



Structure, UV spectroscopic and electrochemical properties of 2-methyl-8-quinolinolato rhodium (I) complexes, containing carbonyl, triphenylphosphine or triphenylphosphite ligands

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ABSTRACT

The known $\text{Rh}(2\text{-Me-8-Oxq})(\text{CO})_2$ complex (1) was prepared through treatment of dicarbonyl(acetylacetonate)rhodium (I) with 2-methyl-8-hydroxyquinoline for the first time. The reactions of 1 with triphenylphosphine and triphenylphosphite result in complexes $\text{Rh}(2\text{-Me-8-Oxq})(\text{PPh}_3)(\text{CO})$ (2) and $\text{Rh}(2\text{-Me-8-Oxq})[\text{P}(\text{OPh})_3](\text{CO})$ (3) that were characterized by IR and NMR spectroscopy. The structures of complexes 2 and 3 were determined by single-crystal X-ray diffraction analysis. The complexes show the 2-methyl-8-quinolinolato ligand in the expected coordination mode with a slightly disordered square planar geometry at the rhodium center. In the crystal, molecules of $\text{Rh}(2\text{-Me-8-Oxq})(\text{CO})(\text{PPh}_3)$ (2) form centrosymmetric dimers due to π -stacking interactions. No intermolecular contacts are observed in the crystal of 3. The UV spectroscopic and electrochemical properties of complexes 1–3 were studied. Their electronic spectra in CH_3CN show three quinoline-centered absorptions. The electrochemical study revealed that the oxidation of the complexes 1–3 is two-electron and leads to the formation of dication $\text{Rh}(\text{III})$ species while their reduction gives radical anions, which undergoes rapid decomposition.

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1. Introduction

Rhodium (I) complexes of the type $\text{Rh}(\text{bident})(\text{CO})(\text{L})$ (where L is a C-, P-, N- or S-donor ligand) with chelating monoanionic bidentate ligands coordinated to rhodium via O,O- or N,O- donor atoms remain one of the predominantly utilized catalysts precursors in hydroformylation, isomerization and hydrogenation of olefins [1,2]. In the last decade, it was found out that these species are also able to catalyze coupling reactions of common reagents in ways that have not been demonstrated with other metal catalysts [3–8]. For example, the team of Fumitoshi Kakiuchi developed efficient protocols for the regioselective synthesis of (Z)-enol ethers, based on the reactions of anti-Markovnikov addition of alcohols to terminal acetylenes catalyzed by rhodium dicarbonyl complexes containing 2-methyl-8-quinolinolato ligand [4,9]. However, the rhodium (I) complexes containing 8-quinolinolato ligands

are less studied than those with β -diketone ligands. To our knowledge, no electrochemical and UV-absorption spectroscopic properties of such 8-quinolinolato rhodium (I) species were described up to date. Herewith, study of physico-chemical properties and determination of structures of new rhodium (I) complexes is essential not only to their chemistry, but also to the understanding their role in different processes.

From our point of view, dicarbonyl rhodium (I) complexes can also be applied as precursors in the construction of heterometallic complexes [10]. For example, previously, our group demonstrated that the treatment of manganese vinylidene $\text{Cp}(\text{CO})_2\text{Mn}=\text{C}=\text{CHPh}$ with $\text{Rh}(\text{acac})(\text{CO})_2$ resulted in binuclear μ -vinylidene MnRh complex $\text{Cp}(\text{CO})_2\text{Re}(\mu\text{-C}=\text{CHPh})\text{Rh}(\text{CO})(\text{acac})$ [11]. The feasibility of the synthesis of such heterobimetallic species is possible due to the lability of one of the carbonyl groups in the dicarbonyl rhodium (I) complexes. Unfortunately, attempts to synthesize any heterometallic complexes via reactions between $\text{Rh}(2\text{-Me-8-Oxq})(\text{CO})_2$ and $\text{Cp}(\text{CO})_2\text{M}=\text{C}=\text{CHPh}$ ($\text{M} = \text{Mn}, \text{Re}$) were unsuccessful. However, a literature search revealed no reports describing the electro-

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chemistry, UV spectra or molecular structures of Rh(I) complexes with the 2-methyl-8-quinolinolato ligand. Therefore, this work has been evolved into a study of series of such complexes, Rh(2-Me-8-Oxq)(CO)₂ (1), Rh(2-Me-8-Oxq)(PPh₃)(CO) (2) and Rh(2-Me-8-Oxq)[P(OPh)₃](CO) (3). Here we report the electrochemical and UV-spectroscopic properties of the Rh(I) 2-methyl-8-quinolinolato complexes for the first time. During this work, we also characterize the complexes 2 and 3 by IR and NMR spectroscopy, perform their X-ray diffraction study and develop a more straightforward synthetic method to 1.

