Clathrochelates Макрогетероциклы **Paper**
Клатрохелаты http://mhc-isuct.ru **Статья**

DOI: 10.6060/mhc224374v

Preparation of a Hybrid Ceramic-Based Material with Immobilized Dicarboxyl-Terminated Ruthenium(II) Clathrochelate and Its Catalytic Activity in Methane Oxidative Conversion

A. S. Chuprin,[a] A. V. Vologzhanina,[a] A. S. Loktev,[b−d] M. G. Bugaenko,[a]
Y. Z. Voloshin,[a−c@] V. M. Buznik,[b,c] and A. G. Dedov[b−d]

[a]*Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 119334 Moscow, Russia*
[b]*Gubkin Russian State University of Oil and Gas (National Research University), 119991 Moscow, Russia*
[c]*Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences, 119991 Moscow, Russia*
[d]*Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, 119991 Moscow, Russia*
[@]*Corresponding author E-mail: voloshin@igic.ras.ru, voloshin@ineos.ac.ru*

New ruthenium(II) clathrochelate with terminal polar and H^+-acidic carboxyl groups, designed for its effective immobilization on a surface of the highly porous silicate fibrous material TZMK, was obtained using the template condensation of cyclohexanedione-1,2-dioxime (nioxime) and 4-carboxyphenylboronic acid on the ruthenium(II) ion as a matrix; the solvatocomplex $[Ru(CH_3CN)_3(COD)Cl](BF_4)$ was used as a source of Ru^{2+} cations. Thus obtained ruthenium(II) clathrochelate was characterized using elemental analysis, MALDI-TOF mass, UV-vis, ^1H and $^{13}C\{^1H\}$ NMR spectra, and by the single crystal X-ray diffraction experiment as well. The hybrid TZMK-based catalytic material, prepared by its immobilization on a surface of this ceramic support, was tested as a catalyst of dry reforming of methane. At the rate of a feeding of the initial reagents (CH_4:CO_2 =1) equal to 12.7 $g^{-1}\cdot L$ per h, their conversions at 900 °C fall in the ranges 7–8 and 11–13 %, respectively, while the yields of H_2 and CO were from 2.2 to 2.5% and 4.4 to 4.6 %, respectively. The CO performance of this ruthenium-containing hybrid system reaches approximately 560 $mL\cdot g^{-1}$ (cat) per h, thus corresponding to 4.3 mol/g-atom of Ru per h. Decrease in the rate of an initial reagents feeding up to 6.4 $mol\cdot L^{-1}$ per h caused an increase in the conversions of CH_4 and CO_2 up to 14 – 15 and 26 – 28 %, respectively, with a simultaneous increase in the yields of H_2 and CO up to 5.3 – 6.3 and 11 – 12 %, respectively. In the latter case, the CO performance reaches 724 $mL\cdot g^{-1}$(cat) per h (5.4 mol/g-atom of Ru per h).

Keywords: Macrocyclic compounds, cage complexes, clathrochelates, ceramic materials, hybrid materials, catalytic materials, ruthenium catalysts, methane oxidative conversion, dry reforming of methane, syngas production.

Получение гибридного керамического материала с иммобилизованным клатрохелатом рутения(II), содержащим терминальные карбоксильные группы, и его каталитическая активность в реакциях окислительной конверсии метана

А. С. Чуприн,[a] А. В. Вологжанина,[a] А. С. Локтев,[b−d] М. Г. Бугаенко,[a]
Я. З. Волошин,[a−c@] В. М. Бузник,[b,c] А. Г. Дедов[b−d]

[a]*Институт элементоорганических соединений им. А.Н. Несмеянова РАН, 119334 Москва, Россия*
[b]*РГУ нефти и газа (НИУ) им. И.М. Губкина, 119991 Москва, Россия*
[c]*Институт общей и неорганической химии им. Н.С. Курнакова РАН, 119991 Москва, Россия*
[d]*Институт нефтехимического синтеза им. А.В. Топчиева РАН, 119991 Москва, Россия*
[@]*E-mail: voloshin@igic.ras.ru, voloshin@ineos.ac.ru*

Новый клатрохелат рутения(II) с терминальными полярными протоногенными карбоксильными группами, предназначенными для его эффективной иммобилизации на поверхности высокопористого силикатного волокнистого материала ТЗМК, был получен темплатной конденсацией циклогександион-1,2-диоксима (ниоксима) и 4-карбоксифенилборной кислоты на ионе рутения(II) как матрице; в качестве источника катионов Ru^{2+} использовали сольватокомплекс $[Ru(CH_3CN)_3(COD)Cl](BF_4)$. Полученный клатрохелат рутения(II) был охарактеризован с использованием данных элементного анализа, MALDI-TOF масс-, ЭСП, ^1H и $^{13}C\{^1H\}$

