ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2018, Vol. 44, No. 8, pp. 496–501. © Pleiades Publishing, Ltd., 2018.
Original Russian Text © M.A. Ogienko, S.N. Konchenko, A.B. Burdukov, A.V. Vologzhanina, E.G. Lebed, Y.Z. Voloshin, 2018, published in Koordinatsionnaya Khimiya, 2018, Vol. 44, No. 4, pp. 244–249.

Unexpected Product of the Reaction of Iron(II) Dichloroclathrochelate with the $[Fe_2(\mu\text{-}S)_2(CO)_6]^{2-}$ Cluster Dianion: Synthesis and X-ray Diffraction Structure of the First Cage Complex with Thiol Groups Inherently Bonded to a Macrobicyclic Framework

M. A. Ogienko[a], S. N. Konchenko[a], A. B. Burdukov[a], A. V. Vologzhanina[b], E. G. Lebed[b], and Y. Z. Voloshin[b, c, *]

[a] *Nikolaev Institute of Inorganic Chemistry, Siberian Branch, Russian Academy of Sciences, Novosibirsk, 630090 Russia*
[b] *Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow, 119991 Russia*
[c] *Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow, 119911 Russia*
**e-mail: voloshin@ineos.ac.ru*

Received November 22, 2017

Abstract—An attempt to prepare a hybrid clusteroclathrochelate by nucleophilic substitution of iron(II) dichloroclathrochelate by substitution of its chlorine atoms with the $[Fe_2(\mu\text{-}S)_2(CO)_6]^{2-}$ cluster dianion as a nucleophilic agent generated *in situ* by the reduction of $Fe_2(\mu\text{-}S_2)(CO)_6$ with lithium triethylborohydride unexpectedly gave the macrobicyclic complex with two inherent thiol groups as the single clathrochelate product. Obviously, the initial iron-sulfide cluster underwent a complete decomposition during the reaction, thus acting only as a source of HS^- and S^{2-} anions. The composition and the structure of the complex obtained were confirmed by elemental analysis, MALDI-TOF mass spectrometry, ^1H and $^{13}C\{^1H\}$ NMR spectroscopy, and single crystal X-ray diffraction (CIF file CCDC 1585112). The encapsulated iron(II) ion is located at the centre of its FeN_6 coordination polyhedron possessing the geometry intermediate between a trigonal prism (the distortion angle $\varphi = 0°$) and a trigonal antiprism ($\varphi = 60°$) with $\varphi \approx 25°$; the height of this polyhedron is 2.33 Å. The presence of two thiol groups in the vicinal positions of the same ribbed moiety of the macrobicyclic molecule substantially affects the crystal packing of the molecular crystal containing clathrochelate dimers formed by four hydrogen bonds of two types (i.e., two S–H···O and two S–H···N bonds). The obtained cage complex and its deprotonated forms seem to be promising *cis*-disulfide bridging or chelating ligand synthons for the synthesis of new types of polynuclear complexes and coordination polymers as well.

