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Unexpected macrocyclization of ruthenium(II) bis-α-benzyldioximate: synthesis and structure of the BF$_2$-cross-linked cyclooctadiene complex

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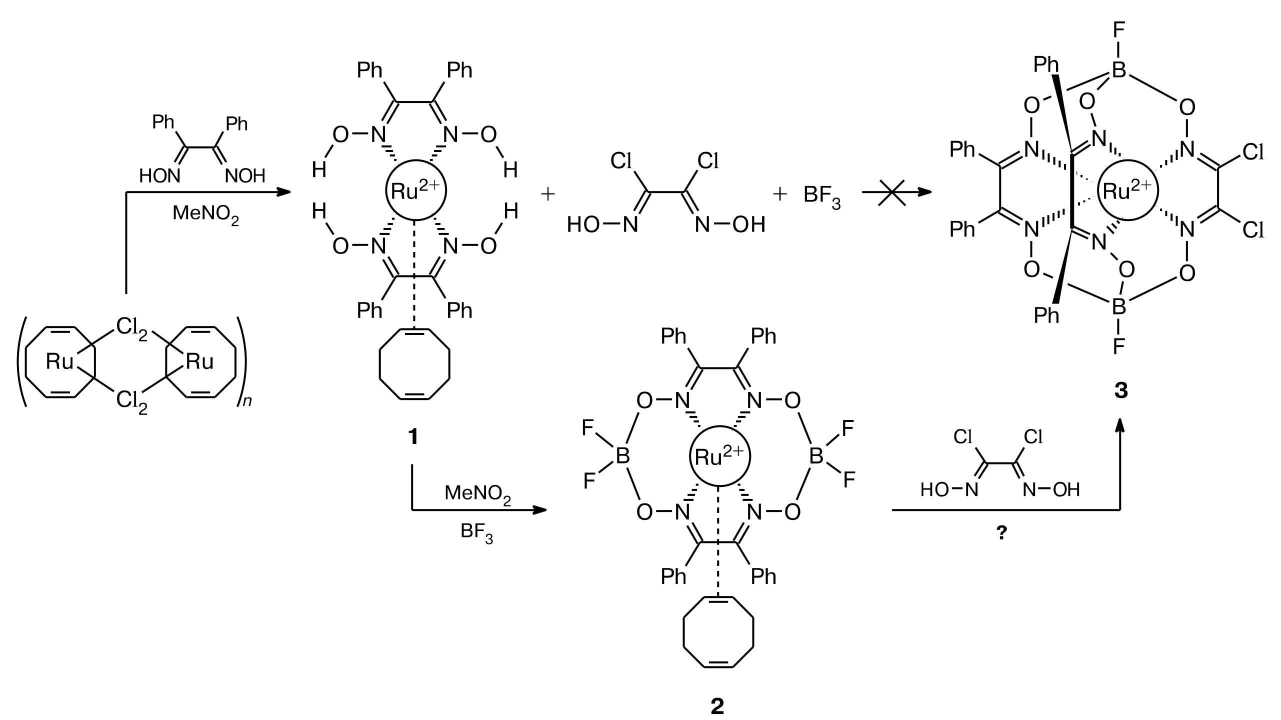
Unique photophysical and photochemical properties of ruthenium(II) diiminates are under intense study, because they can be used in molecular photoelectronic devices, as well as electron and energy carriers, photosensitizers in catalytic systems (in particular, hydrogen production from water), luminescent probes in biochemistry, *etc.* Therefore, ruthenium(II) polyiminates of different structure, symmetry, and functionality have been synthesized. Previously,[1] we obtained triribbed-functionalized ruthenium(II) tris-dioximate clathrochelates starting from their hexachloride precursors. In most practical instances, it is enough to modify only one of the three dioximate fragments.[2] We synthesized both the dichloride α-benzyldioximate precursor and monoribbed-functionalized iron(II) clathrochelates.[2,3]

We intended to prepare the dichloride precursor of the monoribbed-functionalized ruthenium(II) clathrochelates (Scheme 1, complex **3**) using the earlier[2] proposed approach to the synthesis of compounds of this type by the macrocyclization of the ruthenium(II) bis-dioximate complex (**1**) with a Lewis acid followed by the condensation of the macrocyclic compound **2** with dichloroglyoxime.