2. Experimental

2.1. Materials

All operations and manipulations were carried out under an argon atmosphere. Solvents (diethyl ether, petroleum ether, hexane, dichloromethane, acetonitrile) were purified by distillation from the appropriate drying agents and stored under argon. Triphenylphosphine, triphenylphosphite and 2-methyl-8-quinoline (ABCR) were commercially available and used as received. Dicarbonyl(acetylacetonate)rhodium (I) Rh(acac)(CO)₂ was prepared according to literature procedure [12].

2.2. Measurements

Physical-chemical characteristics were obtained in the Krasnoyarsk Regional center of Research Equipment, Siberian Branch of the Russian Academy of Sciences. The IR spectra were recorded on the Shimadzu IR Tracer-100 spectrometer (Japan). The UV spectra were measured from 210 to 700 nm on Shimadzu UV-3600 Plus spectrometer. The ¹H, ¹³C{¹H} and ³¹P{¹H} NMR spectra were obtained using NMR spectrometer AVANCE III 600 (Bruker, Germany). The X-ray data were obtained with the Smart Photon II diffractometer (Bruker AXS, Germany). The course of reactions was monitored by IR spectroscopy.

2.3. Synthesis

2.3.1. Rh(2-Me-8-Oxq)(CO)₂

Rh(acac)(CO)₂ (122 mg, 0.473 mmol) was dissolved in diethyl ether (8 mL), then (2-Me-8-OxqH) (79 mg, 0.497 mmol) were added. The mixture was stirred at room temperature in argon atmosphere. The dark green crystalline precipitate appeared immediately. Petroleum ether (4 mL) was added to the reaction mixture. The precipitate was filtered on a Schott filter, washed with diethyl ether (2×2 mL) and petroleum ether (3×2 mL) and dried in vacuo to yield Rh(2-Me-8-Oxq)(CO)₂ as bronze-colored solid (125 mg, 0.393 mmol, 83%). Anal. Found: C, 43.86; H, 2.30; N, 4.19%. Calc. for C₁₂H₈NO₃Rh (317): C, 45.45; H, 2.54; N, 4.42%. IR, cm⁻¹: 2080 cm⁻¹, 2003 cm⁻¹ (CH₂Cl₂); 2065 cm⁻¹, 2007 cm⁻¹ (KBr). The ¹³C and ¹H NMR data obtained for the CDCl₃ solution of the complex are in good agreement with the literature data [9].

2.3.2. Rh(2-Me-8-Oxq)(CO)(PPh₃)

Rh(2-Me-8-Oxq)(CO)₂ (117 mg, 0.369 mmol) was suspended in diethyl ether (8 mL) with stirring in an argon atmosphere at room temperature, then PPh₃ (97 mg, 0.370 mmol) was added. A yellow precipitate formed, which was filtered on a Schott filter, washed with diethyl ether (2 × 2 mL) and petroleum ether (3 × 2 mL) and dried in vacuo to yield 165 mg (0.299 mmol, 81%) of product. Anal. Found: C, 63.28; H, 3.87; N, 2.90%. Calc. for C₂₉H₂₃NO₂PRh (551): C, 63.17; H, 4.20; N, 2.54%. IR, cm⁻¹: 1961 cm⁻¹(CH₂Cl₂); 1950 cm⁻¹ (KBr).

¹H NMR (CDCl₃, 25°C) δ, ppm [J, Hz]: 3.03 (s, 3H, -CH₃); 6.74 (d, J_{RhH} = 1.1, J_{HH} = 8.0, 1H, H₇); 6.90 (d, J_{HH} = 7.8, 1H, H₅); 7.29

(t, J_{HH} = 8.0, 1H, H₆); 7.33 (d, J_{HH} = 8.5, 1H, H₃); 7.42–7.50 (m, 9H, H of PPh₃); 7.84 (m, 6H, H of PPh₃); 8.11 (d, J_{HH} = 8.5, 1H, H₄).