ЯМР спектров, а также методом монокристального РСА. Гибридный каталитический материал на основе высокопористого керамического материала ТЗМК, полученный иммобилизацией на его поверхность вышеупомянутого клеточного комплекса рутения(II), был испытан в качестве катализатора углекислотной конверсии метана. При скорости подачи исходных реагентов ($CH_4/CO_2 = 1$) равной 12,7 $л{\cdot}г^{-1}$ в час, их конверсия при 900 °С находилась в пределах 7 – 8 и 11 – 13 %, соответственно, а выходы H_2 и CO составили от 2,2 до 2,5 % и от 4,4 до 4,6 %, соответственно. Каталитическая эффективность этой гибридной рутенийсодержащей системы относительно CO достигала 560 $мл{\cdot}г^{-1}$ в час, что соответствует 4.3 моль/г-ат Ru *в час. При уменьшении скорости подачи исходных газов до 6,4 $л{\cdot}г^{-1}$ в час конверсия CH_4 и CO_2 увеличивалась до 14 – 15 % и 26 – 28%, соответственно, с одновременным увеличением выходов H_2 и CO до 5.3 – 6.3 % и 11 – 12 %, соответственно. В последнем случае каталитическая эффективность системы относительно CO достигала 724 $мл{\cdot}г^{-1}$ в час, что соответствует 5.4 моль/г-ат* Ru *в час.*

Ключевые слова: Макроциклические соединения, клеточные комплексы, клатрохелаты, керамические материалы, гибридные материалы, каталитические материалы, рутениевые катализаторы, окислительная конверсия метана, углекислотная конверсия метана, получение синтез-газа.

Introduction

Two prospective methods of hydrogen production, the reactions of partial oxidation and dry reforming of methane (POM and DRM, respectively), include the intermediate step of syngas formation (Scheme 1). These methods are considered as a promising environmental-friendly alternative to the industrial process of producing syngas and hydrogen by steam reforming.[1–4] On the other hand, in the case of DRM process, carbon dioxide that is known[5] to be one of the most unwanted and abundant pollutants, plays the role of an oxidant. This causes its consumption in the course of the latter industrial oxidative process. So, DRM reaction looks a more promising process than POM due to an effective utilization both of CO_2 and of methane, as the most common greenhouse gases, and an opportunity to use biogas, as their renewable raw source. Thus, a search for the suitable catalysts of DRM process seems to be undoubtedly important task of heterogeneous catalysis and modern materials chemistry as well.

Partial oxidation of methane (POM)

$$CH_4 + {}^1/_2\,O_2 \longrightarrow CO + 2\,H_2\ \text{(SG)}$$

$$1\ :\ 2$$

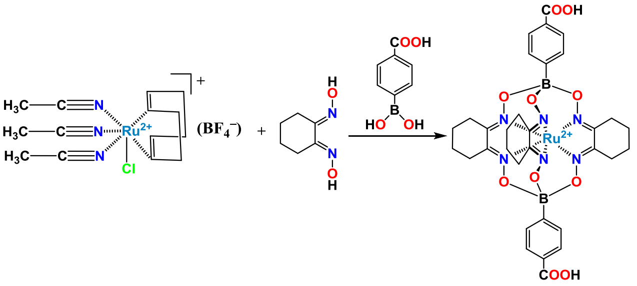
Dry reforming of methane (DRM)

$$CH_4 + CO_2 \rightleftharpoons 2CO + 2\,H_2\ \text{(SG)}$$

$$1\ :\ 1$$

Scheme 1. Prospective processes of a methane conversion to synthesis gas.

Chemical drawing of the ruthenium(II) clathrochelate $RuNx_3(B4\text{-}C_6H_4COOH)_2$ with terminal protonogenic and polar carboxyl groups that was designed for its efficient adsorption on a surface of ceramic materials as the substrates is shown in Scheme 2; an immobilization of this cage complex on such surface *via* their supramolecular interactions can be illustrated by Figure 1. Highly porous (up to 95 %) silica-based ceramic material TZMK* seem to be a promising substrate for efficient immobilization and strong binding of a given ruthenium-containing clathrochelate precursor, the molecule of which is decorated with terminal carboxyl groups. Indeed, the aforementioned material combines a low density and a high specific surface with the presence of opened and interrelated pores sized up to hundreds of μm; it also possesses a high thermal stability (up to 1700 °C). The advantages of their hybrid organo-inorganic derivative, as a promising catalytic material, include (*i*) an opportunity to substantially decrease a consumption of a given platinum group metal by forming of the adsorbed monolayer of a designed ruthenium clathrochelate, thus giving the so-called “single atom (single site) catalyst”, and (*ii*) a high adsorptive capacity of TZMK, thus allowing to substantially increase a surface concentration of the ruthenium-containing catalytically active metallocentres. Therefore, this hybrid material can be considered as prospective highly efficient catalytic system (in particular, that for hydrogen and syngas production using the ruthenium-catalyzed DRM reaction).



