

## "Forgotten" Sulfur Containing Macroheterocycles

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*Brief review of works of V. N. Klyuev (1915-1997) devoted to synthesis and study of properties of sulfur containing macroheterocyclic compounds (MHCC) and their complexes is presented. In particular by gradual heating of the mixture of o-carboxybenzenesulfonic acid, urea, copper(I) chloride and ammonium molybdate the copper complex of tetrabenzotetrathiaporphyrine was synthesized. Other sulfur containing MHCC were synthesized on the basis of 1,3-diiminiothioindolenine. As a result of interaction of the latter with various aromatic and heterocyclic diamines three-unit products were obtained which can be used as initial compounds for synthesis of MHCC of both symmetrical (ABAB) and unsymmetrical (ABAC) structures. The reaction of MHCC with copper acetate in boiling pyridine or butanol gave the corresponding Cu complexes. It was shown that introduction of sulfur atoms into the chain of conjugation leads to hypsochromic shift of the UV-vis absorption bands. Cu complexes were studied as thermo- and light stabilizers of polycapramide fibres.*

**Keywords:** 1,3-Diiminiothioindolenine, sulfur containing phthalocyanine analogs, copper complexes, UV-vis spectra, kinetic stability, thermo- and light stabilization of polymers.

## «Забытые» серосодержащие макрогетероциклы

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*В статье приведен краткий обзор статей В.Н. Ключева (1915-1997), посвященных синтезу и исследованию свойств серосодержащих макрогетероциклических соединений (МГЦС) и их металлокомплексов. В частности, при нагреве смеси о-карбоксібензолсульфиновой кислоты, мочевины, однохлористой меди и молибдата аммония был получен тетрабензотетратиопорфиразин меди. Другие серосодержащие МГЦС были получены на основе 1,3-дииминотиоизоиндоленина. При взаимодействии последнего с различными ароматическими и гетероциклическими диаминами синтезировали трехзвенные продукты, которые дали возможность получить МГЦС как симметричного (АВАВ), так и несимметричного (АВАС) строения. При взаимодействии полученных МГЦС с ацетатом меди в кипящем пиридине или бутаноле были получены соответствующие комплексы с медью. Было показано, что введение атомов серы в контур сопряжения приводит к гипсохромному сдвигу полос поглощения. Комплексы с медью были исследованы в качестве термо- и светостабилизаторов поликапроамидных волокон, причем наилучшие свойства показал комплекс с цикло-1,3-фенилентри-тиоизоиндоленом.*

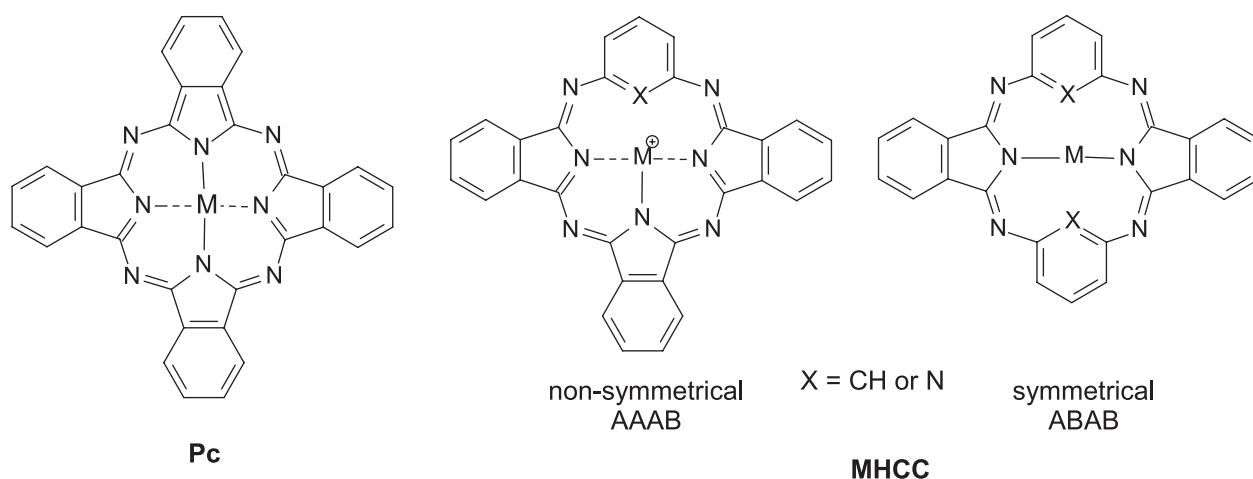
**Ключевые слова:** 1,3-Дииминотиоизоиндоленин, серосодержащие аналоги фталоцианина, Cu<sup>II</sup> комплексы, электронные спектры, кинетическая устойчивость, термо- и светостабилизация полимеров.

