pyrene-fused subphthalocyanine¹⁴, unsubstituted subphthalocyanine can be new receptor for nearly spherical C₆₀ molecules. Dimerization of ketyls in **1** yields diamagnetic products. However, we suppose that similar assemblies with paramagnetic monomeric ketyls can possess promising magnetic properties.

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Notes and references

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† Electronic Supplementary Information (ESI) available: materials, synthesis of **1**, X-ray structure determination for **1**, IR-spectra of **1** and starting materials. See DOI: 10.1039/b000000x/

- (a) I. Beletskaya, V. S. Tyurin, A. Y. Tsivadze, R. Guillard and C. Stern, *Chem. Rev.* 2009, **109**, 1659; (b) C. G. Claessens, D. González-Rodríguez, M. S. Rodríguez-Morgade, A. Medina and T. Torres, *Chem. Rev.* 2014, **114**, 2192.
- (a) A. S. Paton, G. E. Morse, A. J. Lough and T. P. Bender, *CrystEngComm*. 2011, **13**, 914; (b) G. E. Morse, A. S. Paton, A. Lough and T. P. Bender, *Dalton Trans.* 2010, **39**, 3915; (c) T. Fukuda, M. M. Olmstead, W. S. Durfee and N. Kobayashi, *Chem. Commun.*, 2003, 1256; (d) A. K. Eckert, M. S. Rodríguez-Morgade and T. Torres, *Chem. Commun.*, 2007, 4104-4106; (e) L. C. Kasi Viswanath, L. D. Shirlcliff, K. D. Berlin, *J. Porph. Phth.*, 2013, **17**, 1167.
- T. A. Scott, B. A. Ooro, D. J. Collins, M. Shatruk, A. Yakovenko, K. R. Dunbar and H.-C. Zhou, *Chem. Commun.* 2009, 65.
- (a) D. V. Konarev, L. V. Zorina, S. S. Khasanov, E. U. Khakimova and R. N. Lyubovskaya, *Russ. Chem. Bull.*, 2011, **60**, 1063; (b) D. V. Konarev, L. V. Zorina, S. S. Khasanov, R. N. Lyubovskaya, *Dalton Trans.*, 2012, **41**, 9170; (c) D. V. Konarev, A. V. Kuzmin, S. V. Simonov, S. S. Khasanov and R. N. Lyubovskaya, *J. Porph. Phth.*, 2014, **18**, 87; (d) D. V. Konarev, A. V. Kuzmin, S. S. Khasanov, A. Otsuka, H. Yamochi, G. Saito and R. N. Lyubovskaya, *Dalton Trans.*, 2014, **43**, 13061; (e) D. V. Konarev, S. S. Khasanov and R. N. Lyubovskaya, *Coord. Chem. Rev.*, 2014, **262**, 16.

- (a) Z. Hou, T. Miyano, H. Yamazaki and Y. Wakatsuki, *J. Am. Chem. Soc.* 1995, **117**, 4421; (b) Z. Hou, A. Fujita, Y. Zhang, T. Miyano, H. Yamazaki and Y. Wakatsuki, *J. Am. Chem. Soc.* 1998, **120**, 754; (c) Z. Hou, A. Fugita, H. Yamazaki and Y. Wakatsuki, *J. Am. Chem. Soc.* 1996, **118**, 2503.
- Crystal data: Synchrotron X-ray data were collected on the BL14.2 at the BESSY storage ring (Berlin, Germany). C₁₄₆H₄₈B₂Cl₄N₁₂O₂ monoclinic, *P* 2₁, *a* = 15.4619(8), *b* = 16.9321(8), *c* = 19.698(1) Å, β = 110.386(5)°, *V* = 4834.0(4) Å³, *Z* = 2, *T* = 100 K, 21328 reflections, 1708 parameters, 2395 restraints, *R*₁(*F*) = 0.0808 for 16669 reflections with *I* > 2σ(*I*), *wR*₂(all *F*²) = 0.2045, CCDC 1046031.
- H. Kietai, *Monatsh. Chem.* 1974, **105**, 405.
- (a) D. V. Konarev, S. S. Khasanov, G. Saito, A. Otsuka, Y. Yoshida and R. N. Lyubovskaya, *J. Am. Chem. Soc.* 2003, **125**, 10074; (b) D. V. Konarev, S. S. Khasanov and R. N. Lyubovskaya, *Russ. Chem. Bull.* 2007, **56**, 371.
- H. R. Luss and D. L. Smith, *Acta Crystallogr., Sect. B*, 1972, **28**, 884.
- D. V. Konarev and R. N. Lyubovskaya, *Russ. Chem. Rev.* 2012, **81**, 336.
- D. V. Konarev, A. V. Kuzmin, S. V. Simonov, S. S. Khasanov, E. I. Yudanov, G. Saito and R. N. Lyubovskaya, *Phys. Chem. Chem. Phys.* 2013, **15**, 9136.
- D. V. Konarev, S. S. Khasanov, E. I. Yudanov and R. N. Lyubovskaya, *Eur. J. Inorg. Chem.*, 2011, 816.
- (a) D. V. Konarev, E. F. Valeev, Y. L. Slovkhotov, Y. M. Shul'ga and R. N. Lyubovskaya, *J. Chem. Res.* 1997, 442; (b) J. L. Atwood, L. J. Barbour, M. W. Heaven and C. L. Raston, *Chem. Commun.* 2003, 2270; (c) D. Pham, J. C. Bertran, M. M. Olmstead, M. Mascal and A. L. Balch, *Org. Lett.* 2005, **7**, 2805.
- S. Shimizu, S. Nakano, T. Hosoya and N. Kobayashi, *Chem. Commun.* 2011, **47**, 316.