The reflux of dark brown ruthenium bis-α-benzyldioximate **1**, obtained by heating of the polymer [RuCl$_2$(COD)]$_n$ (COD is 1,5-cyclooctadiene) and α-benzyldioxime in a molar ratio of 1 : 2 in nitromethane, with boron trifluoride etherate and dichloroglyoxime in nitromethane produced a bright yellow solid. The product was separated from the initial complex and the reaction by-products by flash chromatography on silica gel

Scheme 1



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Silasorb SPH 300 (Chemapol; eluent: methylene dichloride). The elute obtained was evaporated to dryness, and the solid residue was washed with hexane.

Found (%): C, 54.97; H, 4.05; N, 7.20. $C_{36}H_{32}B_2F_4N_4O_4Ru$. Calculated (%): C, 55.20; H, 4.12; N, 7.15. ^1H NMR (CD_2Cl_2), δ: 2.62 (m, 8 H, CH_2); 2.95 (m, 2 H, =CH); 3.17 (m, 2 H, =CH); 7.05—7.27 (m, 20 H, Ph). $^{13}C\{^1H\}$ NMR (CD_2Cl_2), δ: 30.2, 31.0 (both s, CH_2); 104.2, 109.0 (both s, =CH); 127.6, 129.7, 130.1 (all s, Ph); 161.0, 170.4 (both s, C=N). IR (KBr), ν/cm^{-1}: 1537 (C=N); 881, 992, 1104 (N—O), 1178, 1223 (B—O) + (B—F). UV-VIS spectrum (CH_2Cl_2), λ_{max}/nm ($\varepsilon \cdot 10^{-3}$/L mol^{-1} cm^{-1}): 258 (15), 294 (5.2), 381 (5.8), 432 (12).

Slow evaporation a methylene dichloride—hexane solution of **2** gave single crystals suitable for X-ray diffraction analysis.

The crystals of compound **2** ($C_{36}H_{32}B_2F_4N_4O_4Ru \cdot 0.5\ CH_2Cl_2$) at 120 K are monoclinic, space group $C2/c$, $a = 23.929(6)$ Å, $b = 21.654(5)$ Å, $c = 13.701(3)$ Å, $\beta = 105.855(5)°$, $V = 6829(3)$ Å^3, $Z = 8$, $M = 825.81$, $d_{calc} = 1.606$ g cm^{-3}, and $\mu = 0.608$ mm^{-1}. Intensities of 16 172 reflections were measured on a SMART 1000 CCD diffractometer (λ(Mo-Kα) = 0.71073 Å, graphite monochromator, $2\theta < 50°$) at 120 K. The initial set of intensities measured was processed by the SAINT Plus [4] and SADABS [5] programs, applying an absorption correction ($T_{min} = 0.722$, $T_{max} = 0.968$). The structure was solved by direct method and refined by the full-matrix least-squares method in the anisotropic approximation for non-hydrogen atoms against F^2_{hkl}. The positions of the hydrogen atoms were calculated geometrically and refined using the riding model ($U_{iso}(H) = nU_{eq}(C)$, where $n = 1.2$). In refinement, 6064 independent reflections were used ($R_{int} = 0.1325$). The refinement convergence against all independent reflections was $wR_2 = 0.1409$, GOOF = 0.920 ($R_1 = 0.0633$ against 2934 reflections with $I > 2\sigma(I)$). All calculations were made using the SHELXTL-97 program package.[6]

Table 1. Main geometric parameters of molecule **2**

Parameter	Value
Bond	d/Å
Ru(1)—N(1)	2.003(6)
Ru(1)—N(2)	2.031(6)
Ru(1)—N(3)	2.021(5)
Ru(1)—N(4)	2.032(6)
Ru(1)—C(1)	2.257(7)
Ru(1)—C(2)	2.248(8)
Ru(1)—C(5)	2.262(7)
Ru(1)—C(6)	2.269(7)
O(1)—N(1)	1.387(7)
O(2)—N(2)	1.348(7)
O(3)—N(3)	1.353(7)
O(4)—N(4)	1.348(7)
Bond or interplanar angle	Angle/deg
N(1)—Ru(1)—N(2)	75.7(2)
N(3)—Ru(1)—N(4)	76.1(2)
N(3)—Ru(1)—N(2)	84.7(2)
N(1)—Ru(1)—N(4)	85.2(2)
Ru(1)—N(1)—C(9)—C(16)—N(2)/ Ph (C(10)—C(15))	49.2(3)
Ru(1)—N(1)—C(9)—C(16)—N(2)/ Ph (C(17)—C(22))	42.2(2)
Ru(1)—N(3)=C(23)—C(30)=N(4)/ Ph (C(24)—C(29))	54.4(3)
Ru(1)—N(3)=C(23)—C(30)=N(4)/ Ph (C(31)—C(36))	63.9(2)

