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Encapsulation of ruthenium(II) with macrobicyclic dioxime-functionalized ligands: on the way to new types of DNA-cleaving agents and probes

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The clathrochelate di- and tri-ribbed-functionalized ruthenium(II) tris-dioximates with alkylamine, thioaryl, thioalkyl, phenoxyl, and crown ether substituents in α-dioximate fragments have been synthesized starting from reactive hexachloride clathrochelate precursors, formed by cross-linking with phenyl-, *n*-butyl- and fluoro-boronic capping groups. The IR, UV-vis, ^{1}H, ^{13}C NMR and luminescent spectra as well as X-ray data for complexes obtained have been discussed. The redox characteristics (from cyclic voltammograms) for ruthenium(II) clathrochelates have been correlated with the electrochemical parameters of the corresponding iron(II) complexes and σ_{para} constants for functionalizing substituents.

Introduction

A keen recent interest in polyimine ruthenium(II) complexes and especially in tris-bipyridinates, phenanthrolinates and their analogs[1–19] has largely been evoked by the ample scope they offer as selective DNA-cleaving agents and probes in biochemistry.[20–24] Such ruthenium(II) complexes, as well as their photophysics, are of particular interest in creating devices for molecular electronics (*e.g.*, systems of the "light-switch" type) and in analytical detection of metal ions as well. In the majority of research performed, the chelating ligands have been initially functionalized, and this has permitted the obtention of ruthenium(II) complexes with improved chemical and physicochemical properties. It should be emphasized that through a highly conjugated aromatic system, both the medium (solvent and acidity) and functionalizing substituents influence the energy of the central metal ion d orbitals and ligand π,π*-orbitals.[5,6,13] An electronic effect of aliphatic and aromatic substituents in the dioximate fragments in the series of previously synthesized boron-containing ruthenium(II) clathrochelates is substantially lower.[25] In addition, such substituents exhibit low reactivity, and their modification involving variations in physicochemical parameters (and, consequently, in the corresponding characteristics of the clathrochelate itself) is rather complicated. We have managed to work out several procedures for the synthesis of ribbed-functionalized macrobicyclic iron(II) complexes (with substituents in the α-dioximate fragments) starting from the initially obtained reactive chloride clathrochelates.[26,27] The present study was undertaken first of all to offer convenient methods for the synthesis of halogenide clathrochelate ruthenium(II) precursors with allowance for a kinetic inertness of ruthenium in different oxidation states, and second to obtain ribbed-functionalized ruthenium(II) clathrochelates using the previously developed pathways for modification of precursors and to determine the geometrical and physicochemical characteristics of the complexes obtained.

Experimental

General information

The reagents used, $Ru(OH)Cl_3$, $SbCl_3$, CF_3COOH (TFA), C_6H_5SH, CH_3SH, $BF_3{\cdot}O(C_2H_5)_2$, *n*-butyl- and phenyl-boronic acids, organic bases and their salts, and organic solvents were obtained commercially (Fluka and Reachim). Bis[2-(*o*-oxyphenoxy)]diethyl ether was obtained as described in ref. 28. The dichloroglyoxime (denoted as H_2Cl_2Gm) was prepared by chlorination of glyoxime (H_2Gm) as described in ref. 29. $C_6H_5BCl(O^iC_4H_9)$ was obtained as described in ref. 30.

The $[(CH_3)_4N]_2[Ru(OH)Cl_5]$ salt was obtained from a solution of $Ru(OH)Cl_3$ in 10% hydrochloric acid with an excess of $(CH_3)_4NCl$. The precipitate was filtered and dried *in vacuo*. The sponge lead was prepared by reduction of a 5% $Pb(CH_3CO_2)_2$ solution in 5% aqueous acetic acid with zinc dust. The zinc dust was added to the stirring solution in several portions, and the reaction mixture was left overnight. The sponge metallic lead obtained was washed with water and then acetone, cooled with liquid nitrogen and pulverized. The gray powder was washed with acetone and dried *in vacuo*.

The analyses for the carbon, hydrogen, and nitrogen content were carried out with a Carlo Erba model 1106 microanalyzer.

The plasma desorption (PD) mass spectra were recorded in the positive spectral range on a time-of-flight biochemical mass spectrometer BC MS SELMI using an accelerating voltage of 20 kV. The ionization was induced by ^{252}Cf spontaneous decay fragments, and typically 20000 decay acts were registered. The samples (approximately 1–2 mg) were applied onto a gilded disk or onto a nitrocellulose layer.

The IR spectra of solid samples (KBr tablets) in the range 400–4000 cm^{-1} were recorded on a Specord M-80 spectrophotometer. The bands were assigned using the previous results. The UV-vis spectra of solutions in chloroform in the range of 230–800 nm were recorded on a Lambda 9

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Perkin-Elmer spectrophotometer. The individual Gauss components of these spectra were calculated using the SPECTRA program. The ^1H, ^{13}C, and ^{11}B NMR spectra of the solutions in $CDCl_3$ were recorded on an AC-200 Bruker FT-spectrometer.

Laser photolysis was carried out with the second harmonic of ruby (347 nm, 18 mJ, 15 ns) operated in the Q-switch mode. An Orial 450 W Xe lamp was used as the monitoring light source. The fluorescence was monitored with a Spex-2 photon counting luminescence spectrometer provided with an MX-2 correction unit. The laser photolysis and luminescence measurements in the liquid media (toluene and acetonitrile) were carried out under aerobic conditions. The luminescence spectra were also measured in a frozen toluene glass matrix at 77 K.

Cyclic voltammograms were recorded in dichloromethane under an argon atmosphere using a PI-50-1 potentiostat coupled with a B7-45 teraohmic potentiometer as a current–voltage convertor. The scan rate was varied from 5 to 10 mV s^{-1}, which is close to the steady-state conditions for ultramicroelectrodes.[31,32] Tetraethylammonium tetrafluoroborate (0.1 M) was used as a supporting electrolyte. A platinum microelectrode (100 μm in diameter, throughly polished and rinsed before measurements) was chosen as the working electrode and a platinum wire as the auxiliary electrode. A standard Ag/AgCl reference electrode was connected to the cell *via* a salt bridge. All potentials were referenced to the redox potential of the ferrocene (Fc^+/Fc) couple as an internal standard. This potential is at +0.565 V *vs.* Ag/AgCl reference electrode under the present experimental conditions.

Syntheses

$Ru(Cl_2Gm)_3(BF)_2$ (1). $[(CH_3)_4N]_2[Ru(OH)Cl_5]$ (2.35 g, 5 mmol) and sponge lead (1.5 g) were dissolved/suspended in dry nitromethane (25 ml) under argon, and H_2Cl_2Gm (3.14 g, 20 mmol) was added. The reaction mixture was heated to 60 °C, and a mixture of triethylamine (4.2 ml, 30 mmol) and freshly distilled $BF_3{\cdot}O(C_2H_5)_2$ (18 ml, 150 mmol) was added dropwise for 30 min. The reaction mixture was heated for 2 h at 60 °C, and an additional portion of sponge lead (1.5 g) was added. The reaction mixture was refluxed for 1 h with partial evaporation of solvent (≈10 ml), and an additional portion of H_2Cl_2Gm (1 g) was added. The reaction mixture was left overnight at room temperature and then evaporated to a small volume. The oil-like residue was diluted with a three-fold volume of methanol and filtered. The filtrate was precipitated with water, and the yellow solid was reprecipitated with chloroform–heptane (2 : 1) mixture. The product was washed with hexane and dried *in vacuo*. Yield: 1.75 g (54%). Anal. calc. for $C_6N_6O_6B_2Cl_6F_2Ru$: C, 11.51; N, 13.42; Cl, 34.04. Found: C, 11.56; N, 13.42; Cl, 34.16 %. MS PD: *m*/*z* 626 $(M)^{+\bullet}$. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 131.3 (s, ClC=N). ^{11}B NMR [$CDCl_3$, rel. to $NaB(C_6H_5)_4$]: δ 11.1 d ($J_{^{11}B-^{19}F}$ = 18 Hz). IR (cm^{-1}, KBr): 906, 947 ν(N–O), 1176, 1242 ν(B–O) + ν(B–F), 1506 ν(C=N). UV-Vis ($CHCl_3$): λ_{max} ($10^{-3}\varepsilon/mol^{-1}\ l\ cm^{-1}$) 255(8.6), 278(5.0), 349(5.2), 384(4.8), 417(19), 457(4.0) nm.