$RuNx_3(B4\text{-}C_6H_4COOH)_2$

Scheme 2. Template synthesis of a given ruthenium(II) clathrochelate decorated with terminal carboxyl groups.

Earlier, we have tested two ruthenium(II) clathrochelates (**1** and **2**) shown in Chart 1, the designed molecules of which contain terminal polar groups in their ribbed and apical fragments, respectively, as the precatalysts for obtaining of the corresponding TZMK-based catalytic materials for the oxidative methane conversion (OMC) processes.[6–8] In this paper, we describe the synthesis of a new dicarboxyl-terminated ruthenium(II) clathrochelate, its sin-

---

* TZMK is a brand name of one of the materials, which have been designed and obtained at the All-Russian Scientific Research Institute of Aviation Materials.[9–11]

gle crystal X-ray structure and the catalytic activity of its hybrid ceramic-based derivative in DRM reaction.

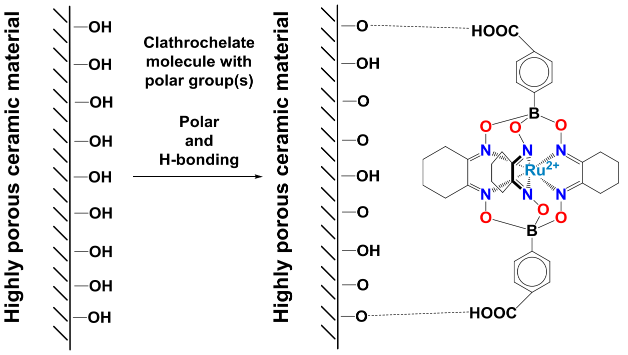
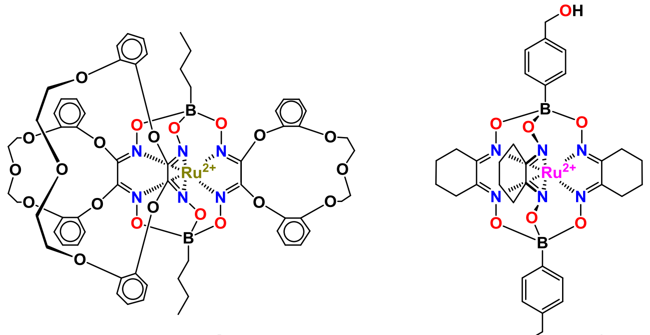


Figure 1. Immobilization of the dicarboxyl-terminated ruthenium(II) clathrochelate on a surface of ceramic material.



1

2

Chart 1.

Experimental

Materials and Methods

The reagents used, 4-carboxyphenylboronic acid (Acros), 1,2-cyclohexane-dion-1,2 dioxime (nioxime, H_2Nx, Sigma-Aldrich®), sorbents and organic solvents were obtained commercially (SAF). The initial solvatocomplex $[Ru(CH_3CN)_3(COD)Cl](BF_4)$ was prepared as described elsewhere.[12]

Analytical data (C, H, N contents) were obtained with a Carlo Erba model 1106 microanalyzer.

MALDI-TOF mass spectra of the obtained ruthenium(II) complex were recorded with and without the matrix using a MALDI-TOF-MS BrukerAutoflex II (Bruker Daltonics) mass spectrometer in a reflecto-mol mode. The ionization was induced by an UV-laser with the wavelength of 337 nm. The samples were applied to a nickel plate, 2,5-dihydroxybenzoic acid was used as the matrix. The accuracy of measurements was 0.1%.

^1H and $^{13}C\{^1H\}$ NMR spectra were recorded from its pyridine-d_5 solution with a Varian Inova 400 spectrometer. The ^1H and $^{13}C\{^1H\}$ NMR measurements were done using the residual signals of the deuterated solvent.

UV-Vis spectrum in DMSO was recorded in the range 250 – 800 nm with a Agilent Cary 60 spectrophotometer. The individual Gaussian components of this spectrum were calculated using the Fityk program.[13]