¹³C{¹H} NMR (CDCl₃, 25°C) δ, ppm [J, Hz]: 29.9 (d, ³J_{RhC} = 1.7, -CH₃); 111.4 (s, C₅); 114.9 (d, ³J_{RhC} = 1.7, C₇); 122.7 (d, ³J_{RhC} = 3.5, C₃); 128.2 (d, J_{CP} = 10.4, C_{meta} of PPh₃); 128.9 (s, C₆); 130.3 (d, J_{CP} = 2.4, C_{para} of PPh₃); 132.1 (d, ³J_{RhC} = 10.1, C_{4a}); 132.8 (d, J_{CP} = 50.3, C_{ipso} of PPh₃); 134.7 (d, J_{CP} = 11.4, C_{ortho} of PPh₃); 138.5 (s, C₄); 144.3 (d, ²J_{RhC} = 1.7, C_{8a}); 157.8 (d, ²J_{RhC} = 1.7, C₂); 164.4 (d, ²J_{RhC} = 4.5, C₈); 191.3 (dd, J_{RhC} = 70.1, -CO).

³¹P{¹H} NMR (CDCl₃, 25°C) δ, ppm [J, Hz]: 43.52 (J_{PRh} = 172.0).

2.3.3. Rh(2-Me-8-Oxq)(CO)[P(OPh)₃]

Rh(2-Me-8-Oxq)(CO)₂ (50 mg, 0.158 mmol) was suspended in diethyl ether (6 mL) with stirring in an argon atmosphere at room temperature, then P(OPh₃) (0.043 mL, 51 mg, 0.165 mmol) was added. A yellow precipitate formed, which was filtered on a Schott filter, washed with diethyl ether (2 × 2 mL) and petroleum ether (3 × 2 mL) and dried in vacuo to yield 78 mg (0.131 mmol, 82%) of product. Anal. Found: C, 58.13; H, 3.72; N, 2.66%. Calc. for C₂₉H₂₃NO₅PRh (599): C, 58.02; H, 4.03; N, 2.33%. IR, cm⁻¹: 1988 cm⁻¹ (CH₂Cl₂); 1983 cm⁻¹ (KBr).

¹H NMR (CDCl₃, 25°C) δ, ppm [J, Hz]: 2.87 (s, 3H, -CH₃); 6.91 (m, 2H, H_{5±H7}); 7.18 (t, J_{HH} = 7.8, 3H, H_{para} of PPh₃); 7.26 (d, J_{HH} = 8.2, 1H, H₃); 7.34 (m, 7H, H of PPh₃ + H₆); 7.47 (m, 6H, H of PPh₃); 8.08 (d, J_{HH} = 8.5, 1H, H₄).

¹³C{¹H} NMR (CDCl₃, 25°C) δ, ppm [J, Hz]: 29.6 (d, ³J_{RhC} = 1.7, -CH₃); 111.7 (s, C₅); 115.1 (d, ³J_{RhC} = 1.7, C₇); 121.2 (d, ⁶J_{PC} = 5.2, C_{para} of P(OPh)₃); 122.4 (d, ³J_{RhC} = 5.2, C₃); 124.8 (d, ⁴J_{PC} = 1.0, C_{meta} of P(OPh)₃); 128.4 (s, C_{4a}); 129.0 (s, C₆); 129.5 (s, C_{ortho} of P(OPh)₃); 139.1 (s, C₄); 143.7 (d, ²J_{RhC} = 3.1, C_{8a}); 151.4 (d, ²J_{PC} = 6.6, C_{ipso} of P(OPh)₃); 157.9 (d, ²J_{RhC} = 2.1, C₂); 168.0 (d, ²J_{RhC} = 4.9, C₈); 188.6 (dd, J_{RhC} = 68.7, -CO).

³¹P{¹H} NMR (CDCl₃, 25°C) δ, ppm [J, Hz]: 120.07 (J_{PRh} = 292.5).

2.3. X-ray diffraction studies

Crystal data and X-ray experimental details for the complexes 2 and 3 are given in Table 1 and in the supplementary materials.