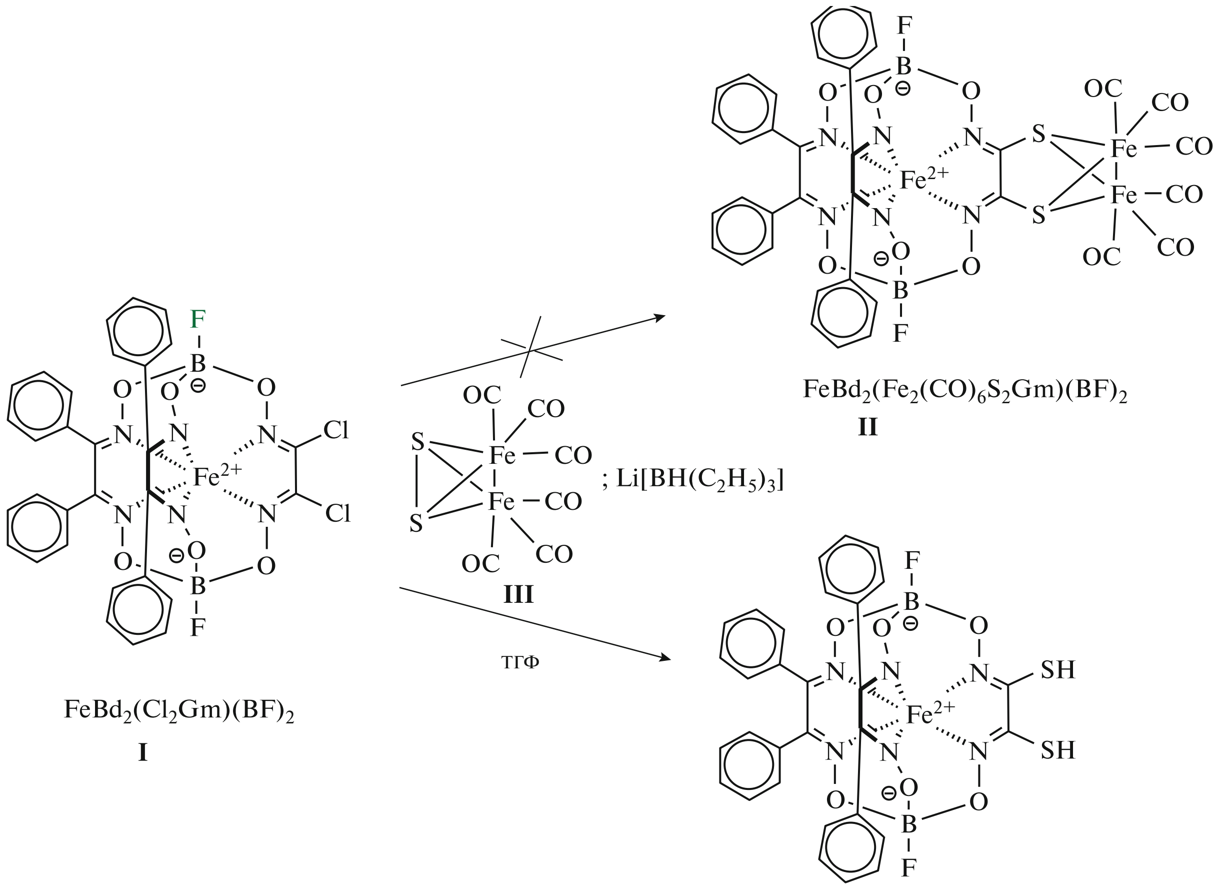
Keywords: clathrochelate, cluster, iron complexes, ligand reactivity, nucleophilic substitution

DOI: 10.1134/S1070328418080055

INTRODUCTION

The clathrochelate precursors with labile cross-linking groups and the reactive ribbed substituents have been widely used as the molecular platforms for the synthesis of new types of hybrid and multicenter systems, such as phthalocyanino- and porphyrino-clathrochelates [1–3], *closo*-borato- and carborano-clathrochelates [4–6], and calixarenoclathrochelates [7, 8]. Most of these compounds have been easily prepared in high yields using a high reactivity of the halo-clathrochelates towards their nucleophilic substitution.

In this study, we made an attempt to prepare the first representative of a new class of hybrid compounds, clusteroclathrochelates, the complex $FeBd_2(Fe_2(CO)_6S_2Gm)(BF)_2$ (**I**) (Scheme 1), by nucleophilic substitution of iron(II) dichloroclathrochelate as a macobiclycylic precursor with a deprotonated form of an iron-sulfide cluster [9] as a nucleophilic agent.



$FeBd_2(Cl_2Gm)(BF)_2$
I

$FeBd_2(Fe_2(CO)_6S_2Gm)(BF)_2$
II

$FeBd_2((HS)_2Gm)(BF)_2$
IV

Scheme 1.