Synthesis of the $RuNx_3(B4\text{-}C_6H_4COOH)_2$ complex

Solvatocomplex $[Ru(CH_3CN)_3(COD)Cl](BF_4)$ (0.069 g, 0.15 mmol) and nioxime (0.062 g, 0.44 mmol) were dissolved/suspended in chloroform – methanol 1:1 mixture (10 mL) under argon. This mixture was refluxed for 6 h and then 4-carboxyphenylboronic acid (0.034 g, 0.02 mmol) was added. The reaction mixture was stirred for 20 h at 80 ºC, the obtained yellowish-brown precipitate was filtered off, washed with ethanol (15 mL), chloroform (5 mL), diethyl ether (5 mL), hexane (5 mL) and dried *in vacuo*. Yield: 0.016 g (20%). Anal. Calcd. for $C_{32}H_{34}B_2RuN_6O_{10}$: C, 48.94; H, 4.36; N, 10.70. Found (%): C, 49.13; H, 4.28; N, 10.92. MS (MALDI-TOF): *m/z*: 785.15 $[M]^{+\bullet}$. ^1H NMR (pyridine-d_5) δ_H ppm: 1.38 {br m, 12H, β-CH_2 (Nx)}, 2.74 {br.t, 12H, α-CH_2(Nx)}, 5.20 (br.s, 2H, COOH + H_2O), 8.58 (d, 4H, *ortho*-Ph), 8.77 (d, 4H, *meta*-Ph). $^{13}C\{^1H\}$ NMR (pyridine-d_5) δ ppm: 21.81 {s, β-CH_2(Nx)}, 25.95 {s, α-CH_2(Nx)}, 129.73 (s, *meta*-Ph), 132.54 (s, *para*-Ph), 133.20 (s, *ortho*-Ph), 149.09 (s, C=N), 170.12 (s, COOH). UV-Vis ν cm^{-1} ($\varepsilon\times10^{-3}$, mol^{-1} L cm^{-1}): 38632 (32), 36258 (12), 32841 (1.7), 28071 (4.7), 25757 (12), 23864 (8.5), 22149 (6.4).

X-Ray crystallography

Single crystals of the complex $RuNx_3(B4\text{-}C_6H_4COOH)_2\cdot 8Py\text{-}d_5$, suitable for the XRD experiment, have been formed in the NMR tube containing its pyridine-d_5 solution. The orange-plate crystal of $C_{72}H_{34}D_{40}B_2N_{14}O_{10}Ru$ (M = 1458.38) with the dimensions of 0.35×0.33×0.07 mm is triclinic; at 120.0(2) К a = 10.9771(5), b =14.4757(7), c = 22.1935(11) Å, α =88.427(2), β = 81.091(2), g = 77.068(2)°, V = 3395.6(3) Å^3, space group $P\text{-}1$, Z = 2, $D_{calcd.}$ = 1.387 g·cm^{-3}, μ = 0.302 mm^{-1}. The intensities of 45905 reflections were collected on a Bruker Apex II diffractometer using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). Data collection was performed using an Oxford CryoJet (Oxford Cryosystems). Data integration was carried out using the SADABS software. The structure was solved by the direct method and refined by full-matrix least squares method against F^2 of all data using the SHELXL-2014[14] and OLEX2[15] programs. Non-hydrogen atoms were found on the difference Fourier maps and refined with anisotropic displacement parameters, except those for the disordered carbon and nitrogen atoms of two deuteropyridine solvate molecules and carbon atoms of two ribbed six-membered α-dioximate fragments. The positions of hydrogen atoms were calculated and included in refinement in an isotropic approximation by the riding model with the $U_{iso}(H)$ = $1.2U_{eq}(X)$, where $U_{eq}(X)$ are equivalent thermal parameters of the parent atoms. Refinement converged to R_1 = 0.056 (for 13806 observed reflections), wR_2 = 0.127 and GOF = 1.01 (for 13806 independent reflections; R_{int} = 0.057). Crystallographic information file is available from the Cambridge Crystallographic Data Center upon request (*https://ccdc.cam.ac.uk/structure*, deposition number is 2165876).

Immobilization of the ruthenium(II) clathrochelate on ceramic material

The hybrid catalytic system was obtained by immobilization of a new macrobicyclic complex $RuNx_3(B4\text{-}C_6H_4COOH)_2$ on a surface of the silicate fibrous material TZMK, as a solid support. This ruthenium(II) clathrochelate is intensively colored in the near UV–visible range (380 – 460 nm). It was immobilized of a surface of TZMK by its dissolution in pyridine, followed by evaporation the obtained solution, easily penetrated into a bulk pores of this ceramic material. Thus obtained hybrid system was dried in air atmosphere. This procedure allowed an effective immobilization of the ruthenium(II) clathrochelate $RuNx_3(B4\text{-}C_6H_4COOH)_2$ with terminal polar and H-acidic groups on this support due to its adsorption on a whole (inner and outer) surface of TZMK. Then, the obtained material was washed with a small amount of pyridine; a removal of the clathrochelate complex $RuNx_3(B4\text{-}C_6H_4COOH)_2$ that has been not immobilized on its surface during such adsorption stage was visually controlled.