In the second half of last century in order to expand the colour scale of phthalocyanine pigments limited to blue and green a large group of compounds similar to phthalocyanine was synthesized.<sup>[1-5]</sup> They differed from the phthalocyanines (Pc) by replacement of one or two isoindole units with benzene ring or other aromatic fragments (*e.g.* by pyridine unit).

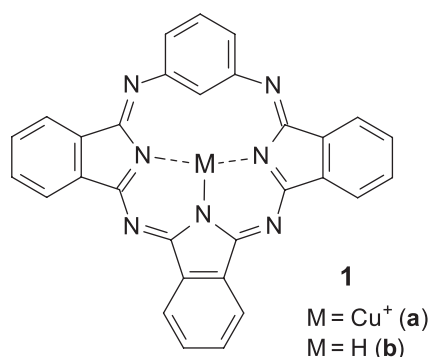
The first examples of such macroheterocyclic compounds (MHCC) were described in 1952 by Linstead.<sup>[1,2]</sup> In 1960-70<sup>th</sup> MHCC containing combination of isoindole fragments with benzene rings were most actively studied in the USSR because of their potential application properties.<sup>[1-16]</sup> Thus, it was reported that the copper(II) complex of cyclo-1,3-phenylenetriisoindole ("Stabilin-9") (**1a**) can be used as stabilizer of polycapromide,<sup>[5]</sup> as fire-retarding and antioxidant agent.<sup>[6]</sup> Besides, there are data on possible application MHCC as pigments,<sup>[3]</sup> dyes,<sup>[7]</sup> thermo- and light stabilizers of polymeric materials,<sup>[4,8,9]</sup> catalysts in a number of chemical and electrochemical oxidation-reduction processes,<sup>[4,9,10]</sup> inhibitors of siloxane polymers burning.<sup>[11]</sup> Data on electrophysical

A considerable contribution to synthetic chemistry and study of MHCC was made by scientists of Ivanovo school of macroheterocyclic compounds – Professors V.F. Borodkin, R.P. Smirnov and their numerous pupils and colleagues.<sup>[6-8,10-12,17-22]</sup> One of them was *Vasily Nikolaevich Klyuev*, whose centenary was celebrated in February 2015.

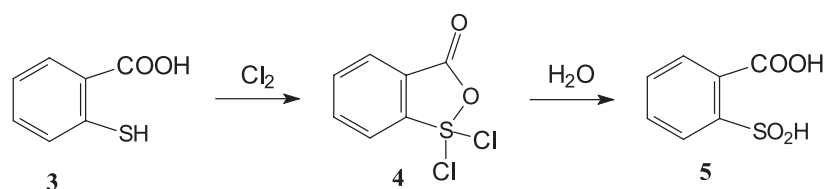
In order to expand the range of the macroheterocyclic compounds V.N. Klyuev suggested to replace one of carbon atoms in the isoindole fragments of phthalocyanine macrocycle with sulfur, hoping to obtain new MHCC interesting from the practical point of view. In 1958 the first work devoted to the sulfur containing analogue of copper phthalocyanine has been published by V.N. Klyuev (together with V.F. Borodkin).<sup>[23]</sup> Instead phthalic acid derivatives as common precursors for phthalocyanines for the synthesis of their thioanalogues they have suggested to use *o*-carboxybenzenesulfonic acid **5**, which is available starting from thiosalicylic acid **3** by hydrolysis of intermediate dichloro-anhydride **4**.<sup>[24]</sup>