In molecule **2** (Fig. 1), both the macrocyclic and one 1,5-cyclooctadiene ligands are coordinated to the ruthenium(II) ion. The η^4-coordinated COD ligand has a *twist-boat* conformation. The macrocyclic ligand is formed by two dioximate fragments "cross-linked" by the tetrahedral BF_2 bridges (bond angles at the boron atoms are

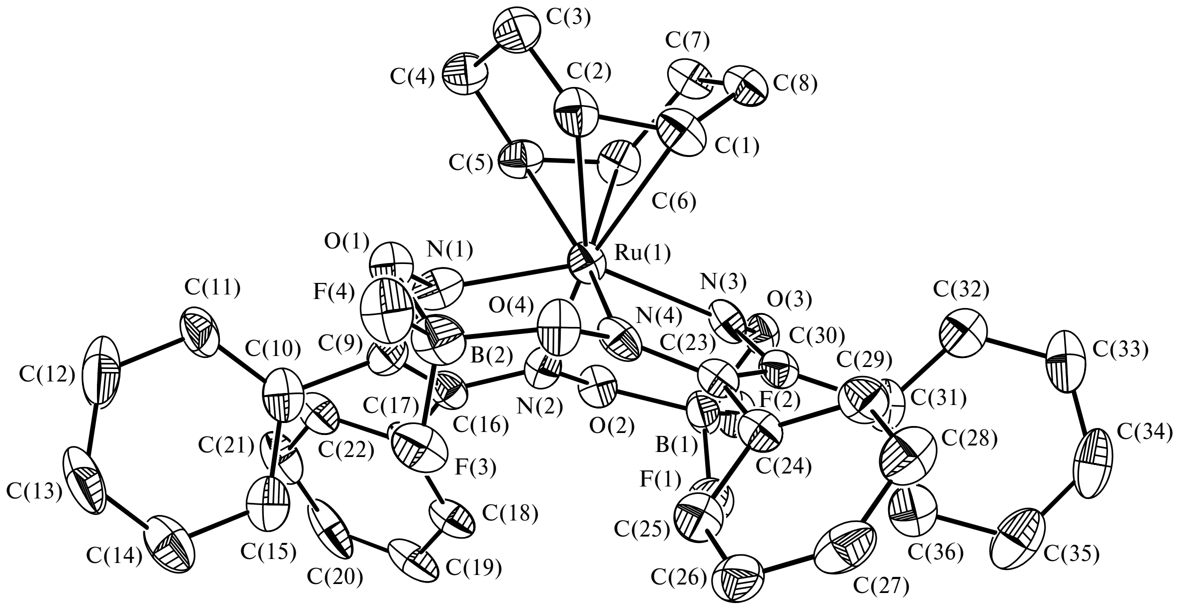

Fig. 1. General view of molecule **2**. The thermal ellipsoids are drawn at the 50% probability level.