Testing of the hybrid TZMK – $RuNx_3(B4\text{-}C_6H_4COOH)_2$ catalytic material

Catalytic activity of this hybrid system in DRM reaction was studied in a heated flow quartz reactor with a thermocouple pocket; the end of thermocouple was placed into a middle of the catalyst bed. Size of the catalytic particles with a weight of 0.253 g was 0.5 – 1 mm; the content of a given ruthenium clathrochelate was 5 %, and a ruthenium content was 0.6 %. The reactor was fed with a CH_4/CO_2 mixture (with a purity of 99.9 %), which has been not diluted with an inert gas, at a component CH_4/CO_2 ratio of equal to 1. The feed space velocity of this gas mixture was 12.7 and 6.4 $L \cdot g^{-1}$ per hour. The catalyst was heated for 1 h to 900 °C in a hydrogen stream and reduced for 1 h. Then, a gas mixture was fed into the reactor. Analysis of the gaseous products was performed using a gas chromatograph GALS-311 equipped with a thermal conductivity detector (Lumeks-marketing); the carrier gas was helium (40 mL/min at an outlet of the columns). Gaseous products were injected into a given chromatograph using a gas-tight syringe. 2m-in-length and 3mm-in-inner diameter steel gas chromatography column; packed with NaX zeolite adsorbent (fraction 0.2–0.25 mm) was used to obtain the contents of H_2, O_2, N_2, CH_4 and CO at room temperature. Steel gas chromatography column with a packed with the Porapak-Q adsorbent with a grain size of 80 – 100 mesh was used to obtain a sum of O_2 and CO, and the contents of CH_4, CO_2, C_2H_4 and C_2H_6 at 80 °C as well. These gas chromatograms were operated and processed using the Ekokhrome hardware–software program an complex for automating chromatographic analysis, which is registered in the State Register of Measuring Instruments of the Russian Federation (no. 16616-03).

Results and Discussion

For preparation of the target ruthenium(II) cage complex with terminal carboxyl groups in its apical aromatic substituents at the capping boron atom, the template condensation on ruthenium(II) ion, as a matrix, of nioxime and 4-carboxyphenylboronic acid in chloroform–methanol 1:1 mixture, as a solvent, at 80 °C was performed; the solvatocomplex $[Ru(CH_3CN)_3(COD)Cl](BF_4)$ was used as a source of Ru^{2+} ions (Scheme 2). We observed a change in the coloration of the reaction mixture from a dark brown (on an initial stage) to a dark yellow (after an addition of 4-carboxyphenylboronic acid as a cross-linking Lewis-acidic agent), and a precipitation of the ruthenium(II) clathrochelate $RuNx_3(B4\text{-}C_6H_4COOH)_2$ as well. We used an excess of nioxime as an α-dioximate ligand synthon (its 4.5 eq instead of 3 eq), trying to increase the yield of the target cage ruthenium(II) complex. It was characterized using elemental analysis, MALDI-TOF mass, UV-Vis, ^1H and $^{13}C\{^1H\}$ NMR spectra, and by the single crystal X-ray diffraction experiment as well.

MALDI-TOF mass spectrum of the obtained new ruthenium(II) clathrochelate shown in Figure S1 (see *Supporting Information* section) contains the peak of the corresponding molecular ion in positive range. This peak possesses a characteristic isotopic distribution, which is in good agreement with that theoretically calculated.

The number and positions of the signals in the solution ^1H and $^{13}C\{^1H\}$ NMR spectra of the ruthenium(II) macrobicyclic complex $RuNx_3(B4\text{-}C_6H_4COOH)_2$ (in particular, protons of its apical aromatic substituents and those of methylene groups in its α-dioximate ligand synthons), together with the ratios of their integral intensities in the ^1H NMR spectrum, confirmed the composition and the symmetry its cage molecule. The number of lines in the $^{13}C\{^1H\}$ NMR spectrum of $RuNx_3(B4\text{-}C_6H_4COOH)_2$ suggests an equivalence of the chelate ribbed α-dioximate fragments of an encapsulating macrobicyclic ligand.

Solution UV-Vis spectrum of $RuNx_3(B4\text{-}C_6H_4COOH)_2$ (SI, Figure S4), contains in its visible and UV ranges two intensive asymmetric bands at 24630 and 38461 cm^{-1}, respectively, assigned to the metal-to-ligand charge transfer (MLCT) Ru$d \rightarrow L\pi^*$ and to the intraligand $\pi - \pi^*$ transitions as in its quasiaromatic framework as in the apical aromatic substituents at this framework. Substantial (approximately 60 nm) short-wavelength shift of this complex MLCT band in the spectrum of $RuNx_3(B4\text{-}C_6H_4COOH)_2$ as compared with that of its iron(II)-containing analog is observed. Deconvolution of the spectrum of $RuNx_3(B4\text{-}C_6H_4COOH)_2$ into its Gaussian bands in its visible range; two of them a less intensive than the gave third one, whereas maxima of the ligand-localized UV bands. The aforementioned ruthenium(II)- and iron(II)-encapsulating cage analogs of the same macrobicyclic ligands, are almost equal. In passing from iron(II) to ruthenium(II) complexes, the position of bands of high intensity in the UV region, stipulated by the π–π^* transitions in dioximate fragments, changed insignificantly.