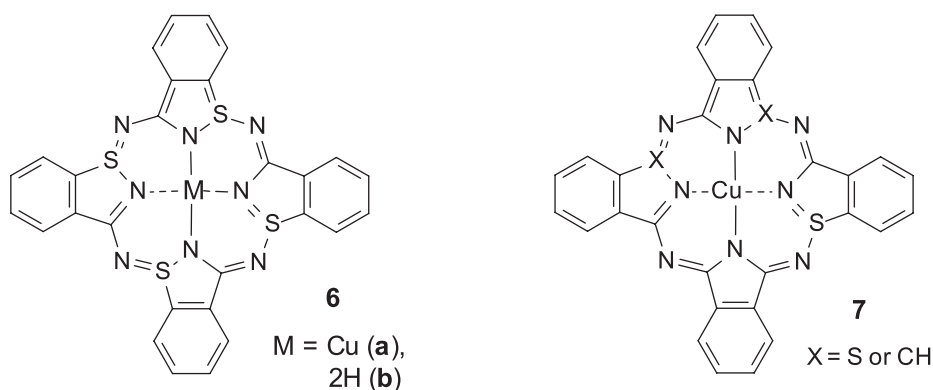


characteristics of MHCC were published in <sup>[12]</sup>. The new wave of interest to MHCC containing isoindole fragments and benzene rings appeared in the last 10 years.<sup>[13]</sup> MHCC containing heteroaromatic fragments (pyridine, triazole, *etc.*) in place of benzene rings were more actively studied and their synthesis and properties were reviewed.<sup>[14-17]</sup>

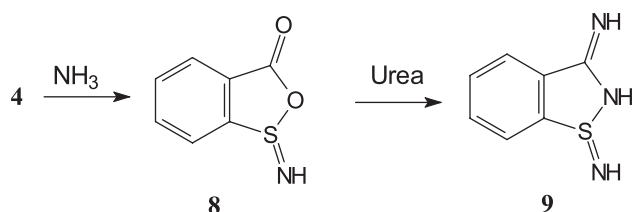


Heating the mixture of *o*-carboxybenzenesulfonic acid **5**, urea, copper(I) chloride and ammonium molybdate with gradual increase of temperature from 130 to 180 and finally to 210 °C they have obtained the olive product **2** which was named Cu-tetrabenzotetrathioporphyrzine or Cu tetrathiophthocyanine.<sup>[23]</sup> Unlike Cu phthalocyanine which can be obtained similarly from phthalic acid derivatives, its tetrathioanalogue **6a** is soluble in the majority of organic solvents. It was noted that it is stable to alkalis and acids. Upon treatment with 100 % sulfuric acid or oleum at elevated temperature it easily undergoes sulfonation forming sulfo derivative which can be used as olive dye for cotton. Initially **6a** was characterized only by elemental analysis. Joint condensation of *o*-carboxybenzenesulfonic acid with phthalic anhydride in 1:1 ratio gave according to the authors blue-green phthalocyanine analogues **7** with the smaller sulfur content, which were not further studied.

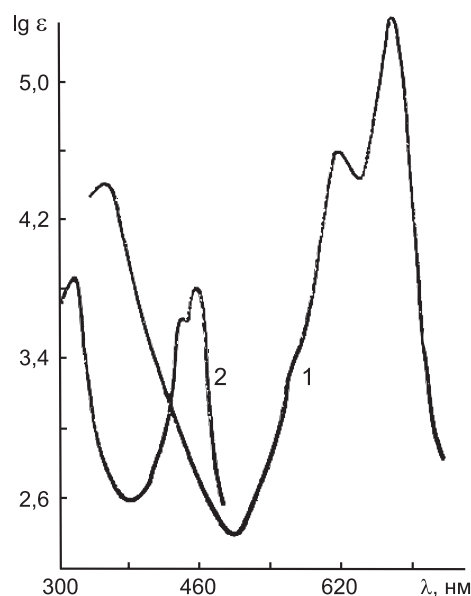




Later V.N. Klyuev and F.P. Snegireva have prepared the more reactive precursor for tetrathioisindolenines – 1,3-diiminothioisindolenine (**9**) heating the mixture of *S*-imine of *o*-carboxybenzenesulfonic acid anhydride (**8**), urea and ammonium molybdate to 170 °C.<sup>[24]</sup>