from 104.3° to 114.8°). Two phenyl substituents in the chelating dioximate fragments are arranged as a "propeller" (Table 1). As a whole, the molecule has the symmetry pseudo-axis C_2. The N—Ru—N bite 2α angles in the chelate cycles are somewhat smaller than the angle in the N—Ru—N moieties, whose nitrogen atoms belong to different chelating fragments (see Table 1). A similar decrease was observed for the earlier studied iron and ruthenium(II) clathrochelate complexes, whose macrobicyclic ligands contain three dioximate fragments.[7,8] The Ru(1)—N(1) bond is shortened and the N(1)—O(1) bond is elongated compared to other bonds of these types, which can be due to both specific features of thermal vibrations (thermal ellipsoid of the N(1) atom is extended along the Ru(1)—N(1) bond) and the involvement of the O(1) atom in the O(1)...H(1S)—C(1S) hydrogen bond (the O...C and O...H distances are 3.327(8) and 2.26 Å, respectively; and the O...H—C angle is 165.5° assuming that the C—H distance is 1.08 Å). Molecules **2** in crystal form hydrogen-bonded dimers (Fig. 2, *a*) packed in stacks (Fig. 2, *b*). The latters are surrounded by the phenyl groups and directed along the crystallographic axis *c*. Channels containing solvate methylene dichloride molecules are formed along the same axis (Fig. 2, *b*, *c*). Inside the stacks we also can emphasize the C(4)—H(4a)...Cl(1S) contact $(2 - x; -y; 1 - z)$ (see Fig. 2, the C...Cl, H...Cl, and C—H distances are 3.296(8), 2.81, and 1.08 Å, respectively; and the C—H...Cl angle is 107°). We believe that this contact