General view of the clathrochelate molecule $RuNx_3(B4\text{-}C_6H_4COOH)_2$ that was obtained using the single crystal XRD experiment is shown in Figure 2; main geometrical parameters of its cage framework, as well as those for its iron(II)-containing analog[16] are listed in Table 1. Their characteristic B–O, N–O and C=N bond lengths are similar to each other. Only that of the chelate C–C bonds in ribbed α-dioximate fragments of the molecule $RuNx_3(B4\text{-}C_6H_4COOH)_2$ are shorter than those for its iron(II)-containing analog. On the other hand, the larger physical ionic (Schannon) radius of the low-spin Ru^{2+} ion, as compared with Fe^{2+} cation (the corresponding radii are more than 0.82 Å and equal to 0.75 Å, respectively,[17]) causes a rotational-translational expansion of a given rigid cage framework along its molecular B…Ru…B C_3-pseudoaxis. As a result, the average Ru–N distance (1.980 Å) in the $RuNx_3(B4\text{-}C_6H_4COOH)_2$ molecule is greater, as compared with the average Fe–N distance (1.920 Å) in the $FeNx_3(B4\text{-}C_6H_4COOH)_2$ molecule.[16] Nevertheless, both these encapsulated low-spin ions are situated in the centres of their $M^{II}N_6$-coordination polyhedra, possessing the geometry intermediate between a trigonal prism (the distortion angle φ = 0°) and a trigonal antiprism (φ = 60°). The corresponding values φ are equal to 11.7 and 18.9°, and the heights h of these polyhedra are equal to 2.45 and to 2.37 Å, respectively. The crystal $RuNx_3(B4\text{-}C_6H_4COOH)_2 \cdot 8Py\text{-}d_5$ contains the solvate deuteropyridine molecules. Therefore, in the contrast to a majority of the crystals of dicarboxylic acids, which have been earlier studied using the XRD method, and that of the dicarboxyl-terminated complex $Fe((CH_3OOCCH_2S)_2Gm)_3(B\text{-}3\text{-}C_6H_4COOH)_2$,[18] the terminal carboxyl groups of the $RuNx_3(B4\text{-}C_6H_4COOH)_2$ molecule are included in a hydrogen bonding with the corresponding solvent molecules, instead of a bifurcate intermolecular bonding between two carboxyl groups of neighboring molecules of the former compounds. The clathrochelate $RuNx_3(B4\text{-}C_6H_4COOH)_2$ molecules are included in their crystal in the intermolecular O–H…N interactions with two solvate deuteropyridine molecules {*r*(O…N) falls in the range 2.633(3) – 2.639(3) Å, the corresponding O…H…N angle varies from 172.8(2) to 175.8(2)°}. Other solvent molecules are included only in the weak C–H…N and H…H contacts.

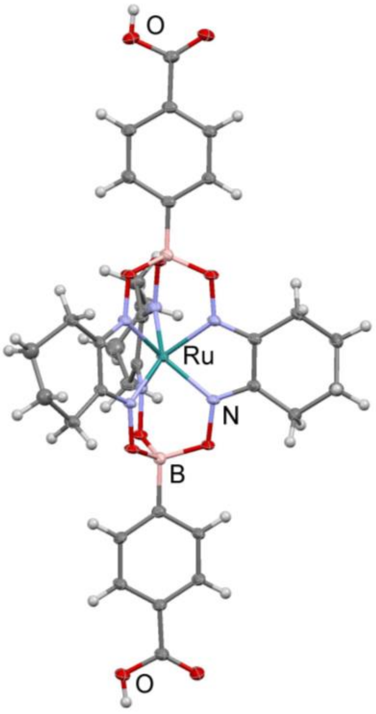


Figure 2. General view of the molecule $RuNx_3(B4\text{-}C_6H_4COOH)_2$.

Table 1. Main geometrical parameters of the quasiaromatic cage frameworks of the obtained dicarboxyl-terminated ruthenium(II) tris-nioximate clathrochelate and its iron(II)-containing analog.