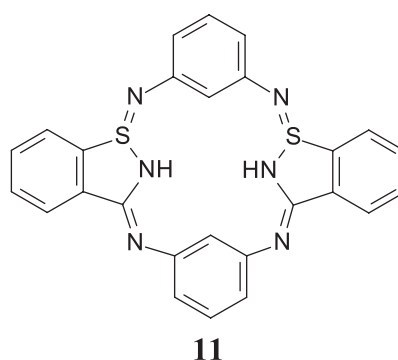
By analogy with a known 1,3-diiminoisindolenine it was assumed that from 1,3-diiminothioisindolenine it will be possible to obtain sulfur-containing analogues of Pc and MHCC, as later it was confirmed in <sup>[25,26]</sup>. Thus, heating of 1,3-diiminothioisindolenine (**9**) with urea and copper(II) acetate in butanol leads to the Cu<sup>II</sup> complex **6a** with 61 % yield, while the metal free tetrathioisindolenine (**6b**) was obtained upon refluxing of **9** with urea and NaHSO<sub>3</sub> in butanol with 72 % yield.<sup>[26]</sup> In this work the constitution of thioisindolenine **6b** and its Cu complex **6a** was confirmed by elemental analysis and by molecular weight measurements using Beckman ebullioscopy method in pyridine. In the same work UV-vis spectra of **6a,b** were reported and their stability to hydrolytic destruction (degradation) in 18M sulfuric acid solutions were studied. It was shown that thio-substitution in isoindole fragment of Pc leads to significant hypsochromic shift of the long-wave absorption bands (150-200 nm). The absorption maxima in DMF for **6a** are observed by 312, 445 and 465 nm and for **6b** by 310, 440 and 455 nm and characterized by ca 10 times lower extinction coefficients as compared to corresponding phthalocyanines. An attempt to explain theoretically the hypsochromic shift of the absorption bands was made in <sup>[29]</sup> on the basis of simplified metallic model of conjugated compounds and ascribed to higher electronegativity of S<sup>IV</sup> as compared to C<sup>IV</sup>. In 18 M sulfuric acid **6a** and **6b** form red-brown solutions with maxima at *ca.* 490 nm (for **6b**). The solution of **6a** is stable at room temperature and decolorized only upon heating to 100 °C. The hydrolytic destruction of **6b** at 25 °C is only 6 times faster than for phthalocyanine. High stability of the macrocyclic chromophore in concentrated sulphuric acid was considered by the authors as an important indication of the phthalocyanine nature of the synthesized compounds.

