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Soluble $\{[Rh_2(\mu\text{-}OOCCH_3)_2(dbbpy)_2][BF_4]\}_n$ molecular wire and $[Rh_2(\mu\text{-}OOCCH_3)_2(dbbpy)_2L_2]^{2+}$ complexes; dbbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine: Synthesis and physicochemical characterization

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ABSTRACT

Binuclear Rh(II) compounds $[Rh_2(\mu\text{-}OOCCH_3)_2(dbbpy)_2(H_2O)_2](CH_3COO)_2$ (**1**) (dbbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine), $[Rh_2(\mu\text{-}OOCCH_3)_2(dbbpy)_2(H_2O)_2](BF_4)_2\cdot H_2O\cdot CH_3CN$ (**2**), $[Rh_2(CH_3COO)_2(C_{18}H_{24}N_2)_2(CH_3CN)_2](BF_4)_2\cdot 4CH_3CN$ (**3**) and $\{[Rh_2(\mu\text{-}OOCCH_3)_2(dbbpy)_2][BF_4]\}_n$ (**4**) have been synthesized and characterized with spectroscopic methods. Structure of complex **3** has been determined using X-ray crystallography. Rhodium atoms in compound **3** have distorted octahedral coordination with O and N atoms in equatorial positions and Rh atom and CH_3CN molecule in axial coordination sites. Reduction of rhodium(II) compounds with aqueous 2-propanol leads to the formation of polymetallic compound $\{[Rh_2(\mu\text{-}OOCCH_3)_2(dbbpy)_2][BF_4]\}_n$ (**4**) containing $[Rh_2]^{3+}$ core. Compound **4** shows strong antiferromagnetic properties, $\mu = 0.18\text{–}1.73$ M.B. in the range 1.8–300 K, $J = -597\ cm^{-1}$. Electrochemistry of compounds **3** and **4** in CH_3CN has been investigated. Compound **4** exhibits a poorly reversible oxidation system at $E_{1/2} = -0.92$ V ($\Delta E_p = 0.19$ V) and in solution in DMF is slowly oxidized to **3** even in total absence of oxygen. Complex **3** is irreversibly oxidized to Rh(III) compound at $E_{pa} = 1.48$ V and irreversibly reduced at $E_{pc} = -1.02$ V to lead to the unstable polynuclear complex **4** in CH_3CN.

1. Introduction

Binuclear rhodium(II) carboxylato complexes $[Rh_2Cl_2(OOCR)_2(N\text{–}N)_2]$ and $[Rh_2(OOCR)_2(N\text{–}N)_2(H_2O)_2]^{2+}$ (R = H, Me, Et, Pr, Bu, Ph, PhCHOH, N–N = 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen) and their derivatives) are very thoroughly investigated compounds, because of their very interesting reactivity and catalytic, antibacterial and antitumor properties [1–7]. These compounds also exhibit rich redox properties. They can be very easily reduced with relatively mild reducers to the Rh(I)Rh(II) molecular wires (MWs) with infinite Rh–Rh chains [8–14]. It has been previously shown that the $[Rh_2(OOCR)_2(N\text{–}N)_2(H_2O)_2]^{2+}$ complexes can be effectively reduced with ethanol and 2-propanol and other alcohols to MWs $[Rh_2(\mu\text{-}OOCR)_2(bpy)_2]_nX_n$ and $[Rh_2(\mu\text{-}OOCR)_2(phen)_2]_nX_n$ (R = H, Me, X = BF_4^-, PF_6^-, $RCOO^-$) [8–10]. In the acetate complex with phen, the binuclear units $[Rh_2(\mu\text{-}OOCR)_2(phen)_2]^+$ are associated into tetranuclear moieties which in turn form infinite Rh–Rh wires with Rh–Rh bonds equal to 2.562, 2.739 and 2.832 Å [8].