$Ru(Cl_2Gm)_3(B^nC_4H_9)_2$ (2). *Procedure I.* $[(CH_3)_4N]_2[Ru(OH)Cl_5]$ (0.84 g, 1.9 mmol), H_2Cl_2Gm (1.28 g, 8 mmol), *n*-butylboronic acid (0.41 g, 4 mmol), and sponge lead (1 g) were dissolved/suspended in TFA (15 ml) under argon. The reaction mixture was refluxed with stirring for 1 h with partial evaporation of solvent (≈8 ml), and then additional portions of TFA (10 ml), H_2Cl_2Gm (0.6 g), *n*-butylboronic acid (0.2 g) and sponge lead (0.4 g) were added. The reaction mixture was refluxed for 40 min with partial evaporation of solvent (≈2 ml) and precipitated with water. The precipitate was filtered, washed with water and then a small amount of methanol, and extracted with chloroform. The chloroform solution was filtered through a Silasorb SPH-300 layer (10 mm), evaporated to a small volume, and precipitated with hexane. The yellow solid was washed with a small amount of methanol and then hexane and dried *in vacuo*. Yield: 0.29 g (22%).

Procedure II. $Ru(OH)Cl_3$ (2.25 g, 10 mmol), freshly distilled $SbCl_3$ (11.5 g, 50 mmol), H_2Cl_2Gm (5.2 g, 33 mmol), and sponge lead (4.0 g, 2 mmol) were dissolved/suspended in dry nitromethane (50 ml) with stirring under argon. The stirring reaction mixture was heated to boiling, and a solution of $(^nC_4H_9BO)_3$ in chloroform was added dropwise [this solution was obtained by dehydration of a solution/suspension of *n*-butylboronic acid (2.6 g, 25 mmol) in chloroform (50 ml) for 6 h under argon in a flask equipped with a Soxhlet extractor containing 4 Å molecular sieves (15 g)]. The reaction mixture was refluxed for 3 h (the temperature of the bath was 110 °C) with partial evaporation of solvent (≈50 ml) and left overnight at room temperature. Then the reaction mixture was evaporated to a small volume and precipitated with a three-fold volume of methanol. The solid was filtered, washed with 5% aqueous HCl solution and then a small amount of methanol, and extracted with chloroform. The subsequent purification was as described in Procedure I. Yield: 2.2 g (31%). Anal. calc. for $C_{14}H_{18}N_6O_6B_2Cl_6Ru$: C, 23.94; H, 2.57; N, 11.97; Cl, 30.35. Found: C, 23.94; H, 2.54; N, 11.98; Cl, 30.30%. MS PD: *m*/*z* 702 $(M)^{+\bullet}$. ^1H NMR ($CDCl_3$): δ 0.97 (m, 10H, BCH_2 + CH_3), 1.49 (m, 8H, CH_2CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 14.1 (s, CH_3), 16.8 (br s, BCH_2), 25.7 (s, CH_2), 25.8 (s, CH_2), 129.1 (s, ClC=N). IR (cm^{-1}, KBr): 908, 936 ν(N–O), 1098 ν(B–O), 1493 ν(C=N). UV-vis ($CHCl_3$): λ_{max} ($10^{-3}\varepsilon/mol^{-1}\ l\ cm^{-1}$) 265(6.9), 291(3.0), 354(3.9), 385(5.1), 417(15), 455(4.5) nm.

$Ru(Cl_2Gm)_3(BC_6H_5)_2$ (3). *Procedure I.* This complex was synthesized by a similar method to **2** (Procedure II) except that $(C_6H_5BO)_3$, obtained from phenylboronic acid (3.05 g, 2.5 mmol), was used instead of $(^nC_4H_9BO)_3$. The reaction mixture after heating was left overnight and filtered. The solid was washed with water, 10% aqueous hydrochloric acid, methanol, diethyl ether and then a small amount of chloroform. The desired complex was extracted with benzene or chloroform in a Soxhlet extractor and precipitated with hexane. The yellow product was washed with hexane and dried *in vacuo*. Yield: 1.1 g (15%).

Procedure II. The complex $[RuPy_4Cl_2]$ (3.0 g, 6.2 mmol), $(C_6H_5BO)_3$, obtained as described in Procedure I from phenylboronic acid (1.60 g, 13 mmol), and H_2Cl_2Gm (2.98 g, 19 mmol) were dissolved/suspended in TFA (50 ml). The reaction mixture was refluxed for 10 h, left overnight, and diluted with methanol. The precipitate obtained was purified as described in Procedure I. Yield: 0.41 g (9%).

Procedure III. $[(CH_3)_4N]_2[Ru(OH)Cl_5]$ (1.68 g, 38 mmol), H_2Cl_2Gm (2.56 g, 16 mmol), and sponge lead (1.7 g, 8.0 mmol) were dissolved/suspended in dry nitromethane (50 ml) with stirring under argon. The reaction mixture was heated to boiling, and a solution of $C_6H_5BCl(O^iC_4H_9)$ (2.24 ml, 11.5 mmol) in chloroform (50 ml) was added dropwise. The reaction mixture was refluxed for 2 h, and an additional portion of H_2Cl_2Gm (1.28 g, 8.0 mmol) was added. The reaction mixture was then refluxed for 3 h with partial evaporation of solvent (≈30 ml) and diluted with a two-fold volume of methanol. The precipitate obtained was purified as described in Procedure I. Yield: 0.45 g (16%). Anal. calc. for $C_{18}H_{10}N_6O_6B_2Cl_2Ru$: C, 29.12; H, 1.35; N, 11.33; Cl, 28.72. Found: C, 29.06; H, 1.44; N, 11.23; Cl, 28.82%. MS PD: *m*/*z* 742 $(M)^{+\bullet}$. ^1H NMR ($CDCl_3$): δ 7.48 (m, 6H, Ph), 7.89 (m, 4H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 127.8 (s, Ph), 129.1 (s, Ph), 130.2 (s, ClC=N), 131.8 (s, Ph). IR (cm^{-1}, KBr): 888, 975 ν(N–O), 1229 ν(B–O), 1501 ν(C=N). UV-Vis ($CHCl_3$): λ_{max} ($10^{-3}\varepsilon/mol^{-1}\ l\ cm^{-1}$) 265(15), 350(4.5), 388(5.1), 420(13), 457(4.3) nm.

Preparation of $Ru[(CH_3S)_2Gm]_3(BF)_2$ (4). Methanethiol (0.12 ml, 2.4 mmol) was dissolved in dry THF (20 ml) and a 0.843 M solution of $^tC_5H_{11}ONa$ (1.9 ml), obtained from metallic sodium with *tert*-amylalcohol in THF, was added under argon. The reaction mixture was cooled to −30 °C, and the complex $Ru(Cl_2Gm)_3(BF)_2$ (0.12 g, 0.19 mmol) was added in 10 portions over 12 h. The reaction mixture was stirred for 1 h at −30 °C and left overnight at 0 °C. Then K_2CO_3 (0.5 g) and CH_3I (0.5 ml) were added to the reaction mixture, and it was stirred for 2 h at room temperature. The reaction mixture was filtered, and the filtrate was evaporated to dryness. The oil-like residue was dissolved in warm methanol (≈15 ml) and precipitated with a small amount of water at 0 °C. The solid was dissolved in chloroform, and chloroform solution was filtered through the Silasorb SPH-300 layer (20 mm), evaporated to a small volume, and precipitated with hexane. The precipitate was washed with hexane and dried *in vacuo*. Yield: 0.081 g (61%). Anal. calc. for $C_{12}H_{18}N_6O_6S_6B_2F_2Ru$: C, 20.72; H, 2.59; N, 12.09; S, 27.68. Found: C, 20.69; H, 2.57; N, 12.12; S, 27.58%. MS PD: *m*/*z* 695 $(M)^{+\bullet}$. ^1H NMR ($CDCl_3$): δ 2.76 (s, 18H, SCH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 17.4 (s, SCH_3), 147.2 (s, C=N). ^{11}B NMR [$CDCl_3$, rel. to $NaB(C_6H_5)_4$]: δ 10.8 d, ($J_{^{11}B-^{19}F}$ = 17 Hz). IR (cm^{-1}, KBr): 923, 960sh ν(N–O), 1157,1222 ν(B–O)+ ν(B–F), 1479 ν(C=N). UV-Vis ($CHCl_3$): λ_{max} ($10^{-3}\varepsilon$/mol^{-1} l cm^{-1}) 259(13), 286(5.2), 391(4.3), 432(15), 479(22), 516(7.9) nm.