Bright yellow crystals of carbonyl(2-methyl-8-quinolinolato)(triphenylphosphane)rhodium Rh(2-Me-8-Oxq)(CO)(PPh₃) (2) and carbonyl(2-methyl-8-quinolinolato)(triphenyl phosphite)rhodium Rh(2-Me-8-Oxq)(CO)[P(OPh)₃] (3) complexes suitable for the X-ray crystallography were grown from methylene chloride solutions under argon atmosphere at +5 °C. The experimental data were collected on a Smart Photon II diffractometer (Bruker AXS) with CCD area detector and graphite monochromator using MoKα (λ = 0.71073 Å) radiation at room temperature. Absorption corrections have been applied using multiscan procedure [13]. The structures were solved by direct methods and refined by full-matrix least squares on F², using SHELX programs [14,15]. Hydrogen atoms have been placed in calculated positions and taken into account in the final stages of refinement in the “riding model” approximation.

2.4. Electrochemistry

The electrochemical measurements were carried out in acetonitrile solutions with 0.1 M [Et₄N][BF₄] as a supporting electrolyte. The cyclic voltammograms (CV) and polarograms were recorded on an IPC-Pro M potentiostat (Volta, Saint-Petersburg, Russia) using a three-electrode system. The working electrode¹ was a stationary platinum (Pt) electrode of 1 mm diameter or a stationary glassy

¹ The application of different working electrodes offers an opportunity to study the oxidation and reduction properties of compounds in the wide range of accessible potentials. The measurement region of potentials in acetonitrile (vs. Ag/0.1 M

Table 1
Crystallographic data and the details of X-ray diffraction experiments.

	2	3
CCDC	2078783	2078782
Empirical formula	RhPNC ₂₉ O ₂ H ₂₃	RhPNC ₂₉ O ₅ H ₂₃
Formula weight	551	599
T(K)	296	
Crystal system	Triclinic	
Space group	P-1 (2)	
a (Å)	9.3599(5)	9.3211(3)
b (Å)	9.8661(5)	11.6208(4)
c (Å)	14.4994(7)	12.6026(5)
α (°)	98.1870(10)	96.5100(10)
β (°)	93.0600(10)	106.1780(10)
γ (°)	114.9920(10)	94.8790(10)
V (Å ³)	1191.56(11)	1292.82(8)
d _{calc} (g/cm ⁻³)	1.537	1.540
Z	2	2
μ (mm ⁻¹)	0.811	0.763
F(000)	560	608
Radiation	MoKα (λ=0.71073)	
2θ-range for data collection (°)	2.86 to 54.334	3.4 to 58
Index ranges	-12 ≤ h ≤ 12, -12 ≤ k ≤ 12, -18 ≤ l ≤ 18	-12 ≤ h ≤ 12, -15 ≤ k ≤ 15, -17 ≤ l ≤ 17
Reflections collected	13,531	15,255
Uniq. refl./R _i /R _σ	5280/ 0.0370/ 0.0428	6845/ 0.0408/ 0.0541
Number of parameters/restraints	308/ 0	336/ 0
R1 [I > 2σ(I)]	0.0349	0.0398
R1/wR2 [all data]	0.0486/0.0756	0.0634 / 0.0867
Goof	1.037	1.023
Δρ _{min} /Δρ _{max}	-0.28/0.36	-0.35/0.41

carbon (GC) electrode of 4 mm diameter in a Teflon housings or a dropping mercury electrode (DME) with a positive margin drop ($m = 3.6$ mg/s, $\tau = 0.23$ s). The reference electrode was Ag/0.1 M AgNO₃ in MeCN. Potentials are given versus Ag/0.1 M AgNO₃ in MeCN (they can be converted to V versus SCE by adding 0.337 V). The auxiliary electrode was a platinum wire. The reference electrode and the auxiliary electrode were separated from the bulk solution in a glass tube filled with an electrolyte solution and fitted with a porous plug. The number of the electrons transferred in a particular redox process was estimated by comparison of the wave height observed with those of the one-electron ferrocene⁺⁰ of the same concentration as well as through usual diagnostic electrochemical parameters.