Recently electrochemical and chemical syntheses of $\{[Rh_2(\mu\text{-}OOCCH_3)_2(phen)_2][BF_4]\}_n$ and $\{[Rh_2(\mu\text{-}OOCCH_3)_2(dmbpy)_2][BF_4]\}_n$ have also been performed and their electrochemical and physicochemical properties investigated [11,12]. It has been demonstrated that the compounds obtained chemically are similar to those prepared electrochemically. A simpler Rh(I)–Rh(II) MW $[Rh_2(NCCH_3)_8]_n(BF_4)_{3n}$ was previously obtained by electrochemical reduction of dinuclear rhodium(II) complex $[Rh_2(NCCH_3)_{10}](BF_4)_2$. In this compound the Rh–Rh distances are longer (2.8442 and 2.9277 Å) [13,14], thus rhodium MWs containing carboxylato bridging ligands are more stable. This conclusion was confirmed by formation of formato complexes $[Rh_4(\mu\text{-}OOCH)_4(bpy)_4][PF_6]_2$ and $\{[Rh_4(\mu\text{-}OOCH)_4(bpy)_4](BF_4)\}_n\cdot 0.5nC_4H_8O_2$ containing $[Rh_4]^{6+}$ and $[Rh_4]^{5+}$ cores, respectively [9,10].

More generally polymetallic complexes with metal–metal bonded chains are of interest because of their unusual and valuable properties. For instance they can be useful for electronics

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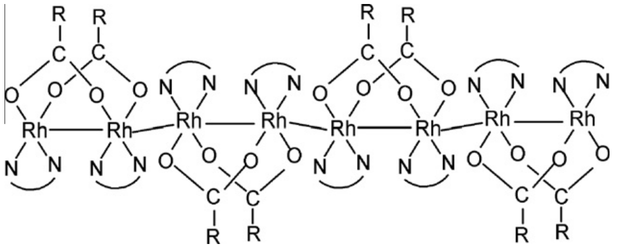

Scheme 1.

applications as semiconductors or conducting MWs [15,16]. MWs with infinite M–M bonds can be synthesized by chemical reduction of mononuclear or dinuclear metal complexes. The other, very convenient method is the electrochemical reduction of the appropriate coordination compounds especially developed for Ru and Os wires [17–19]. The properties of $\{[Rh_2(OOCR)_2(N\text{–}N)_2]X\}_n$ molecular wires depend both on carboxylato bridging ligands and polypyridyl ligands (Scheme 1).

Earlier properties and spectra of Rh(II) carboxylato complexes $[Rh_2(OOCR)_2(NN)_2L_2](X)_2$ (R = H, Me, Et, Pr, Bu, NN = bpy, phen, 4,4′-Me_2bpy, 4,4′-Ph_2bpy, 4,7-Ph_2phen, L = solvent molecule) were described [1–12,20–22]. However, complexes with bpy derivatives containing very bulky *tert*-butyl substituents were not investigated. Until now only rhodium carboxylato MWs with bpy, 4,4′-dimethyl-2,2′-bipyridine and phen ligands were characterized [1,4–6,8–12,21,22]. In order to have a better understanding of the influence of polypyridyl ligands substitution on the properties of rhodium complexes and corresponding MWs we report here properties of $[Rh_2(\mu\text{-}OOCCH_3)_2(dbbpy)_2(H_2O)_2](CH_3COO)_2$ (**1**) (dbbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine), $[Rh_2(\mu\text{-}OOCCH_3)_2(dbbpy)_2(H_2O)_2](BF_4)_2{\cdot}H_2O{\cdot}CH_3CN$ (**2**), $[Rh_2(CH_3COO)_2(C_{18}H_{24}N_2)_2(CH_3CN)_2](BF_4)_2{\cdot}4CH_3CN$ (**3**) and $\{[Rh_2(\mu\text{-}OOCCH_3)_2(dbbpy)_2][BF_4]\}_n$ (**4**), the X-ray structure of the complex (**3**) and chemical and electrochemical characterizations of $\{[Rh_2(\mu\text{-}OOCCH_3)_2(dbbpy)_2][BF_4]\}_n{\cdot}2nH_2O$ (**4**) molecular wire. Utilizing of the dbbpy ligand is expected to render the molecular wire more soluble in CH_3CN than other polypyridyl rhodium molecular wires.