Parameter	$RuNx_3(B4\text{-}C_6H_4COOH)_2$	$FeNx_3(B4\text{-}C_6H_4COOH)_2$[16]
M – N (Å)	1.970(2) – 1.989(2)	1.906(4) – 1.933(4)
B – O (Å)	1.496(3) – 1.521(4) *av.* 1.508	1.488(7) – 1.504(7) *av.* 1.499
N – O (Å)	1.375(3) – 1.386(3) *av.* 1.381	1.377(5) – 1.389(5) *av.* 1.382
C=N (Å)	1.311(3) – 1.322(3) *av.* 1.318	1.295(6) – 1.310(6) *av.* 1.302
C – C (Å)	1.434(3) – 1.440(3) *av.* 1.437	1.445(7) – 1.461(7) *av.* 1.455
N=C–C=N (°)	4.1(3) – 6.2(3) *av.* 5.4	5.8(6) – 6.1(6) *av.* 6.4
φ (°)	11.7	18.9
α (°)	77.0	78.2
h (Å)	2.45	2.37

Hybrid TZMK-based catalytic material with immobilized ruthenium(II) clathrochelate $RuNx_3(B4\text{-}C_6H_4COOH)_2$, obtained as described in the Experimental section, was tested as a catalyst of DRM process; main obtained results are complied in Table 2 and shown in Figure 3. At the feed rate of the initial reagents (CH_4 and CO_2) equal to 12.7 g^{-1} L per hour, their conversions at 900 °C fall in the ranges 7–8 and 11–13 %, respectively, while the yields of H_2 and CO were from 2.2 to 2.5 % and 4.4 to 4.6 %, respectively. So, the stoichiometric ratio of these products is in the range 0.5 – 0.6 (therefore, the CO/H_2 ratio in a given products mixture is close to 2). The CO performance of this ruthenium-containing hybrid system reaches approximately 560 mL g^{-1} (cat) per hour, thus corresponding to 4.3 mol/g-atom of Ru per hour. Decrease in the rate of a feeding reagents up to 6.4 mol L^{-1} per hour caused an increase in the conversions of methane and carbon dioxide up to 14 – 15 and 26 – 28 %, respectively, with a simultaneous increase in the yields of molecular hydrogen and carbon monoxide up to 5.3 – 6.3 and 11–12%, respectively. On the other hand, the same CO/H_2 ratio (2:1) persists. The CO performance in this case at 900 °C reaches 724 mL g^{-1}(cat) per h (5.4 mol/g-atom of Ru per hour). Therefore, a catalytic activity of the hybrid material under study is substantially affected by the rate of the feeding reagents.

Conclusions

Thus, we performed the molecular design of a new ruthenium(II) clathrochelate for its efficient immobilization on a surface of ceramic materials and prepared the dicarboxyl-terminated cage complex decorated with polar and H-acidic functionalizing groups in its apical aromatic substituents at a diboron-capped macrobicyclic framework.

$$CH_4 + CO_2 \rightleftharpoons CO + H_2 \text{ (syngas)}$$

t = 900°C

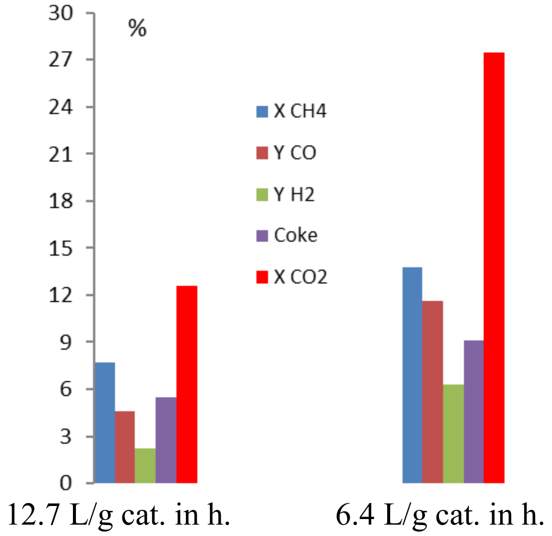


Figure 3. Influence of the rate of reagents feeding on the results of DRM reaction (900 °C) catalyzes by a given ruthenium-containing TZMK-based catalytic material, obtained by immobilization of the complex $RuNx_3(B4\text{-}C_6H_4COOH)_2$.

Table 2. Products of the DRM process in the presence of the clathrochelate RuNx$_3$(B4-C$_6$H$_4$COOH)$_2$-containing TZMK-based catalytic material *versus* time (min).

CH_4/CO_2	W, $L\cdot g^{-1}\cdot h^{-1}$	T, °C	X CH_4, %	X CO_2, %	Y, mol. %		Coke Y, %	CO productivity, $mL\cdot g^{-1}\cdot h^{-1}$
					H_2	CO		
1.02	12.7	900	7.7	12.6	2.2	4.6	5.5	581
1.02	12.7	900	7	11	2.5	4.4	4.5	558
1.01	6.4	900	14.7	25.8	5.3	11	9.3	686
0.99	6.4	900	13.8	27.5	6.3	11.6	9.1	724

Hybrid catalytic material, obtained by its immobilization on TZMK, as a heat-resistance highly porous silicate fibrous support, was tested in DRM process at various reaction conditions. As follows from the data of these catalytic experiments, this cage complex is still not such effective precatalyst of DRM reaction, as compared with its synthetically much less available triribbed-functionalized analog **1**, the molecule of which is functionalized by a number of the polar oxygen-containing groups. We suggest that the catalytic activity of hybrid materials of this type may be increased by using of the clathrochelate precatalysts, the cage 3D-molecules of which are decorated with a number of the terminal carboxyl groups, thus allowing to increase their surface concentration on a surface of the ceramic supports (substrates), and, therefore, that of the catalytically active single-atom metallocenters.