$Ru[(C_6H_5S)_2Gm]_3(BF)_2$ (5). This complex was synthesized by an analogous method to that used for **4** except that thiophenol (0.21 ml, 1.9 mmol) was used instead of methanethiol and the realkylation stage was omitted. The reaction mixture was refluxed for 12 h, filtered, and precipitated with a three-fold volume of ethanol. The solid was reprecipitated from chloroform solution with hexane. Yield: 0.15 g (74%). Anal. calc. for $C_{42}H_{30}N_6O_6S_6B_2F_2Ru$: C, 47.23; H, 2.81; N, 7.87; S, 18.03. Found: C, 47.18; H, 2.82; N, 7.80; S, 17.94%. MS PD: *m*/*z* 1067 $(M)^{+\bullet}$. ^1H NMR ($CDCl_3$): δ 7.07 (m, 12H, Ph), 7.19 (m, 18H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 128.5 (s, Ph), 129.3 (s, Ph), 131.2 (s, SPh), 131.5 (s, Ph), 147.5 (s, C=N). ^{11}B NMR [$CDCl_3$, rel. to $NaB(C_6H_5)_4$]: δ 10.8 d, ($J_{^{11}B-^{19}F}$ = 14 Hz). IR (cm^{-1}, KBr): 904, 926 ν(N–O), 1158–1163, 1227 ν(B–O) + ν(B–F), 1578 ν(C=N). UV-Vis ($CHCl_3$): λ_{max} ($10^{-3}\varepsilon$/mol^{-1} l cm^{-1}) 266(17), 307(5.1), 366(6.9), 428(19), 480(25), 516(9.0) nm.

$Ru[(C_6H_5O)_2Gm]_3(B^nC_4H_9)_2$ (6). Phenol (0.66 g) was added to a solution of potassium methoxide, obtained from metallic potassium (0.30 g, 7.7 mmol) with dry methanol (10 ml). The reaction mixture was evaporated to dryness, and the solid residue was heated at 100 °C for 1 h *in vacuo*. The solution/suspension of the complex $Ru(Cl_2Gm)_3(B^nC_4H_9)_2$ (0.8 g, 1.14 mmol) in THF (10 ml) was added to the solution/suspension of the resulting potassium phenolate in dry THF at −35 °C. The reaction mixture was stirred for 2 h at this temperature and then for 5 h at room temperature and filtered. The THF solution was evaporated to dryness, and the solid residue was washed with water and a water–methanol mixture (1 : 1) and then dried *in vacuo*. The solid was dissolved in chloroform and the solution was filtered through a Silasorb SPH-300 layer (20 mm). The filtrate was evaporated to a small volume (≈3 ml), and a three-fold volume of hexane was added. The resulting solution/suspension was evaporated to dryness, and the dark-yellow product was washed with hexane and dried *in vacuo*. Yield: 0.75 g (63%). Anal. calc. for $C_{50}H_{48}N_6O_{12}B_2Ru$: C, 57.32; H, 4.59; N, 8.03. Found: C, 57.31; H, 4.57; N, 8.04%. MS PD: *m*/*z* 1047 $(M)^{+\bullet}$. ^1H NMR ($CDCl_3$): δ 0.50 (m, 4H, BCH_2), 0.65 (t, 6H, CH_3), 1.03 (m, 8H, CH_2CH_2), 6.86 (m, 12H, Ph), 7.14 (m, 6H, Ph), 7.30 (m, 12H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 14.0 (s, CH_3), 17.2 (br s, BCH_2), 25.4 (s, CH_2), 25.5 (s, CH_2), 116.7 (s, Ph), 124.5 (s, Ph), 129.6 (s, Ph), 142.0 (s, OPh), 155.1 (s, C=N). IR (cm^{-1}, KBr): 918, 988 ν(N–O), 1090 δ(B–O), 1556 ν(C=N). UV-Vis ($CHCl_3$): λ_{max} ($10^{-3}\varepsilon$/mol^{-1} l cm^{-1}) 260(11), 275(5.9), 367(4.5), 417(22), 453(4.3) nm.

$Ru(CwGm)_2(Cl_2Gm)(B^nC_4H_9)_2$ (7). Bis[2-(*o*-oxyphenoxy)]-diethyl ether (1.5 g, 5.1 mmol) was added to a solution of sodium methoxide, obtained from metallic sodium (0.19 g, 8.2 mmol) with dry methanol (15 ml). The reaction mixture was refluxed for 30 min and evaporated to dryness, and the solid residue was left at 90–100 °C for 1 h *in vacuo*. The resulting salt and interphase carrier $[(^nC_4H_9)_4N]Br$ (0.77 g, 5.1 mmol) were dissolved/suspended in dry THF (50 ml), and a solution of the complex $Ru(Cl_2Gm)_3(B^nC_4H_9)_2$ (1.2 g, 1.7 mmol) in THF (30 ml) was added dropwise to the stirring reaction mixture for 2 h at 50 °C. The solution/suspension was stirred for 5 h at 50 °C, cooled to room temperature, and filtered. The filtrate was evaporated to dryness. The solid residue was washed with water and then methanol, dried *in vacuo*, and dissolved in chloroform. The chloroform solution was filtered through a Silasorb SPH-300 layer (20 mm), evaporated to dryness and washed with methanol, a small amount of diethyl ether and then hexane, and dried *in vacuo*. Yield: 0.35 g (18%). Anal. calc. for $C_{46}H_{50}N_6O_{16}B_2Cl_2Ru$: C, 48.60; H, 4.40; N, 7.40; Cl, 6.25. Found: C, 48.65; H, 4.44; N, 7.38; Cl, 6.17%. MS PD: *m*/*z* 1136 $(M)^{+\bullet}$. ^1H NMR ($CDCl_3$): δ −0.12 (m, 4H, BCH_2), 0.33 [m, 4H, CH_2(Bu)], 0.63 (t, 6H, CH_3), 0.82 [m, 4H, CH_2(Bu)], 3.40 (m, 4H, OCH_2), 3.68 (m, 4H, OCH_2), 4.03 (m, 8H, OCH_2), 6.83 (m, 8H, Ph), 7.09 (m, 8H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 14.0 (s, CH_3), 17.1 (br s, BCH_2), 25.1 [s, CH_2(Bu)], 25.5 [s, CH_2(Bu)], 67.0 (s, OCH_2), 69.7 (s, OCH_2), 111.7 (s, Ph), 119.1 (s, Ph), 120.4 (s, Ph), 123.7 (s, ClC=N), 125.5 (s, Ph), 139.8 (s, OC=N), 143.6 (s, OPh), 148.9 (s, OPh). IR (cm^{-1}, KBr): 936, 1004 ν(N–O), 1118 ν(B–O), 1512, 1540sh ν(C=N). UV-Vis ($CHCl_3$): λ_{max} ($10^{-3}\varepsilon$/mol^{-1} l cm^{-1}) 276(10), 307(2.4), 395(12), 433(12) nm.

$Ru(CwGm)_3(B^nC_4H_9)_2$ (8). This complex was synthesized by an analogous method to **7** except that an excess of the disodium salt of bis[2-(*o*-oxyphenoxy)]diethyl ether, obtained from metallic sodium (0.28 g, 12.3 mmol) and bis[2-(*o*-oxyphenoxy)]-diethyl ether (2.2 g, 7.7 mmol), was used and the reaction time was 30 h.