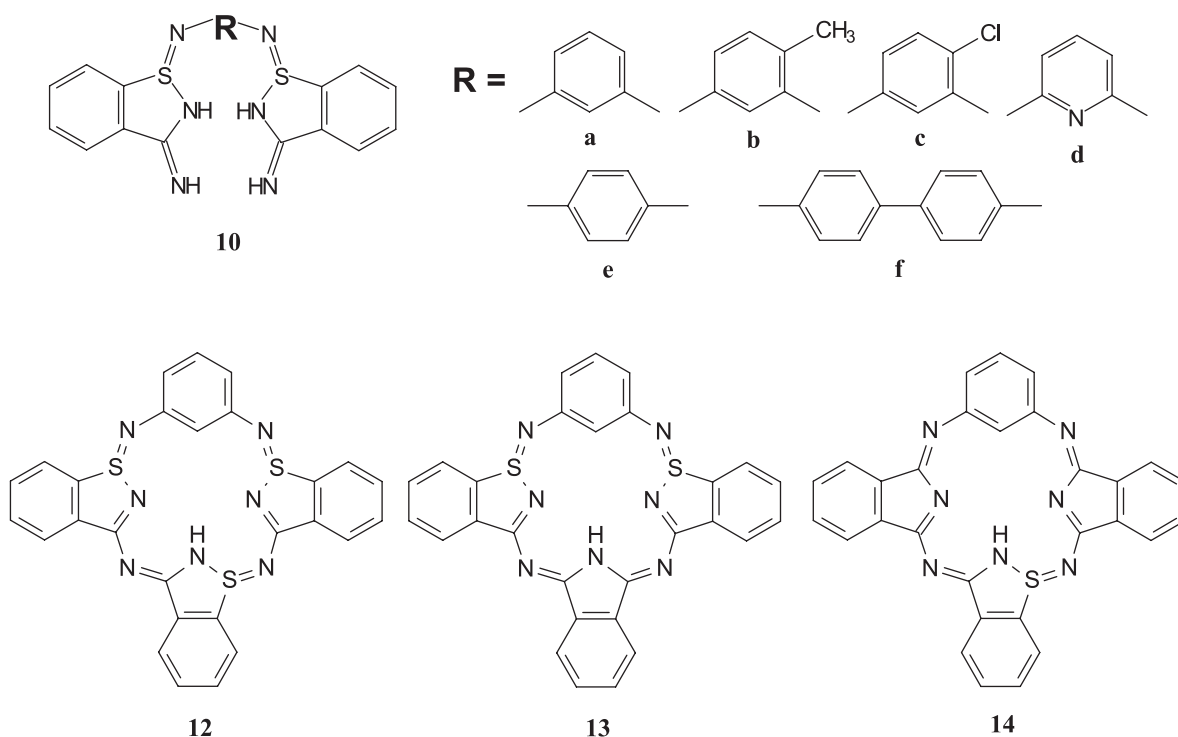


**Figure 1.** UV-Vis spectra of Cu phthalocyanine (**1**) and tetrathioisindolenine (**2**) in DMF (adapted from <sup>[29]</sup>).

It was shown that 1,3-diiminothioisindolenine (**9**) has larger reactivity of the *S*-iminegroup as compared to the *C*-iminegroup.<sup>[24]</sup> The reaction of this diimine **9** with various aromatic and heterocyclic diamines (2:1 molar ratio) in methanol under reflux leads to yellow three-unit products of the general formula **10** with 40-50 % yields.<sup>[27]</sup> They were characterized by elemental analysis, UV-Vis, IR spectra and molecular weight measurement by Rast method.

These three-unit products **10a-f** can be used as initial compounds for synthesis of MHCC of both symmetric (ABAB) and unsymmetrical (ABAC) structure.<sup>[25]</sup>

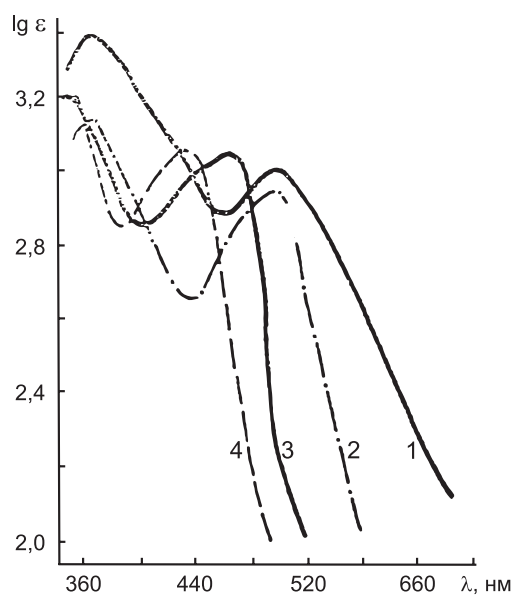




Symmetrical MHCC **11** was prepared by interaction of *m*-phenylenediamine with **10a** (1:1 ratio) or directly with diimine **9** (1:1) in butanol under reflux with *ca.* 50 % yield as yellow-brown crystals (mp 313-315 °C). The reaction between **10a** and 1,3-diiminothioisindolenine (**9**) leads to non-symmetrical AAAB type MHCC **12** with three S atoms (59 %), while ABAC type MHCC **13** with two S atoms was prepared from **10a** and 1,3-diiminoisindolenine (57 %). MHCC containing one S atom (**14**) was also prepared from **9** and 1,3-bis(1-imino-3-isindoleninidenamino) benzene with 63 % yield. MHCC **12-14** were obtained as red-orange crystals which have melting points above 380 °C.