EXPERIMENTAL

The reactions were carried out under argon using the standard Schlenk line; the reactants were charged in an argon box. The subsequent isolation, purification, and crystallization stages were performed in air. The dichloroclathrochelate precursor $FeBd_2(Cl_2Gm)(BF)_2$ **(II)**, where Bd^{2-} and Cl_2Gm^{2-} are the α-benzyldioxime and dichloroglyoxime dianions, respectively) were prepared as described [10]. The $Fe_2(\mu\text{-}S_2)(CO)_6$ cluster **(III)** (1) was synthesized using a known procedure [9]. The solvents were dried and degassed by refluxing and distillation under argon using standard procedures [11].

The ^1H and $^{13}C\{^1H\}$ NMR spectra were measured on a Bruker Avance 400 spectrometer operating at 400.13 MHz for ^1H and 100.61 MHz for ^{13}C. The chemical shifts were referred to the residual $CHDCl_2$ signals in the CD_2Cl_2 solvent (5.34 ppm) for the ^1H NMR spectra and to CD_2Cl_2 signals (53.8 ppm) for the ^{13}C NMR spectra.

Elemental analysis for C, H, and N was carried out on a Carlo Erba 1106 instrument at the Laboratory of Microanalysis of the Nesmeyanov Institute of Organoelement Compounds.

MALDI-TOF mass spectra in the negative and positive ranges were measured on a Bruker Autoflex II (Bruker Daltonics) MALDI-TOF-MS mass spectrometer in a reflecto-mol mode. The ionization was carried out by an UV laser at 337 nm. The sample was placed on a nickel plate and 2,5-dihydroxybenzoic acid was used as the matrix. The accuracy of measurements was 0.1%.

Synthesis of $FeBd_2((HS)_2Gm)(BF)_2$ (IV). The cluster $Fe_2(\mu\text{-}S_2)(CO)_6$ (0.046 g, 0.13 mmol) was dissolved in THF (15 mL), and a 1 M solution of $Li[BH(C_2H_5)_3]$ in THF (0.27 mL) was added dropwise at –75°C. The reaction mixture turned a dark-green, thus indicating a formation of the $[Fe_2(\mu\text{-}S)_2(CO)_6]^{2-}$ dianion. Then a suspension of $FeBd_2(Cl_2Gm)(BF)_2$ (0.100 g, 0.13 mmol) in THF (20 mL) was slowly added to the reaction mixture using a Teflon tube. The reaction mixture acquired a dark-claret color; it was heated to room temperature and then evaporated *in vacuo* to dryness. After thorough washing of the solid residue with hexane, thus removing the unreacted $Fe_2(\mu\text{-}S_2)(CO)_6$ cluster and the formed compound $Fe_3(CO)_9S_2$, the product was isolated by multiple extraction with diethyl ether. The extract was evaporated to dryness and dried *in vacuo*; its purity was controlled by TLC on a Silufol plate. The yield of **IV** was 0.033 (34%).

For $C_{30}H_{22}N_{26}O_6B_2F_2S_2Fe$

Anal. calcd., %	C, 48.56	H, 2.99	N, 11.32
Found, %	C, 48.69	H, 2.87	N, 11.10

MS (MALDI-TOF), *m/z*: 742 $[M]^{+\bullet}$. ^1H NMR (CD_2Cl_2, δ, ppm): 0.75 (s., 2H, SH), 7.25 (m, 20H, Ph). $^{13}C\{^1H\}$ NMR (CD_2Cl_2; δ, ppm): 127.41, 128.10, 129.84 (all s, Ph), 129.87 (s, SC=N), 156.99 (s, PhC=N).

The red needle single crystals of $\mathbf{IV} \cdot 0.5C_8H_{18}$ suitable for X-ray diffraction were obtained by slow evaporation of a clathrochelate solution in a benzene–isooctane 1 : 1 mixture.