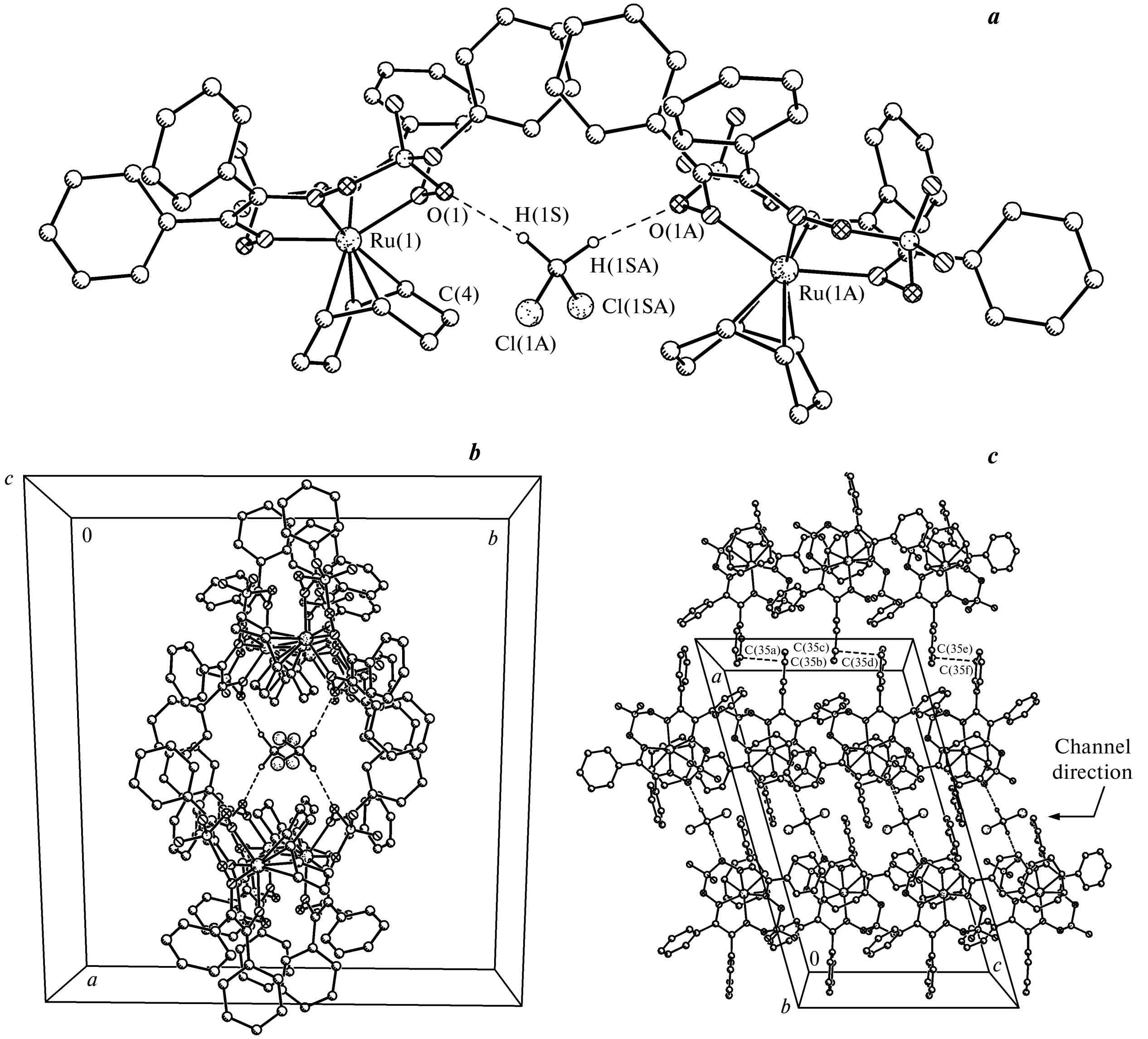

Fig. 2. Fragments of the crystal packing of complex **2**: (***a***) hydrogen-bonded dimer structure; (***b***) view along the *c* axis demonstrates the formation of channels containing solvate molecules; and (***c***) projection of the crystal packing on the *ac* plane (directions of the channels and π-stacking are shown).

cannot be considered as a hydrogen bond because of the long H—Cl distance and the small angle at the H(4a) atom. A shortened contact between the carbon atoms of one of the phenyl rings C(35)...C(35) ($1 - x$, y, $0.5 - z$) equal to 3.15(2) Å was found between the molecules of the adjacent piles. These rings are superimposed by the C(33)—C(34)—C(35) fragments, indicating the π-stacking between the corresponding aromatic substituents.

The ratio of integral intensities and the number of signals of aromatic protons of the dioxime fragments and signals of protons of the axial cyclooctadiene ligand in the ^{1}H NMR spectrum, as well as the number of signals in the ^{13}C{^{1}H} NMR spectrum, were in agreement with the supposed composition and symmetry of complex **2**.

The solution UV-VIS spectrum of complex **2** contains intense bands in the visible and near-UV regions (λ_{max} = 381 nm, $\varepsilon = 5.8 \cdot 10^3$ L mol^{-1} cm^{-1} and λ_{max} = 432 nm, $\varepsilon = 1.2 \cdot 10^4$ L mol^{-1} cm^{-1}), which were assigned to the metal-to-ligand charge transfer Ru$d \rightarrow$Lπ^*, while the bands in the far-UV region are caused by intraligand π,π^*-transitions.[7]

The obtained macrocyclic ruthenium(II) bis-dioximate can be used as starting material for the syntheses of mono- and dichloride precursors of mono- and difunctionalized ruthenium(II) clathrochelates by its condensation with mono- and dichlorodioximes under rigid conditions.

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References

1. Ya. Z. Voloshin, O. A. Varzatskii, T. E. Kron, V. K. Belsky, V. E. Zavodnik, N. G. Strizhakova, V. A. Nadtochenko, and V. A. Smirnov, *J. Chem. Soc., Dalton Trans.*, 2002, 1203.
2. Ya. Z. Voloshin, V. E. Zavodnik, O. A. Varzatskii, V. K. Belsky, A. V. Palchik, N. G. Strizhakova, I. I. Vorontsov, and M. Yu. Antipin, *J. Chem. Soc., Dalton Trans.*, 2002, 1193.
3. Ya. Z. Voloshin, V. E. Zavodnik, O. A. Varzatskii, V. K. Belsky, I. I. Vorontsov, and M. Yu. Antipin, *Inorg. Chim. Acta*, 2001, **321**, 116.
4. *SMART and SAINT*, *Release 5.0, Area Detector control and Integration Software, Bruker AXS, Analytical X-Ray Instruments*, Madison, Wisconsin, USA, 1998.
5. G. M. Sheldrick, *SADABS: A Program for Exploiting the Redundancy of Area-detector X-Ray Data*, University of Göttingen, Göttingen, Germany, 1999.
6. G. M. Sheldrick, *SHELXTL-97 Program for Solution and Refinement of Crystal Structure*, Bruker AXS Inc., Madison, WI-53719, USA, 1997.
7. Ya. Z. Voloshin, N. A. Kostromina, and R. Krämer, *Clathrochelates: Synthesis, Structure and Properties*, Elsevier, Amsterdam, 2002.
8. Ya. Z. Voloshin and M. Yu. Antipin, *Izv. Akad. Nauk, Ser. Khim.*, 2004, 2009 [*Russ. Chem. Bull., Int. Ed.*, 2004, **53**, 2097].

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