The reaction mixture was filtered, and the filtrate was precipitated with a three-fold volume of hexane. The precipitate was removed by filtration, and the filtrate was evaporated to dryness. The solid was washed with water and then methanol, and the product was dissolved in chloroform. The chloroform solution was filtered through a Silasorb SPH-300 layer (20 mm), evaporated to dryness, and extracted with a small amount of diethyl ether. The extract was evaporated to dryness, and the resulting orange solid was washed with hexane and dried *in vacuo*. Yield: 0.32 g (14%). Anal. calc. for $C_{62}H_{66}N_6O_{21}B_2Ru$: C, 55.00; H, 4.88; N, 6.21. Found: C, 55.02; H, 4.81; N, 6.17%. MS PD: *m*/*z* 1353 $(M)^{+\bullet}$. ^1H NMR ($CDCl_3$): δ −0.12 (m, 4H, BCH_2), 0.38 (m, 4H, CH_2), 0.67 (t, 6H, CH_3), 0.83 (m, 4H, CH_2), 3.68 (m, 12H, OCH_2), 4.05 (m, 12H, OCH_2), 6.82 (m, 12H, Ph), 7.09 (m, 12H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 14.0 (s, CH_3), 25.1 (s, CH_2), 25.5 (s, CH_2), 67.1 (s, OCH_2), 69.7 (s, OCH_2), 111.8 (s, Ph), 119.2 (s, Ph), 120.4 (s, Ph), 125.5 (s, Ph), 139.6 (s, C=N), 143.7 (s, OPh), 149.0 (s, OPh). IR (cm^{-1}, KBr): 937, 1006 ν(N–O), 1117 ν(B–O), 1540 ν(C=N). UV-Vis ($CHCl_3$): λ_{max} ($10^{-3}\varepsilon$/mol^{-1} l cm^{-1}) 274(15), 304(6.0), 357(5.8), 394(11), 430(20), 458(30) nm.

$Ru[(^nC_4H_9NH)_2Gm]_2(Cl_2Gm)(BC_6H_5)_2$ (9). The complex $Ru(Cl_2Gm)_3(BC_6H_5)_2$ (0.37 g, 0.5 mmol) was dissolved/suspended in dry DMF at −5 °C, and a solution of an excess of *n*-butylamine (0.9 ml, 9 mmol) in DMF (10 ml) was added dropwise to the stirring reaction mixture for 2 h at this temperature. The reaction mixture was left overnight at room temperature and precipitated with a two-fold volume of water. The brown product was filtered, dried *in vacuo*, and dissolved in chloroform. The chloroform solution was filtered through a Silasorb SPH-300 layer (20 mm), diluted with twice the volume of hexane, and evaporated to dryness. The solid residue was

Table 1 Crystallographic data and refinement details for $Ru(Cl_2Gm)_3(B^nC_4H_9)_2$ (**2**), $Ru[(CH_3S)_2Gm]_3(BF)_2$ (**4**), and $Ru[(C_6H_5O)_2Gm]_3(B^nC_4H_9)_2$ (**6**)

	2	**4**	**6**
Empirical formula	$C_{14}H_{18}B_2Cl_6N_6O_6Ru$	$C_{12}H_{18}B_2F_2N_6O_6RuS_6$	$C_{50}H_{48}B_2N_6O_{12}Ru$
FW	701.73	695.37	1047.64
Color, habit	Orange, prism	Red, prism	Brown, prism
Crystal dimensions/mm	0.58 × 0.36 × 0.15	0.36 × 0.28 × 0.26	0.48 × 0.36 × 0.28
a/Å	26.238(5)	10.518(2)	17.654(2)
b/Å	7.999(2)	12.517(2)	25.336(4)
c/Å	13.927(3)	19.574(4)	13.483(1)
β/°	116.76(3)	91.83(3)	120.99(1)
V/Å^3	2610(1)	2504.5(8)	5170(1)
Z	4	4	4
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/n$	$C2/c$
D_{calc}/g cm^{-3}	1.786	1.844	1.346
μ/mm^{-1}	1.258	1.183	0.369
Data/restraints/parameters	1840/0/196	2744/0/389	3757/0/398
Weighting scheme[a]	$1/[\sigma^2(F_o^2) + (0.0722P)^2 + 2.84P]$	$1/[\sigma^2(F_o^2)_o + (0.0428P)^2 + 1.18P]$	$1/[\sigma^2(F_o^2) + (0.0561P)^2 + 3.16P]$
R[b] (%)	0.0275	0.0212	0.0289
R_w[c] (%)	0.0724	0.0558	0.0837
F(000)	1392	1392	2160
GooF[d]	1.077	1.063	1.153

[a] $P = (F_o^2 + 2F_c^2)/3$. [b] $R = (\Sigma|F_o| - |F_c|)/\Sigma|F_o|$. [c] $R_w = [(\Sigma(w|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. [d] $\mathrm{GooF} = [(\Sigma w|F_o| - |F_c|)^2/(N_{obs} - N_{param})^{1/2}$.

washed with a small amount of hexane and dried *in vacuo*. Yield: 0.085 g (19%). Anal. calc. for $C_{34}H_{50}N_{10}O_6B_2Cl_2Ru$: C, 45.96; H, 5.63; N, 15.77. Found: C, 45.87; H, 5.58; N, 15.69%. MS PD: m/z 888 $(M)^{+\bullet}$. ^{1}H NMR ($CDCl_3$): δ 0.93 (t, 12H, CH_3), 1.42 (m, 16H, CH_2CH_2), 3.29 (m, 8H, NCH_2), 5.26 (br s, 4H, NH), 7.46 (m, 6H, Ph), 7.93 (m, 4H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 13.6 (s, CH_3), 19.4 (s, CH_2), 33.3 (s, CH_2), 44.5 (s, NCH_2), 124.6 (s, ClC=N), 127.4 (s, Ph), 127.8 (s, Ph), 131.7 (s, Ph), 148.6 (s, NC=N). IR (cm^{-1}, KBr): 905, 982 ν(N–O), 1221 ν(B–O), 1512, 1560 ν(C=N). UV-Vis ($CHCl_3$): λ_{max} ($10^{-3}\varepsilon$/mol^{-1} l cm^{-1}) 263(9.0), 278(7.8), 436(7.3), 461(12) nm.

X-Ray crystallography

The details of crystal data collection and refinement parameters for $Ru(Cl_2Gm)_3(B^nC_4H_9)_2$ (**2**), $Ru[(CH_3S)_2Gm]_3(BF)_2$ (**4**), and $Ru[(C_6H_5O)_2Gm]_3(B^nC_4H_9)_2$ (**6**) are listed in Table 1. Single crystals of these complexes were grown from chloroform–heptane (**2**), THF–*iso*-octane (**4**), and toluene–*iso*-octane (**6**). Data were collected at 293 K on a CAD4 diffractometer using Mo-Kα (β-filtered) radiation (λ = 0.71073 Å) by $\theta/2\theta$ scans. The structures were solved by the heavy-atom method, and refinements were made by full-matrix least squares on F^2 for all data with anisotropic thermal parameters for non-hydrogen and isotropic parameters for hydrogen atoms. All calculations were made using the SHELXTL-97 program package.[33]

CCDC reference numbers 168668–168670.