X-ray diffraction. The crystals of $IV \cdot 0.5C_8H_{18}$ ($M = 799.24$) are monoclinic; at 100.0(2) K, $a = 13.8046(17)$ Å, $b = 17.488(2)$ Å, $c = 22.265(3)$ Å, $\beta = 133.582(3)°$, $V = 3893.8(8)$ Å^3, space group $P2_1/c$, $Z = 4$, ρ(calcd.) = 1.363 g/cm^3, $\mu = 0.554$ mm^{-1}. The experimental set of 40 664 reflections was collected on a Bruker APEX II diffractometer equipped with a CCD array detector using emission of the molybdenum anode ($\lambda = 0.71073$ Å) and graphite monochromator. The absorption corrections were applied empirically using the SADABS program [12]. The structure was solved by the direct method. All non-hydrogen atoms were located in difference electron density maps and refined on F^2_{hkl} in the anisotropic approximation using the SHELXL-14 program package [13]. The hydrogen atoms were located geometrically and refined in the isotropic approximation in the rigid body model, with $U_{iso}(H) = 1.5U_{eq}(X_i)$ for the methyl and thiol groups and $1.2U_{eq}(X_i)$ for all other atoms, where $U_{eq}(X)$ are the equivalent thermal parameters of atoms bearing this hydrogen atom. The final R-factors were $R_1 = 0.068$ (for 6355 measured reflections with $I > 2\sigma(I)$), $wR_2 = 0.168$ (for 10 937 unique reflections), GOOF = 1.00.

The atom coordinates, thermal parameters, and the whole list of reflections are deposited with the Cambridge Crystallographic Data Centre (no. 1585112; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

We suggested that the reaction of the dichloroclathrochelate $FeBd_2(Cl_2Gm)(BF)_2$ (**II**) with the cluster dianion $[Fe_2(\mu\text{-}S)_2(CO)_6]^{2-}$, generated *in situ* by the reduction of $Fe_2(\mu\text{-}S_2)(CO)_6$ (**III**) with lithium triethylborohydride, could give the hybrid clusteroclathrochelate **I** as a result of nucleophilic substitution of two chlorine atoms of the macrobicyclic precursor by a cluster fragment. However, in a course of the reaction, the cluster fragment underwent a destruction and, hence, it served only as a source of HS^- and S^{2-} ions. Consequently, the macrobicyclic complex $FeBd_2((HS)_2Gm)(BF)_2$ (**IV**) with two thiol groups inherently bonded to a macrobicyclic framework was isolated from the reaction mixture as the only clathrochelate product of this reaction. The dry residue resulting from an evaporation of the reaction mixture was found also to contain the noticeable amounts of carbonyl sulfide clusters $Fe_2(\mu\text{-}S_2)(CO)_6$ and $Fe_3(\mu_3\text{-}S)_2(CO)_9$; the latter is the major product of a transformation of $Fe_2(\mu\text{-}S_2)(CO)_6$. After elimination of these clusters by extracting of the solid residue with hexane, the above-mentioned clathrochelate product **IV** was isolated using the procedure described in the Experimental part.

The composition and the structure of the obtained complex were confirmed using elemental analysis, MALDI-TOF mass spectrometry, ^1H and $^{13}C\{^1H\}$ NMR spectroscopy, and by the single crystal X-ray diffraction.

The molecular structure of the complex **IV** is shown in Fig. 1; the main geometric parameters of this complex as well as those for the fluoroboron-capped monoribbed functionalized alkyl and allyl sulfide iron(II) clathrochelates with known X-ray diffraction structures. As can be seen from Table 1, even the bulky *tert*-butyl sulfide substituents in a vicinal position of the ribbed chelating group of the clathrochelate molecule do not affect substantially the geometric parameters of the macrobicyclic framework. In all of these iron(II) cage complexes, like in the molecule $FeBd_2((HS)_2Gm)(BF)_2$, the encapsulated iron(II) ion is located at the center of the FeN_6-coordination polyhedron possessing the geometry intermediate between a trigonal prism (TP, distortion angle $\varphi = 0°$) and a trigonal antiprism (TAP; $\varphi = 60°$). The φ angle in all X-ray characterized alkyl-sulfide iron(II) clathrochelates is close to 25°, while the heights of the TP–TAP coordination polyhedra slightly vary in the range 2.31–2.34 Å [17, 18]. Other geometric parameters of the clathrochelate framework are also similar for all of the above cage complexes.