MHCCs **11-14** were characterized by elemental analysis, UV-Vis spectra and molecular weight measurements using Beckman method. It was shown that the reaction of MHCCs **11-14** with copper acetate in boiling pyridine or butanol gives the corresponding Cu complexes.<sup>[28]</sup> The IR spectra of **12** and its Cu complex were reported.<sup>[28]</sup> It was observed that increase of the number of the S atoms in MHCC from 0 to 3 leads to the hypsochromic shift of the absorption bands in the series **1b** (0S, 340, 510 nm), **14** (1S, 370, 510 nm), **13** (2S, 370, 480 nm), **12** (3S, 335, 430 nm). The similar trend exists also for the series of corresponding Cu complexes (370, 540, 680 nm for 0S, 360, 490, 540 for 1S, 335, 450, 530 nm for 2S, 335, 430, 510 nm for 3S). Some theoretical interpretation of the observed hypsochromic shift was attempted and it was connected with influence of electronegativity of S<sup>IV</sup>.<sup>[29]</sup>

In 1974 the last work of V.N. Klyuev devoted to the sulfur containing MHCCs was published in which the possibility of using the copper complexes as thermo- and light stabilizers of polycaproadid fibers has been shown.<sup>[30]</sup> It was found that Cu complex of MHCC **12** has the best performance.



**Figure 2.** UV-Vis spectra of cyclo-1,3-phenylenetriisindole macrocycle **1b** (1) and its monothio **14** (2), dithio **13** (3), and trithio **12** (4) derivatives in DMF (adapted from <sup>[29]</sup>).

After 1974 the studies of S-containing phthalocyanine analogues were not carried out to the best of our knowledge. However taking into account modern achievements in the macroheterocyclic chemistry we would like to draw attention of the researchers to sulfur containing MHCCs which were perhaps unfairly forgotten but have undoubtedly perspectives as new organic materials.