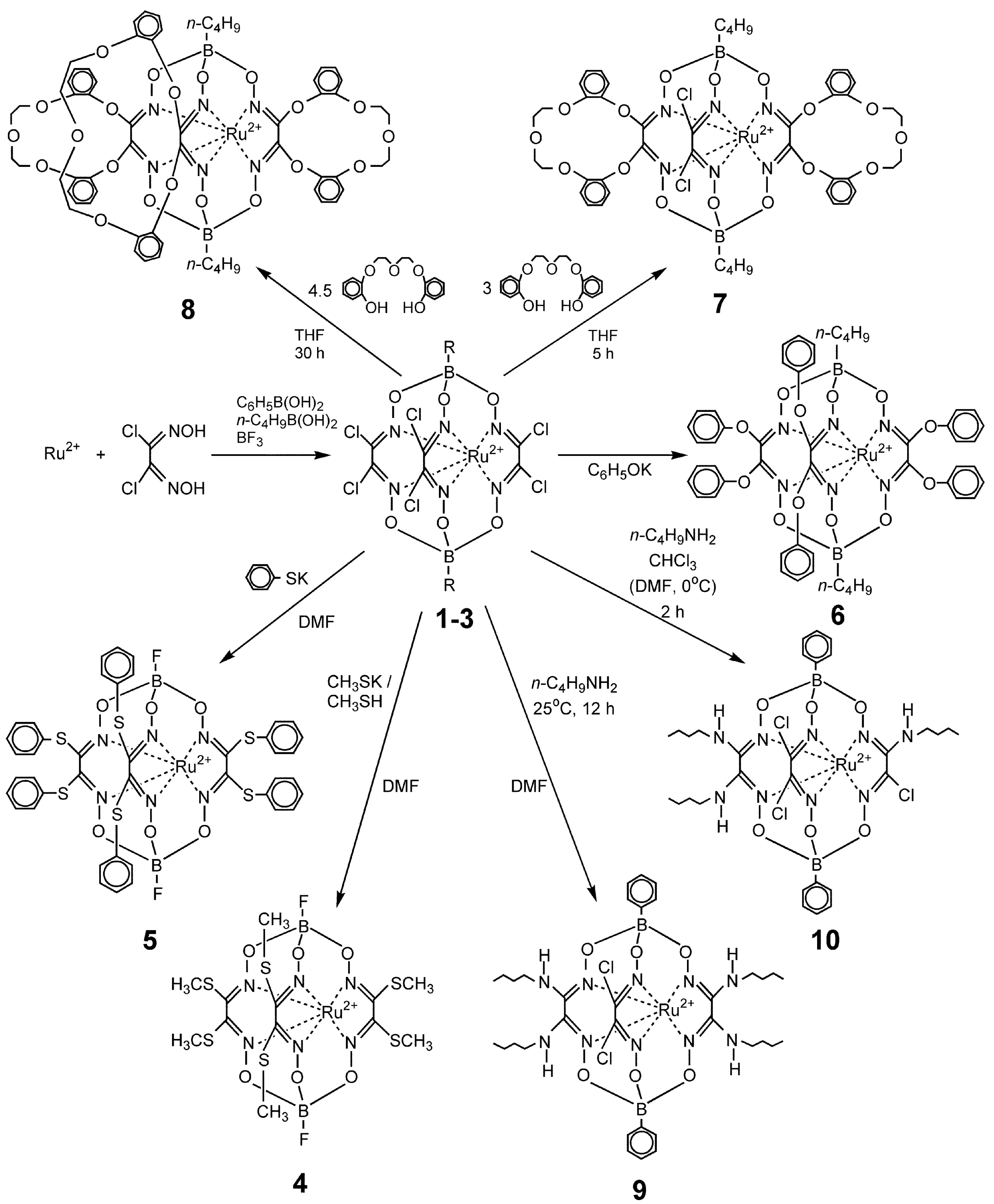
See http://www.rsc.org/suppdata/dt/b1/b107172f/ for crystallographic data in CIF or other electronic format.

Results and discussion

Synthesis of precursors

Several pathways for the synthesis of ribbed-functionalized trisdioximate clathrochelate complexes (*i.e.*, clathrochelates with functionalizing substituents in α-dioximate fragments) have been thoroughly analyzed earlier.[26] The optimal synthetic route is based on a preliminary isolation of a reactive halogenide precursor and its further functionalization *via* the typical nucleophilic substitution reactions so well known in organic chemistry. The synthesis of ruthenium(II) clathrochelates is complicated by a kinetic inertness of the starting ruthenium solvato complexes in the reactions of coordinated ligand substitution, as well as by the ability of ruthenium complexes to undergo intra- and inter-molecular redox reactions, frequently with participation of coordinated ligands. In particular, we have unexpectedly isolated an organic $[(CH_3)_3S]^+(CH_3SO_3)^-$ salt[34] in the course of the synthesis of a dimethylsulfoxide $Ru(DMSO)_4Cl_2$ solvate by the procedure described earlier.[35] Moreover, the Ru^{3+} ion is apt to form stable square-planar bis-dioximate complexes. Therefore, the attempt to extend the procedures of the precursor synthesis, developed earlier for iron(II),[26] to ruthenium(II) without any modification met with failure. The poor donor ability displayed by the H_2Cl_2Gm did not permit us to obtain clathrochelate ruthenium(II) precursors starting from $Ru(DMSO)_4Cl_2$ in the manner proposed by Grzybowski and co-workers for boron-containing ruthenium(II) clathrochelates with aromatic, alicyclic, and acyclic dioximes.[25] Therefore, we managed to implement the synthesis of hexachloride ruthenium(II) precursors under rigid conditions [in particular, a mixture of nitromethane and $SbCl_3$, boiling TFA and $BF_3\cdot O(C_2H_5)_2$ were used as reaction media] with much lower yields compared to iron(II).

The fact that the approach employed met with success was to a great extent caused by the low basicity and high protolytic stability of the H_2Cl_2Gm. In most cases, the Ru^{2+} ion generated *in situ* during the reduction of oxychloride ruthenium compounds in the higher oxidation states with metallic lead in the presence of electron-accepting $SbCl_3$-type ligands also favored the elimination of chloride ions from the inner coordination sphere of ruthenium ions. As a result, we managed to obtain the $Ru(Cl_2Gm)_3(BF)_2$ and $Ru(Cl_2Gm)_3(B^nC_4H_9)_2$ complexes in reasonable yields. However, the rigid conditions required for the activation of the Ru^{2+} ions in the reaction with poorly coordinating H_2Cl_2Gm imposes restrictions on the use of the synthetic routes worked out in our laboratory. Such methods can be employed only when capping agents (in particular, BF_3, alkylboronic acids, and their derivatives) are stable to protolytic dissociation. When arylboronic acids and their derivatives (especially, phenylboronic acid), which are more apt to protolytic dissociation and transmetallization, were employed as capping agents, one could observe an abrupt decrease in the desired product yield induced by the destruction of the capping agent. Thus, the reaction involved two competitive processes: the formation of a clathrochelate, which was removed from the reaction mixture because of its low solubility (this shifted the equilibrium in the desired direction), and a protolytic dissociation of the capping agent. Consequently, one should determine the optimal conditions for a synthetic route (time and temperature) that make it possible on the one hand to achieve a maximal formation of the desired complex and, on the other, to



Scheme 1

avoid significant decomposition of the capping agent, which can eventually lead to the decomposition of the already-formed complex. To avoid such negative phenomena during the synthesis, we believe that it is expedient to add the capping agent in excess at periodic intervals.

Synthesis of functionalized complexes

The pathways implemented for the modification of synthesized hexachloride ruthenium(II) precursors are shown in Scheme 1. The reactivity of such precursors in the reactions of nucleophilic substitution was somewhat lower than that of their analogs with an encapsulated iron(II) ion. In particular, the attempts to prepare a hexathiophenol ruthenium(II) clathrochelate using a C_6H_5SH/K_2CO_3 system in 1,4-dioxane proved to be unsuccessful: the ^1H and ^{13}C NMR and PD mass spectra indicated that a mixture of partial substitution products is formed [as well as in the case of earlier-studied $Fe(Cl_2Gm)_3(BC_6H_5)_2/CH_3SH/K_2CO_3$ system].[26]

The reaction of $Ru(Cl_2Gm)_3(BC_6H_5)_2$ with a 15% excess of *n*-butylamine (calculated from a tetrasubstituted clathrochelate) in DMF at 0 °C for 2 h resulted solely in trisubstituted clathrochelate, and the substitution took place in two of the three dioximate fragments (Scheme 1). In the case of the $Fe(Cl_2Gm)_3(BC_6H_5)_2$ precursor, only tetrasubstituted product was obtained under analogous conditions. To produce its ruthenium analog, a two-fold excess of *n*-butylamine was used, and the reaction mixture was stirred in the final stage for 10 h at room temperature. It should also be emphasized that when the reaction with *n*-butylamine was carried out in DMF, it afforded a great variety of clathrochelate framework destruction products and a mixture of square-planar bis-complexes and this significantly decreased the desired product yield. Therefore, in this case the reaction was started at a low temperature and gradually increased up to room temperature (unlike the reaction with iron complexes). When kept in air for a long time, the $Ru[(^nC_4H_9NH)_2Gm]_2(Cl_2Gm)(BC_6H_5)_2$ complex underwent partial destruction, presumably because of redox reactions with the participation of oxygen. A somewhat unexpected result was obtained when DMF was replaced by chloroform: the interaction of $Ru(Cl_2Gm)_3(BC_6H_5)_2$ with *n*-butylamine both at room temperature and with prolonged stirring at 50–60 °C yielded only one trisubstituted product, **10**, as evidenced by the NMR and mass spectra.