However, the presence of thiol groups in a vicinal position of the ribbed substituent in **IV** substantially affected its crystal packing, because the hydrogen atoms of these groups are the efficient hydrogen bond donors. Indeed, the single crystal X-ray diffraction of

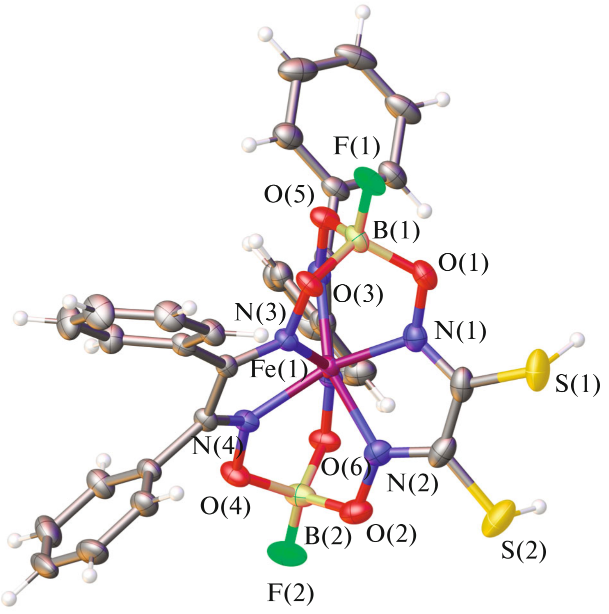


Fig. 1. Molecular structure of the clathrochelate $FeBd_2((HS)_2Gm)(BF)_2$ shown in thermal ellipsoids ($p = 50\%$).

IV · $0.5C_8H_{18}$ revealed the presence of clathrochelate dimers shown in Fig. 2. These dimers are formed by four hydrogen bonds of two types, two S–H···O and two S–H···N bonds. The corresponding r_i(S···O) and r_i(S···N) distances are 3.459(1) and 3.884(1) Å. In this crystal, the above clathrochelate dimers are coplanar with each other, while their molecular B···Fe···B C_3 pseudoaxes are collinear with the crystallographic *c* axis. The cavities between these clathrochelate dimers are filled by disordered solvent isooctane molecules (Fig. 3).

Thus, a cage complex with the inherent HS-groups was prepared and characterized for the first time. It is noteworthy that our earlier attempts to obtain this complex by using nucleophilic substitution of dichloroclathrochelate precursor with H_2S and its derivatives as nucleophilic agents were unsuccessful. The obtained cage complex and its deprotonated forms seem to be promising *cis*-disulfide chelating or bridging ligand synthons for the synthesis of new types of polynuclear complexes and coordination polymers as well.

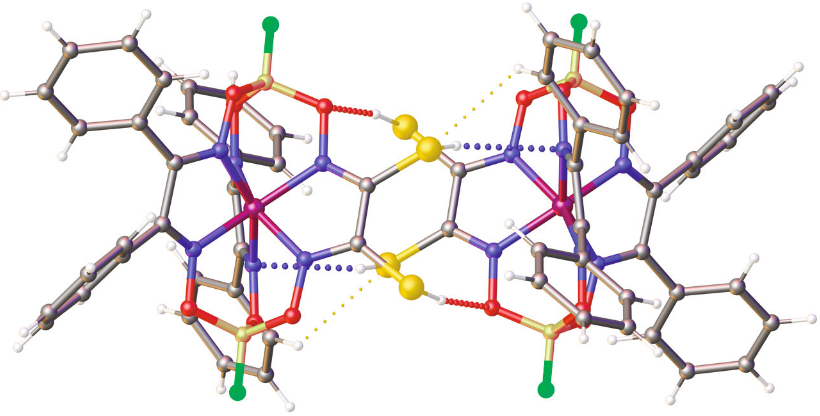


Fig. 2. Formation of the clathrochelate dimer $[FeBd_2((HS)_2Gm)(BF)_2]_2$ via the S–H···O and S–H···N hydrogen bonding (depicted with dashed line).