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## References

1. Elvidge J.A., Linstead R.P. *J. Chem. Soc.* **1952**, 20, 5008-5012.
2. Campbell J.B. Patent 2765308 (USA); announced 15.08.52; published 02.10.56.
3. Krolik L.G., Vitkina B.F. *Zhurnal VKhO im. D.I. Mendeleeva* **1966**, 11, 60-69 (in Russ.).
4. Siling S.A. In: *Uspekhi Khimii Porfirinov [The Advances in Porphyrin Chemistry]*. Vol. 2 (Golubchikov O.A., Ed.), St. Petersburg: NII Khimii SPbGU, **1999**, pp. 320-329 (in Russ.).
5. Maslova I.P., Zolotareva K.A., Glazunova N.R. *Chemical Additions to Polymers*, Moscow: Khimiya, **1973**. 113 p. (in Russ.) [Маслова И.П., Золотарева К.А., Глазунова Н.Р. *Химические добавки к полимерам*, М.: Химия, **1973**. 113 с.].
6. Smirnov L.N. In: *Proceedings of the 1<sup>st</sup> International Conference on Polymer Materials of the Lowered Combustibility*, Alma-Ata, **1990**, Vol. 2, p. 53 (in Russ.).
7. (a) Borodkin V.F., Volkova N.A., Makarycheva A.V. *Izv. Vyssh. Uchebn. Zaved. SSSR., Khim. Khim. Tekhnol.* **1973**, 16, 951-954 (in Russ.). (b) Borodkin V.F., Makarycheva A.V. *Izv. Vyssh. Uchebn. Zaved. SSSR., Khim. Khim. Tekhnol.* **1974**, 17, 942-944 (in Russ.).
8. (a) Smirnov R.P., Kharitinov V.N., Smirnov L.N. *Trudi IKhTI [Works of Ivanovo Institute of Chemistry and Technology]* **1972**, 4, 111-116 (in Russ.). (b) Smirnov L.N., Snegirev D.G. *Russian Polymer News* **2000**, 5, 6-12.
9. Siling S.A., Margolin F.L., *et al.* *Acta Polymerica* **1991**, 42, 133-135.
10. (a) Kolesnikov N.A., Maizlish V.E., Borodkin V.F. Avt. Svid. SSSR [Copywrite certificate of USSR] № 505654, publ. 05.03.1976, Bull. N 9. (b) Bazanov M.I., Kudrinskii V.V., Kolesnikov N.A., Smirnov R.P. *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* **1993**, 36, 59-64 (in Russ.).
11. Smirnov L.N., Zdorikova G.A., Smirnov A.L., Snegirev D.G. *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* **1992**, 35, 71-76 (in Russ.).
12. (a) Smirnov R.P. *Izv. Vyssh. Uchebn. Zaved. SSSR., Khim. Khim. Tekhnol.* **1969**, 12, 1259-1261 (in Russ.). (b) Fedorov L.N., Smirnov R.P., Kolesnikov N.A., Alyanov M.I. *Izv. Vyssh. Uchebn. Zaved. SSSR., Khim. Khim. Tekhnol.* **1972**, 15, 537-540 (in Russ.).
13. (a) Çetin A., Durfee W.S., Ziegler C.J. *Inorg. Chem.* **2007**, 46, 6239-6241. (b) Çetin A., Sripothongnak S., Kawa M., Durfee W.S., Ziegler C.J. *Chem. Commun.* **2007**, 4289-4290. (c) Sripothongnak S., Pischera A.M., Espe M.P., Durfee W.S., Ziegler C.J. *J. Porphyrins Phthalocyanines* **2009**, 13, 304. (d) Durfee W.S., Ziegler C.J. *J. Porphyrins Phthalocyanines* **2009**, 13, 304. (e) Sripothongnak S., Baronea N., Ziegler C.J. *Chem. Commun.* **2009**, 4584-4586. (f) Sripothongnak S., *et al.* *J. Porphyrins Phthalocyanines* **2010**, 14, 170. (g) Bonner E.S., Engle J.T., Sripothongnaka S., Ziegler C.J. *Dalton Trans.* **2010**, 39, 1932-1934.
14. Fernández-Lázaro F., Torres T., Haushel B., Hanack M. *Chem. Rev.* **1998**, 98, 563-575.
15. Rodríguez-Morgade M.S., de la Torre G., Torres T. In: *The Porphyrin Handbook*, Vol. 15 (Kadish K.M., Smith K.M., Guillard R., Eds.), Academic Press: San Diego, **2003**, pp. 125-159.
16. Rodríguez-Morgade M.S., Stuzhin P.A. *J. Porphyrins Phthalocyanines* **2004**, 8, 1129-1165.
17. Islyaikin M.K., Danilova E.A., Kudrik E.V. In: *Uspekhi Khimii Porfirinov [The Advances in Porphyrin Chemistry]*, Vol. 2 (Golubchikov O.A., Ed.), St. Petersburg: NII Khimii SPbGU, **1999**, pp. 300-319 (in Russ.).
18. Stepanov B.I. *Introduction to Chemistry and Technology of Organic Dyes*, Moscow: Khimiya, **1984**. 592 p. (in Russ.) [Степанов Б.И. *Введение в химию и технологию органических красителей*, М.: Химия, **1984**. 592 с.].
19. Borodkin V.F. *Zh. Obshch. Khim.* **1960**, 30, 1547-1553 (in Russ.).
20. Smirnov R.P., Borodkin V.F. *Izv. Vyssh. Uchebn. Zaved. SSSR., Khim. Khim. Tekhnol.* **1960**, 3, 718-720 (in Russ.).
21. Smirnov R.P., Gnedina V.A., Borodkin V.F. *Izv. Vyssh. Uchebn. Zaved. SSSR., Khim. Khim. Tekhnol.* **1963**, 6, 1022-1024 (in Russ.).
22. Vorob'eva S.M., Smirnov R.P., Vorob'ev Y.G. *Izv. Vyssh. Uchebn. Zaved. SSSR., Khim. Khim. Tekhnol.* **1978**, 21, 1521-1525 (in Russ.).
23. Borodkin V.F., Klyuev V.N. *Trudi IKhTI [Works of Ivanovo Institute of Chemistry and Technology]*, **1958**, pp. 105-106 (in Russ.).
24. Klyuev V.N., Snegireva F.P. *Izv. Vyssh. Uchebn. Zaved. SSSR., Khim. Khim. Tekhnol.* **1967**, 10, 891-894 (in Russ.).
25. Klyuev V.N., Snegireva F.P. *Izv. Vyssh. Uchebn. Zaved. SSSR., Khim. Khim. Tekhnol.* **1969**, 12, 170-172 (in Russ.).
26. Klyuev V.N., Snegireva F.P. *Izv. Vyssh. Uchebn. Zaved. SSSR., Khim. Khim. Tekhnol.* **1971**, 14, 258-261 (in Russ.).
27. Klyuev V.N., Snegireva F.P. *Izv. Vyssh. Uchebn. Zaved. SSSR., Khim. Khim. Tekhnol.* **1968**, 11, 1357-1360 (in Russ.).
28. Klyuev V.N., Snegireva F.P. *Izv. Vyssh. Uchebn. Zaved. SSSR., Khim. Khim. Tekhnol.* **1969**, 12, 1236-1239 (in Russ.).
29. Klyuev V.N., Berezin B.D., Snegireva F.P. *Izv. Vyssh. Uchebn. Zaved. SSSR., Khim. Khim. Tekhnol.* **1970**, 13, 209-213 (in Russ.).
30. Klyuev V.N., Smirnov L.N., Snegireva F.P., Merkureva E.V., Tikhomirova I.S., Kharitonov V.M. *Izv. Vyssh. Uchebn. Zaved. SSSR., Khim. Khim. Tekhnol.* **1974**, 17, 1209-1212 (in Russ.).