As with iron(II), we managed to isolate di- and tri-crown ether ruthenium(II) complexes **7** and **8** depending on the molar ratio of precursor : salt of bis[2-(*o*-oxyphenoxy)]diethyl ether and on the reaction time.

Structure and spectra

The composition and purity of the isolated functionalized ruthenium(II) clathrochelates were first confirmed by ^1H and ^{13}C NMR spectroscopy (the integral intensities of functionalizing and apical substituent protons in the ^1H NMR spectra, and the number of signals in the ^{13}C NMR spectra was in accordance with the proposed composition and symmetry of the molecule). A small (from 1 to 2 ppm) systematic decrease in the chemical shift of the signals assigned to azomethine fragments in the ^{13}C NMR spectra of ruthenium complexes compared with their iron-containing analogs should be emphasized. A substantial (from 30 to 40 cm^{-1}) systematic short-frequency shift in the stretching vibrations $\nu_{C=N}$ of such fragments was also observed in the IR spectra of the synthesized complexes compared with iron(II) compounds. The magnitudes of chemical shifts and spin–spin interaction constants ($J_{^{11}B-^{19}F} \approx 15$ Hz) in the ^{11}B NMR spectra of a fluoroboronic $Ru(Cl_2Gm)_3(BF)_2$ precursor and its ribbed-functionalized derivatives confirmed a tetrahedral character of the apical boron atom coordination polyhedron and the high symmetry of the O_3BF moiety.

The crystal and molecular structures of three clathrochelates obtained (one precursor and two functionalized complexes) were determinated by X-ray analysis (Figs. 1–3). As expected, the Ru–N distances (approximately 1.98–1.99 Å, Table 2) are longer than the Fe–N ones (approximately 1.90–1.91 Å), but the increase (0.07–0.08 Å) is not significant. A similar variation in the metal–nitrogen distance has also been observed in the series of cyclohexanedion-1,2-dioximate clathrochelates.[36] Judging from the magnitude of the physical ionic radius of a low-spin Ru^{2+} ion in an octahedral environment,[37] one might have expected a more significant increase in the Ru–N distance. However, such an increase is impeded by strong π-back-bonding effects in the ruthenium(II) complexes.[36] The increase in the metal–nitrogen distance in ruthenium complexes led to a decrease in the magnitude of the distortion angle φ of the coordination polyhedron with a geometry intermediate between a trigonal prism (TP, $\varphi = 0°$) and a trigonal antiprism (TAP, $\varphi = 60°$).

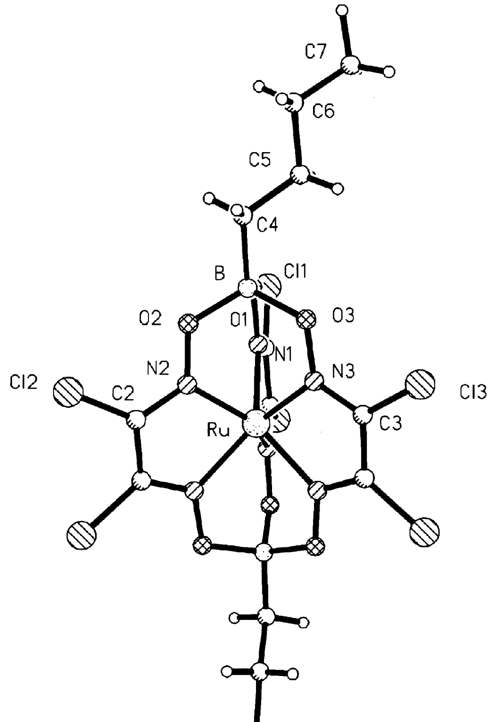


Fig. 1 Molecular structure of $Ru(Cl_2Gm)_3(B^nC_4H_9)_2$ (**2**).

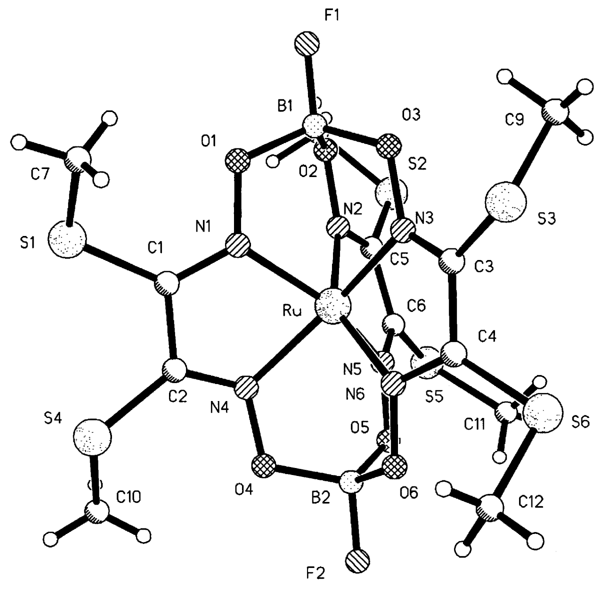


Fig. 2 Molecular structure of $Ru[(CH_3S)_2Gm]_3(BF)_2$ (**4**).

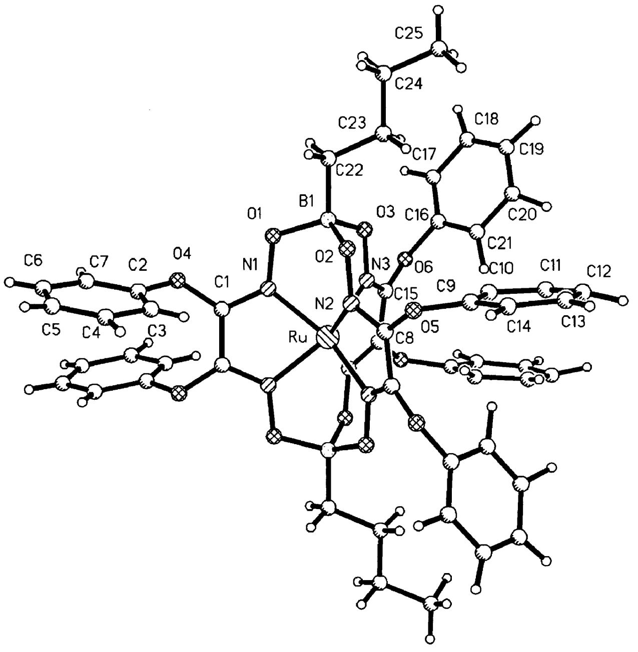


Fig. 3 Molecular structure of $Ru[(C_6H_5O)_2Gm]_3(B^nC_4H_9)_2$ (**6**).