Acknowledgements. The synthesis of a given ruthenium cage complex was supported by the Russian Foundation for Basic Research (grant 18-29-23007). Catalytic experiments were supported by the Russian Science Foundation (grant 20-13-00138). The optical measurements was performed in a framework of the IGIC RAS state assignment in the field of basic scientific research. NMR and XRD experiments were performed with a financial support from Ministry of Science and Higher Education of the Russian Federation using an equipment of Center for molecular composition studies of INEOS RAS.

References

1. Holmen A. *Catal. Today* **2009**, *142*, 2. DOI: 10.1016/j.cattod.2009.01.004.
2. Enger B.C., Lodeng R., Holmen A. *Appl. Catal.* A, **2008**, *346*, 1. DOI: 10.1016/j.apcata.2008.05.018.
3. York A.P.E., Xiao T., Creen M.L.H., Claridge J.B. *Catal. Rev.* **2007**, *49*, 511. DOI: 10.1080/01614940701583315.
4. Moiseev I.I., Loktev A.S., Shlyakhtin O.A., Mazo G.N., Dedov A.G. *Petroleum Chem.* **2019**, *59*, S1–S20. DOI: 10.1134/S0965544119130115.
5. Esswein A.J., Nocera D.G. *Chem. Rev.* **2007**, *107*, 4022. DOI: 10.1021/cr050193e.
6. Dedov A.G., Loktev A.S., Voloshin Y.Z., Buznik V.M., Sandzhieva D.A. RF Patent No. 2719176, **2020** [Дедов А.Г., Локтев А.С., Волошин Я.З., Бузник В.М., Санджиева Д.А. *Способ получения синтез-газа*, Патент РФ № 2719176, 17.04.2020].
7. Dedov A.G., Voloshin Y.Z., Belov A.S., Loktev A.S., Bespalov A.S., Buznik V.M. *Mendeleev Commun.* **2019**, *29*, 669. DOI: 10.1016/j.mencom.2019.11.022.
8. Voloshin Y.Z., Buznik V.M., Dedov A.G. *Pure Appl. Chem.* **2020**, *92*, 1159. DOI: 10.1515/pac-2019-1105.
9. Belunova L.V., Gribkov V.N., Chernyak A.I., Mizyurina G.T., Mordovin O.A., Mukhanova E.E., Patent US 5.569.423, **1996**.
10. Schetanov B.V., Ivakhnenko Yu.A., Babashov V.G. *Russ. J. Gen. Chem.* **2011**, *81*, 978. DOI: 10.1134/S1070363211050288.
11. Armour for 'Buran'. Materials and Technologies of VIAM for the International Space Station 'Energy–Buran' (Kablov E.N., Ed.), Moscow: Nauka i Zhizn', **2013** [Доспехи для Бурана. Материалы и технологии ВИАМ для МКС "Энергия-Буран" (Каблов Е.Н., ред.), М.: Наука и жизнь, **2013**].
12. Chuprin A.S., Belova S.A., Bugaenko M.G., Vologzhanina A.V., Loktev A.S., Voloshin Ya.Z., Buznik V.M., Dedov A.G. *Kin. Cat.* **2022**, *63*, 108. DOI: 10.1134/S0023158422010025.
13. Wojdyr M. *J. Appl. Cryst.* **2010**, *43*, 1126. DOI: 10.1107/S0021889810030499.
14. Sheldrick G.M. *Acta Cryst.* **2015**, *C71*, 3. DOI: 10.1107/S2053229614024218.
15. Dolomanov O.V., Bourhis L.J., Gildea R.J., Howard J.A.K., Puschmann H. *J. Appl. Cryst.* **2009**, *42*, 339. DOI: 10.1107/S0021889808042726
16. Marmier M., Wise M.D., Holstein J.J., Pattison P., Schenk K., Solari E., Scopelliti R., Severin K. *Inorg. Chem.* **2016**, *55*, 4006. DOI: 10.1021/acs.inorgchem.6b00276.
17. Shannon R. D. *Acta Cryst.* **1976**, *A32*, 751. DOI: 10.1107/S0567739476001551.
18. Limarev I.P., Zelinskii G.E., Vologzhanina A.V., Zubavichus Y.V., Voloshin Y.Z. *Macroheterocycles* **2021**, *14*, 229. DOI: 10.6060/mhc210843z.

Received 15.04.2022
Accepted 22.04.2022