2. Experimental

2.1. Starting materials and methods

Reagents 4,4′-di-*tert*-butyl-2,2′-bipyridine (dbbpy) and $RhCl_3{\cdot}3H_2O$ were purchased from Aldrich. Rhodium(II) acetate $[Rh_2(\mu\text{-}OOCCH_3)_4]$ was prepared as described in literature [23]. ^1H NMR spectra were measured with a Bruker AMX 300 and Avance 500 spectrometers, IR spectra on a Bruker IFS 113v spectrometer and Raman spectra on a Nicolet Magna 860 FT-IR spectrometer interfaced with a FT-Raman accessory. The samples were illuminated by a Nd:YVO4 laser line at 1.064 mm with a power of 0.32 W at the sample containing saturated solutions of complexes in water and wet solid compounds, without a converging lens.

EPR spectra were recorded on a Bruker ESP 300E and UV–Vis spectra on a Beckman DU-7500, Cary 5 and Cary 500 spectrometers. The reflectance spectra of the powder samples of complex **4** were recorded using MgO as a reference. The temperature dependence of the magnetic susceptibility was measured with a Quantum Design MPMS-XL-5 SQUID susceptometer operating at a magnetic field of 0.5 T in the temperature range 1.8–300 K. Sample of compound was sealed in quartz tube under argon. The susceptibilities were corrected for the diamagnetism of the constituent atoms using Pascal's constants [24].

2.2. Synthesis of complexes

2.2.1. $[Rh_2(\mu\text{-}OOCCH_3)_2(C_{18}H_{24}N_2)_2(H_2O)_2](OOCCH_3)_2$ (*1*)

Solution of $Rh_2(\mu\text{-}OOCCH_3)_4$ (0.442 g, 1 mmol) and 4,4′-di-*tert*-butyl-2,2′-bipyridine (dbbpy) (0.536 g, 2 mmol) in isopropanol (10 ml) was heated under reflux for 3 h. The red crystals of the product were deposited after addition of diethyl ether. Yield 85%. *Anal.* Calc. for $Rh_2C_{44}H_{64}N_4O_{10}$: C, 52.08; N, 5.52; H, 6.36. Found: C, 52.15; N, 5.43; H, 6.28%. IR (KBr, cm^{-1}): 604 m, 706 m ($\delta_{C\text{–}C}$ Ph), 743 w, 849 m ($\delta_{C\text{–}H}$ Ph), 901 w, 1022 w, 1045 w, 1077 w, 1122 w, 1159 w, 1203 w, 1252 m, 1325 m, 1368 s, 1415 vs (ν^{sym}_{COO}), 1441 s (ν^{sym}_{COO}), 1484 s, 1560 vs (ν^{as}_{COO}), 1618 s, 2872 s (ν_{CH}), 2964 s (ν_{CH}). Raman spectrum (water solution and wet solid, cm^{-1}): 201 m, 228 m, 244 m, 252 m, 267 m (ν_{RhRh}), 348 m, 386 m, 486 m, 560 m, 668 w, 725 m, 804 w, 902 w, 930 w, 950 w, 1047 vs, 1076 w, 1137 w, 1203 w, 1254 w, 1284 m, 1318 m, 1373 w, 1420 w, 1449 w, 1466 w, 1489 m, 1546 m, 1619 m, 2883 vw, 2915 vw, 2939 w, 2986 w, 3106 w. ^1H NMR (δ (ppm) J (Hz), CD_3OD): dbbpy: 8.23 (d, 2H, H (6,6′), ^3J (H^5H^6) = 6.0 Hz), 8.09 (d, 2H, H (3,3′), ^4J (H^3H^5) = 2.0 Hz), 7.45 (dd, 2H, H (5,5′), ^3J (H^5H^6) = 6.0 Hz, ^4J (H^5H^3) = 2.1 Hz), 1.37 (s, 18H, (CH_3)); $OOCCH_3$: 2.53 (s, 3H, μ-$OOCCH_3$), 1.86 (s, 3H, $OOCCH_3$). UV–Vis ($1/\lambda$ (cm^{-1}), (ε, $M^{-1}\ cm^{-1}$), H_2O): 17 500 (160), 24 700 (2650), 27 200 (2960).