Thus, the variation in geometry of coordination polyhedra in passing from iron complexes to their ruthenium analogs may be described as a rotary-translational expansion that gives rise to a considerable (0.06–0.09 Å) increase in the distance, *h*, between the bases of TPs and, consequently, to an increase in the size of a macrobicyclic ligand cavity. In the series of both iron and ruthenium compounds, the maximal distance between the coordination polyhedron bases and minimal distortion angle

Table 2 The main X-ray data for ruthenium complexes and their analogs

Compound	ϕ/°	M–N[a]/Å	h[b]/Å	α[c]/°	C–C[a]/Å	C=N[a]/Å	C–C=N[a]/°	N–O[d]/Å	N–O–B[d]/°	B–O[d]/Å	O–B–C (O–B–F)[d]/°	O–B–O[d]/°	Δ[e]/Å	N=C–C=N[f]/°
$Ru(Cl_2Gm)_3(B^nC_4H_9)_2$	2.6	1.978	2.47	38.8	1.419	1.301	114.0	1.355	114.3	1.502	109.2	109.6	0.08	0.8
$Ru[(CH_3S)_2Gm]_3(BF)_2$	20.2	1.986	2.42	38.6	1.451	1.313	112.8	1.372	113.0	1.494	106.9	111.9	0.11	10.5
$Ru[(C_6H_5O)_2Gm]_3(B^nC_4H_9)_2$	19.5	1.988	2.45	39.0	1.442	1.304	113.8	1.373	113.7	1.513	108.3	110.6	0.10	9.8
$Ru[(CH_2)_4Gm]_3(B^nC_4H_9)_2$[25]	12.0	1.972		38.6	1.425	1.314	113.2	1.370	113.7	1.511		110.1		
$Fe(Cl_2Gm)_3(B^nC_4H_9)_2$[26]	16.1	1.90	2.38	39.1	1.422	1.285	112.4	1.376	111.1	1.504	109.8	109.2	0.089	8.6
$Fe[(C_6H_5O)_2Gm]_3(B^nC_4H_9)_2$[26]	25.2	1.91	2.36	39.8	1.440	1.296	112.8	1.372	112.9	1.502	109.5	109.5	0.096	9.2
$Fe[(CH_3S)_2Gm]_3(BC_6H_5)_2\cdot THF$[26]	25.3	1.91	2.32	39.3	1.461	1.298	111.3	1.377	112.2	1.491	109.7	110.2	0.115	10.9
$Fe[(CH_2)_4Gm]_3(B^nC_4H_9)_2$[25]	20.3	1.916		39.1	1.434	1.302	112.0	1.371	112.9	1.499		109.3		

[a] The average of the main structural parameters of chelate cycles. [b] Distance between the coordination polyhedron bases. [c] Bite angle (half the chelate angle). [d] The average of the main structural parameters of capping fragments. [e] Mean deviation of the coordinated nitrogen atoms from C–Fe–C plane. [f] Dihedral angle values for the chelating fragments.

φ (and, consequently, a maximal cavity size) were observed for hexachloride precursors. Their functionalized derivatives have greater distortion angles φ and smaller h values (Table 2).

The UV-vis spectra of the ruthenium(II) complexes obtained exhibited bands of high intensity in the visible region, characteristic of clathrochelates. A short wavelength shift of such asymmetric Ru d ⟶ L π* charge transfer bands (CTBs) proved to be 15–35 nm compared with the position of CTBs in analogous iron complexes. The CTBs in C_3-symmetric ruthenium complexes were decomposed into three Gaussian components: two of less intensity at the edges and one of higher intensity in the center. The CTBs in the UV-vis spectra of the synthesized sulfur-containing complexes were substantially (by approximately 60 nm) shifted compared with their hexachloride precursors. At the same time, the oxygen-containing substituents in dioximate fragments had practically no effect on the position of the CTB. 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 negligibly as well.

All complexes synthesized in the toluene and acetonitrile solutions exhibited extremely low luminescence quantum yields, at least 500 times lower relative to $[Ru(bpy)_3]^{2+}$ in acetonitrile solution. Also transient signals were not observed during laser photolysis under these conditions. At the same time, luminescence was observed in a frozen toluene matrix at 77 K. The clathrochelates obtained have wide luminescence bands in the range of 500 to 700 nm. Summarized data on luminescence maxima and relative quantum yields of luminescence are presented in Table 3.

Electrochemistry

The cyclic voltammograms of the ruthenium complexes synthesized exhibit reversible or quasi-reversible anodic processes assigned to the Ru(II/III) couples.[25] The oxidation half-wave potentials as well as Tomeš criteria values, which were determined as a wave slope ($\Delta E = E_{3/4} - E_{1/4}$) to characterize the reversibility of a corresponding electrochemical redox process (the ΔE value is equal to 56 mV for a one-electron reversible reaction at 25 °C), are listed in Table 3. The cyclic voltammetry data give some information concerning the stability of electrochemically generated ruthenium(III) clathrochelates. The existence of a reverse wave on backscanning the potential might provide evidence on the relative stability of these complexes on the cyclic voltammetry time scale. Among the ruthenium(II) clathrochelates studied, for $Ru[(CH_2)_4Gm]_3(B^nC_4H_9)_2$, $Ru(CwGm)_2(Cl_2Gm)(B^nC_4H_9)_2$, $Ru(CwGm)_3(B^nC_4H_9)_2$, $Ru[(CH_3S)_2Gm]_3(BF)_2$ and $Ru[(^nC_4H_9NH)_2Gm]_2(Cl_2Gm)(BC_6H_5)_2$ complexes the reverse waves were only observed, both direct and reverse waves being well reproduced at repeated cycling. For the rest of compounds there were no reverse waves due to the reduction processes. Moreover, the oxidation process was accompanied by formation of insoluble products followed by passivation of the working electrode.

The data obtained make it possible to analyze the effects of apical and ribbed substitutes on the half-wave potential $E_{1/2}$ values. Earlier it was found[26] for analogous iron(II) clathrochelates, that both the inductive and mesomeric changes, characteristics of substituents in dioximate fragments with a conjugated π-bond system, have more significant effects on the oxidation potential values than the properties of the apical substituents. These conclusions are also true for ruthenium(II) clathrochelates. As seen from Table 3, there is a relation between $E_{1/2}$ values and the Hammett σ_{para} constants, whereas no agreement has been found for Taft σ_I inductive constants.

Fig. 4 demonstrates the $E_{1/2} - \sigma_{para}$ correlation plot for fluoroboronic ruthenium clathrochelates, and this correlation is compared with that obtained earlier for iron(II) complexes[26] (the correlation coefficient is 0.84 for ruthenium and 0.86 for iron

Table 3 Redox and emission characteristics for hexachloride clathrochelate ruthenium(II) precursors, resultant functionalized complexes and analogous iron(II) clathrochelates