Table 1. Main geometric parameters of the fluoroboron-capped monoribbed functionalized disulfide iron(II) clathrochelates

Parameter	$FeBd_2((HS)_2Gm)(BF)_2$	$FeBd_2((CH_3S)_2Gm)(BF)_2$* [10]	$FeBd_2((CH_2{=}CH{-}CH_2S)_2Gm)(BF)_2$** [14]	$FeBd_2((n\text{-}C_4H_9S)_2Gm)(BF)_2$ [15]	$FeBd_2((tert\text{-}C_4H_9S)_2Gm)(BF)_2$* [16]
Fe–N, Å	1.897(3)–1.922(3) average, 1.911	1.898(5)–1.910(8) average, 1.903	1.902–1.919	1.900(3)–1.922(3) average, 1.911	1.905(2)–1.920(2) average, 1.913
B–O, Å	1.474(1)–1.495(2) average, 1.488	1.468(9)–1.491(9) average, 1.479	1.472–1.497	1.468(5)–1.502(5) average, 1.488	1.486(4)–1.498(4) average, 1.491
N–O, Å	1.350(2)–1.373(2) average, 1.366	1.365(8)–1.380(8) average, 1.373	1.361–1.377	1.357(4)–1.379(4) average, 1.368	1.370(2)–1.378(2) average, 1.373
C=N, Å	1.296(1)–1.309(1) average, 1.304	1.283(8)–1.321(8) average, 1.308	1.303–1.324	1.301(6)–1.317(5) average, 1.309	1.314(3)–1.318(3) average, 1.316
C–C, Å	1.437(1)–1.457(2) average, 1.450	1.42(1)–1.46(1) average, 1.433	1.450–1.467	1.429(7)–1.465(5) average, 1.446	1.457(3)–1.460(4) average, 1.458
B–F, Å	1.350(2)–1.354(2) average, 1.352	1.382(8)	1.355–1.366	1.351(5)–1.352(5) average, 1.552	1.355(4)
C–S, Å	1.694(4)–1.699(4)	1.748(9)	1.744–1.754	1.715(4)–1.716(4)	1.759(3)
N=C–C=N, deg	8.30(2)–9.57(1) average, 8.8	3.9(8)–6.7(7) average, 4.8	0.0–12.7	7.4(6)–9.5(6) average, 8.1	5.4(4)–13.3(4) average, 8.0
φ, deg	25.0	25.8	23.8–24.6	24.8	25.5
α, deg	78.6	78.6	78.2	78.4	78.8
h, Å	2.33	2.31	2.33–2.34	2.33	2.32

* Symmetrically independent moiety comprises only a half of the molecule. ** Data for three solvatomorphs of these complex are given.