2.2.2. $[Rh_2(\mu\text{-}OOCCH_3)_2(dbbpy)_2(H_2O)_2](BF_4)_2{\cdot}H_2O{\cdot}CH_3CN$ (*2*)

Solution of $Rh_2(\mu\text{-}OOCCH_3)_4$ (0.442 g, 1 mmol), 4,4′-di-tert-butyl-2,2′-bipyridine (dbbpy) (0.536 g, 2 mmol) and $NaBF_4$ (0.220 g, 2 mmol) in wet acetonitrile (10 ml) was heated under reflux for 24 h. Mixture was filtered and the red product was deposited from filtrate with ethyl ether and dried in air. *Anal.* Calc. for $Rh_2C_{42}H_{63}B_2F_8N_5O_7$: C, 44.63; N, 6.20; H, 5.58. Found: C, 44.57; N, 5.99; H, 5.40%.

IR (KBr, cm^{-1}): 522 m, 533 m, 604 m, 707 m ($\delta_{C\text{–}C}$ Ph), 743 w, 849 m ($\delta_{C\text{–}H}$ Ph), 901 w, 1038 vs (ν_{BF}), 1063 vs (ν_{BF}), 1084 vs (ν_{BF}), 1123 s, 1203 w, 1253 m, 1266 w, 1281 w, 1305 w, 1368 m, 1416 vs (ν^{sym}_{COO}), 1442 s (ν^{sym}_{COO}), 1483 s, 1558 s (ν^{as}_{COO}), 1618 s, 2210 vw (ν_{CN}), 2873 m (ν_{CH}), 2910 m (ν_{CH}), 2966 s (ν_{CH}). Raman spectrum (water solution and wet solid, cm^{-1}): 194 s, 202 s, 248 s, 259 s, 268 s (ν_{RhRh}), 283 s, 302 s, 348 s, 387 s, 391 s, 414 s, 444 s, 476 s, 502 s, 518 m, 560 m, 726 m, 769 m ($\nu^{s}_{BF_4}$), 784 m ($\nu^{s}_{BF_4}$), 804 m, 826 w, 872 w, 882 w, 903 w, 941 w, 1037 m, 1048 m, 1136 w, 1203 w, 1284 m, 1319 m, 1374 w, 1424 w, 1450 w, 1468 w, 1491 m, 1548 m, 1619 m, 2882 vw, 2914 w, 2940 w, 2987 w, 3074 w, 3100 m.

^1H NMR (δ (ppm) J (Hz), CD_3CN): 8.08 (d, 2H, H (6,6′), ^3J (H^5H^6) = 6.3 Hz), 7.79 (d, 2H, H (3,3′), ^4J (H^3H^5) = 1.8 Hz), 7.36 (dd, 2H, H (5,5′), ^3J (H^5H^6) = 6.2 Hz, ^4J (H^5H^3) = 1.9 Hz), 1.35 (s, 18H (CH_3)); $OOCCH_3$: 2.45 (s, 3H, μ-$OOCCH_3$).

UV–Vis ($1/\lambda$ (cm^{-1}), (ε, $M^{-1}\ cm^{-1}$), EtOH): 17 600 (210), 23 500 (2810), 26 700 (3530).

2.2.3. $Rh_2(CH_3COO)_2(C_{18}H_{24}N_2)_2(CH_3CN)_2(BF_4)_2(CH_3CN)_4$ (*3*)

Single crystals suitable for X-ray investigations were obtained from solution of compound $[Rh_2(\mu\text{-}OOCCH_3)_2(C_{18}H_{24}N_2)_2(H_2O)_2](BF_4)_2{\cdot}H_2O{\cdot}MeCN$ in dry acetonitrile by slow diffusion of vapor of diethyl ether into this solution. The crystals decompose in air atmosphere because of loss of acetonitrile molecules, therefore, single crystals were kept at low temperature in the stream of nitrogen and X-ray measurements were performed at 100 K.

2.2.4. $\{[Rh_2(\mu\text{-}OOCCH_3)_2(C_{18}H_{24}N_2)_2](BF_4)\}_n$ (4)

A solution of $[Rh_2(\mu\text{-}OOCCH_3)_2(C_{18}H_{24}N_2)_2(H_2O)_2](CH_3COO)_2$ (0.508 g, 0.5 mmol) in 2-propanol/water (3/1 v/v; 5 ml) was heated under reflux in argon atmosphere until a deep blue-green solution of the Rh(I)Rh(II) compound was formed and then the solution of