Compound	σ_I[a]		σ_{para}[a]		$E_{1/2}$/mV	ΔE/ mV	λ_{max}^{em}/ nm	φ_{em}[b]
$\mathrm{Ru(Cl_2Gm)_3(BC_6H_5)_2}$	0.47 [0.10]		0.227 [−0.01]		1360	60	570	0.0010
$\mathrm{Fe(Cl_2Gm)_3(BC_6H_5)_2}$[26]					1360	80		
$\mathrm{Ru(Cl_2Gm)_3(B^nC_4H_9)_2}$	0.47 [−0.08]		0.227 [−0.19]		1330	60	550	0.031
$\mathrm{Fe(Cl_2Gm)_3(B^nC_4H_9)_2}$[26]					1320	90		
$\mathrm{Ru(Cl_2Gm)_3(BF)_2}$	0.47 [0.52]		0.227 [0.062]		1340	80	590	0.040
$\mathrm{Fe(Cl_2Gm)_3(BF)_2}$[26]					1415	60		
$\mathrm{Ru[(C_6H_5S)_2Gm]_3(BF)_2}$	0.27 [0.52]		0.15 [0.062]		1120	60	620, 700	0.035
$\mathrm{Fe[(C_6H_5S)_2Gm]_3(BC_6H_5)_2}$[26]	[0.10]		[−0.01]		895	80		
$\mathrm{Ru[(CH_3S)_2Gm]_3(BF)_2}$	0.19 [0.52]		0.00 [0.062]		830	65	610	0.033
$\mathrm{Fe[(CH_3S)_2Gm]_3(BC_6H_5)_2}$[26]	[0.10]		[−0.01]		670	60		
$\mathrm{Ru[(C_6H_5O)_2Gm]_3(B^nC_4H_9)_2}$	0.38 [−0.08]		−0.32 [−0.19]		840	85	500	0.0031
$\mathrm{Fe[(C_6H_5O)_2Gm]_3(B^nC_4H_9)_2}$[26]					800	100		
$\mathrm{Ru(CwGm)_3(B^nC_4H_9)_2}$	0.38 [−0.08]		−0.32 [−0.19]		690	90	580	0.12
$\mathrm{Fe(CwGm)_3(B^nC_4H_9)_2}$[26]					460	60		
$\mathrm{Ru(CwGm)_2(Cl_2Gm)(B^nC_4H_9)_2}$	0.38(OPh) 0.47(Cl)	} 0.41	−0.32(OPh) 0.227(Cl)	} −0.14	780	60	500, 600	0.049
$\mathrm{Fe(CwGm)_2(Cl_2Gm)(B^nC_4H_9)_2}$[26]	[−0.08]		[−0.19]		670	65		
$\mathrm{Ru[(^nC_4H_9NH)_2Gm]_2(Cl_2Gm)(BC_6H_5)_2}$	0.47(Cl) 0.10(^{n}BuNH)	} 0.22	0.227(Cl) −0.63(^{n}BuNH)	} −0.14	560	95	550	0.010
$\mathrm{Fe[(^nC_4H_9NH)_2Gm]_2(Cl_2Gm)(BC_6H_5)_2}$[26]	[−0.10]		[−0.01]		200	170		
$\mathrm{Ru[(CH_2)_4Gm]_3(BF)_2}$	−0.05 [0.52]		−0.15 [0.062]		850	70		
$\mathrm{Fe[(CH_2)_4Gm]_3(BF)_2}$[40]					745	80		
$\mathrm{Ru[(CH_2)_4Gm]_3(B^nC_4H_9)_2}$	−0.05 [−0.08]		−0.15 [−0.19]		645	60		
$\mathrm{Fe[(CH_2)_4Gm]_3(B^nC_4H_9)_2}$[41]					570	70		
$\mathrm{Fe[(C_6H_5)_2Gm]_3(BF)_2}$[40]	0.10 [0.52]		−0.01 [0.062]		940	70		
$\mathrm{Fe[(CH_3)_2Gm]_4(BF)_2}$[40]	−0.05 [0.52]		−0.17 [0.062]		785	60		
$\mathrm{FeGm_3(BF)_2}$[26]	0.00 [0.52]		0.00 [0.062]		1250	65		
$\mathrm{Fe[(C_6H_5)_2Gm]_2(Cl_2Gm)(BF)_2}$[27]	0.10(Ph) 0.47(Cl) [0.52]	} 0.223	−0.01(Ph) 0.227(Cl) [0.062]	} 0.069	1100	70		
$\mathrm{Fe[(C_6H_5)_2Gm]_2(CwGm)(BF)_2}$[27]	0.10(Ph) 0.38(OPh) [0.52]	} 0.193	−0.01(Ph) −0.32(OPh) [0.062]	} −0.113	800	90		
$\mathrm{Fe[(C_6H_5)_2Gm]_2[(^nC_4H_9NH)_2Gm](BF)_2}$[27]	0.10(Ph) 0.10(^{n}BuNH) [0.52]	} 0.10	−0.01(Ph) −0.63(^{n}BuNH) [0.062]	} −0.217	400	75		
$\mathrm{Fe[(C_6H_5)_2Gm]_3[(CH_3S)_2Gm](BF)_2}$[27]	0.10(Ph) 0.19($\mathrm{CH_3S}$) [0.52]	} 0.13	−0.01(Ph) −0.00($\mathrm{CH_3S}$) [0.062]	} −0.007	880	70		

[a] Taft (σ_I) and Hammet (σ_{para}) constants for substituents in α-dioximate fragments [capping groups]. $\sigma_\Sigma = n/(m + n)\sigma_1 + m/(m + n)\sigma_2$, $\sigma_{n+1} = \sigma_n/2.5$.[38,39] [b] Quantum yield of luminescence in the frozen toluene glass matrix relative to $[\mathrm{Ru(bpy)_3}]^{2+}$ acetonitrile solution.

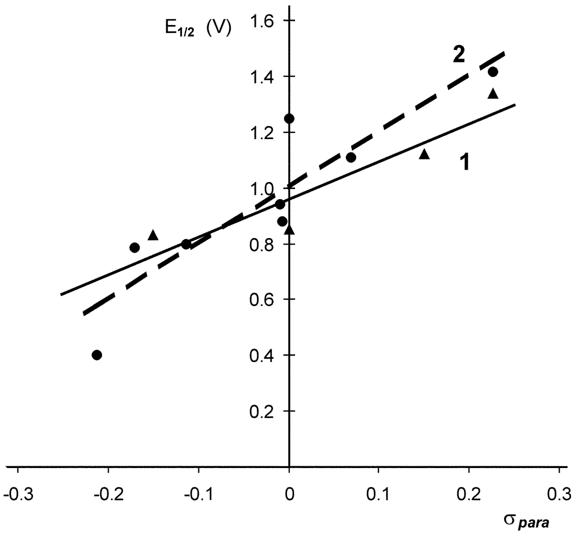


Fig. 4 Correlation of $E_{1/2}$ for $\mathrm{Ru^{3+}/Ru^{2+}}$ (**1**, ●) and $\mathrm{Fe^{3+}/Fe^{2+}}$ (**2**, ▲) couples of the fluoroboronic clathrochelates with Hammett σ_{para} values.

clathrochelates). It should be noted that this correlation is rather qualitative because of the quasi-reversible nature of the oxidation processes for these clathrochelates. However, they enable us to conclude that ruthenium complexes are less sensitive to the change of substituent in dioximate fragments than in iron complexes (the correlation plot slopes are 1.35 and 2.02, respectively). At the same time, an attempt to obtain a similar plot for *n*-butylboronic clathrochelates turned out to be less successful. In our opinion, this might be the result of other effects, in particular structural changes of coordination polyhedra, rather than electromeric properties of the substituents.

The peculiarity of the electrochemical behavior of ruthenium clathrochelates, which distinguishes them from analogous iron(II) complexes, is their lower sensitivity to the replacement of substituents in the capping groups. Moreover, if the dioximate fragments contain electron-accepting substituents, the ruthenium complexes oxidation potential becomes practically independent of apical substituent features as seen from the $E_{1/2}$ values for the hexachloride precursors). At the same time, for the macrobicyclic ruthenium(II) tris-dioximates the replacement of fluoroboronic capping groups onto *n*-butylboronic ones resulted in a cathodic shift of the $E_{1/2}$ value by approximately 200 mV (Table 3).

Conclusion

Ribbed-functionalized clathrochelate ruthenium(II) tris-dioximates were obtained by the nucleophilic substitution of reactive chlorine atoms in the initially obtained hexachloride precursors using procedures proposed earlier for their iron(II) analogs.

However, the synthesis of clathrochelate ruthenium(II) precursors was successfully performed under substantially more rigid conditions than in the case of iron(II). The luminescent characteristics (in particular, quantum yield) of the obtained ruthenium complexes lose to those of ruthenium(II) tris-phenanthrolinates and tris-bipyridinates. At the same time, ruthenium(II) clathrochelates have highly intense absorption bands in the visible region and their maxima depend on the nature of the ribbed-functionalizing substituents.

The directed apical and ribbed functionalization of ruthenium(II) tris-dioximate clathrochelates allows high selectivity in the binding of DNA fragments. The possibility of effective functionalization of both free and DNA-bound complexes is the significant advantage of reactive tris-dioximates compared with most of their phenanthroline and bipyridine analogs. We assume that variation of both apical and ribbed substituents (in particular, increasing the clathrochelate framework rigidity and increasing the number of aromatic substituents) as well as interaction of complexes with DNA will allow improvement of the luminescent parameters of ruthenium(II) clathrochelates.

We also plan to investigate thoroughly the photophysics of both synthesized macrobicyclic ruthenium(II) complexes and products of their interaction with nucleic acids.

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