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## Dedication to Vasily Nikolaevich Klyuev on the occasion of his 100<sup>th</sup> anniversary

Vasily Nikolaevich Klyuev (1915-1997) was born in Kokhma (Ivanovo region). He graduated from Ivanovo Institute of Chemical Technology, and in 1939 was called to the Red Army. He took part in the Great Patriotic War and awarded by 5 orders and many medals for his service and contribution to liberation of the Soviet homeland and Europe from Nazi invaders. After demobilization in 1947 he started to work in Ivanovo Institute of Chemical Technology as an assistant, and after receiving the Degree of the Candidate of Chemical Sciences as associate Professor (dozent) and then as Chief of the Department of the Technology of Plastics. He has published about 150 scientific works and belongs to the scientists who began the research of phthalocyanines and related compounds in the late 1950<sup>th</sup> together with the founders of the Ivanovo scientific school on macroheterocycles professors Vasily Fedorovich Borodkin and Boris Dmirievich Berezin.

On the occasion of centenary of Vasily Nikolaevich Klyuev we have decided to present in this issue a brief review of his results on sulfur analogues of phthalocyanines, which have been published in Russian 50 years ago and remained probably unknown, but might be of interest to scientists studying phthalocyanine-like macroheterocycles.

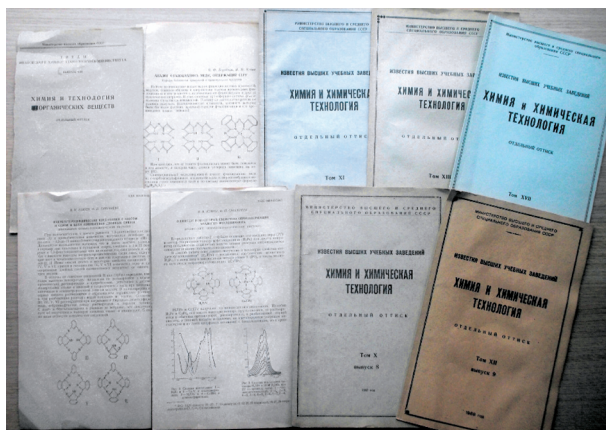
*the Editorial Board*



*V. N. Klyuev in 1945*



*V. N. Klyuev – Head of the Department of Technology of Plastics (1960<sup>th</sup>)*



*Reprints of the articles on S-containing phthalocyanine analogues published by V. N. Klyuev and co-authors in 1958-1974*