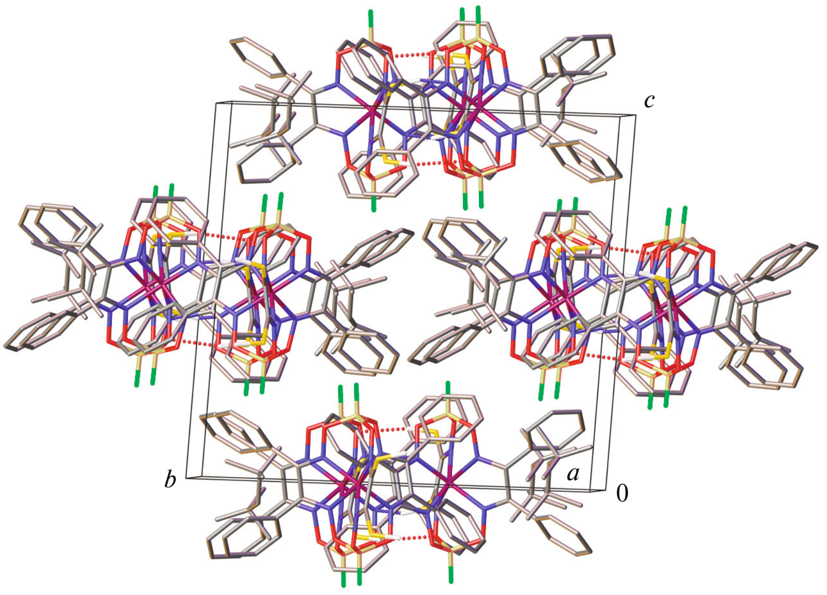


Fig. 3. Fragment of the crystal packing of $FeBd_2((HS)_2Gm)(BF)_2 \cdot 0.5C_8H_{18}$ (view along the crystallographic axis *a*). The hydrogen atoms which are not involved in the strong hydrogen bonding are not shown.

ACKNOWLEDGMENTS

This study was supported by the Russian Foundation for Basic Research (grant nos. 15-03-07414 and 16-03-00408).

REFERENCES

1. Voloshin, Y.Z., Varzatskii, O.A., Korobko, S.V., et al., *Inorg. Chem.*, 2005, vol. 44, p. 822.
2. Voloshin, Y.Z., Varzatskii, O.A., Tomilova, L.G., et al., *Polyhedron*, 2007, vol. 26, p. 2733.
3. Dudkin, S.V., Erickson, N.R., Vologzhanina, A.V., et al., *Inorg. Chem.*, 2016, vol. 55, p. 11867.
4. Voloshin, Y.Z., Varzatskii, O.A., Zhizhin, K.Yu., et al., *Rus. Chem. Bull., Intern. Ed.*, 2006, vol. 55, p. 22.
5. Kuznetsov, N.T., Belaya, I.G., Dolganov, A.V., et al., *Rus. Chem. Bull., Intern. Ed.*, 2011, vol. 60, p. 2518.
6. Svidlov, S.V., Varzatskii, O.A., Potapova, T.V., et al., *Inorg. Chem. Commun.*, 2014, vol. 43, p. 142.
7. Solovieva, S.E., Rovnova, T.A., Latipov, S.K., et al., *Phosphorus, Sulfur, and Silicon*, 2013, vol. 188, p. 503.
8. Solovieva, S.E., Tyuftin, A.A., Muravev, A.A., et al., *Polyhedron*, 2013, vol. 50, p. 90.
9. Seyferth, D., Henderson, R.S., and Song, L., *Organometallics*, 1982, vol. 1, p. 125.
10. Voloshin, Y.Z., Zavodnik, V.E., Varzatskii, O.A., et al., *Dalton Trans.*, 2002, p. 1193.
11. Gordon, A. and Ford, R., *The Chemist's Companion*, New York-London: Wiley, 1972.
12. Sheldrick, G.M., *SADABS. Program for Empirical X-ray Absorption Correction*, Bruker-Nonius, 1990–2004.
13. Sheldrick, G.M., *Acta Crystalogr., Sect. C: Struct. Chem.*, 2015, vol. 71, p. 3.
14. Voloshin, Y.Z., Varzatskii, O.A., Starikova, Z.A., et al., *Rus. Chem. Bull., Intern. Ed.*, 2004, vol. 53, p. 1496.
15. Voloshin, Y.Z., Varzatskii, O.A., Kochubey, D.I., et al., *Inorg. Chim. Acta*, 2009, vol. 362, p. 149.
16. Petrov, P.A., Virovets, A.V., Plyusnin, P.E., et al., *Russ. J. Inorg. Chem.*, 2014, vol. 59, no. 10, p. 1162. doi 10.7868/S0044457X14100134
17. Voloshin, Y.Z., Kostromina, N.A., and Krämer, R., *Clathrochelates: Synthesis, Structure and Properties*, Elsevier, 2002.
18. Voloshin, Y., Belaya, I., and Krämer, R., *Cage Metal Complexes Clathrochelates Revisited*, Springer, 2017.

Translated by Z. Svitanko