3. Results and discussion

3.1. Synthesis

Previously [4], the reaction of dimethylammonium dicarbonyldichlororhodate [NH₂Me₂][RhCl₂(CO)₂] with 2-methyl-8-hydroxyquinoline in DMF was suggested by Kakiuchi's group for the synthesis of the complex 1 (Scheme 1, reaction (a)). However, to isolate the desired product Rh(2-Me-8-Oxq)(CO)₂ (1) obtained by this method, a large amount of solvents was required. At the same time, the team of Varshavsky previously showed that the analogous 8-quinolinolato rhodium (I) complex Rh(8-Oxq)(CO)₂ can be obtained by the substitution of the acetylacetonate ligand in Rh(acac)(CO)₂ with 8-hydroxyquinoline [16]. We found out that complex 1 can also be prepared in high yields by Varshavsky's approach using the reaction of dicarbonyl(acetylacetonate)rhodium (I) with 2-methyl-8-hydroxyquinoline. Moreover, in contrast to the "dicarbonyldichlororhodate" method, the isolation of Rh(2-Me-8-Oxq)(CO)₂ (1), in this case, was more straightforward and required significantly less solvent (see Experimental part and Supplementary material). The addition of triphenylphosphine

AgNO₃ in MeCN) is from 0.30 to -3.20 V at DME, from 2.00 to -2.20 V, and from 2.00 to -2.80 V at the Pt and GC electrodes, respectively.

Table 2
The main structural characteristics of 2-methyl-8-quinolinolato rhodium (I) complexes.

	Rh(2-Me-8-oxq)(CO)(PPh ₃) (2)	Rh(2-Me-8-oxq)(CO)[P(OPh) ₃] (3)
	Lengths, Å	
Rh-C1	1.794(4)	1.807(3)
C1-O1	1.156(4)	1.152(4)
Rh-N	2.155(2)	2.128(2)
Rh-O2	2.024(2)	2.018(2)
C2-O2	1.318(3)	1.326(3)
Rh-P	2.2565(7)	2.1724(7)
	Angles, (°)	
N-Rh-P	167.52(7)	167.08(7)
O2-Rh-C1	175.47(13)	175.37(11)
Rh-C1-O1	176.7(4)	176.0(3)
P-Rh-C1	90.33(10)	89.23(10)
N-Rh-O2	79.67(9)	80.89(9)
P-Rh-O2	87.94(6)	86.32(6)
N-Rh-C1	102.14(12)	103.60(12)

and triphenylphosphite to complex 1 resulted in the formation of complexes Rh(2-Me-8-Oxq)(CO)(PPh₃) (2) and Rh(2-Me-8-Oxq)(CO)[P(OPh)₃] (3), respectively.

3.2. Molecular structures

The molecular structures of complexes 2 and 3 were established by an X-ray diffraction study. Suitable crystals were grown from methylene chloride solutions. The views of the structures are shown in Fig. 1. Crystal data and refinement parameters are shown in Table 1. Selected bond distances and angles of the complexes are given in Table 2.

Both complexes crystallized in the triclinic space group P-1 (2), their molecular structures are similar and display a slightly distorted square planar geometry, with PPh₃ and P(OPh)₃ ligands disposed trans to the nitrogen atom of the 2-methyl-8-quinolinolato chelate (N-Rh-P angles = 167.52(7)° for 2 and 167.08(7)° for 3). Both complexes have the 2-methyl-8-quinolinolato chelate, the carbonyl group and the P atom of phosphorous ligand in the

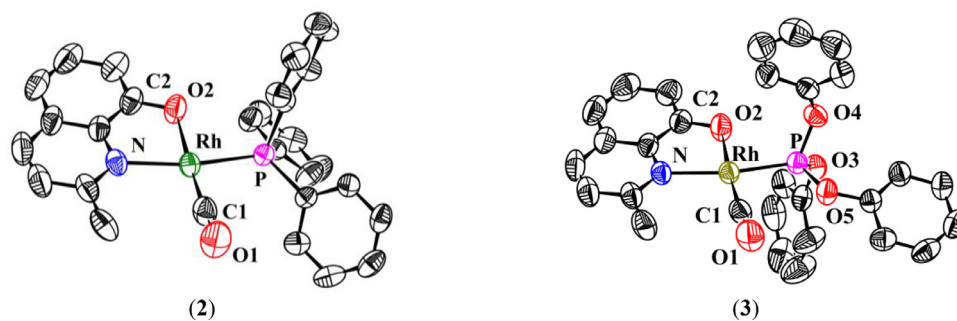


Fig. 1. Molecular structures of: Rh(2-Me-8-Oxq)(CO)(PPh₃) (2), Rh(2-Me-8-Oxq)(CO)[P(OPh)₃] (3).

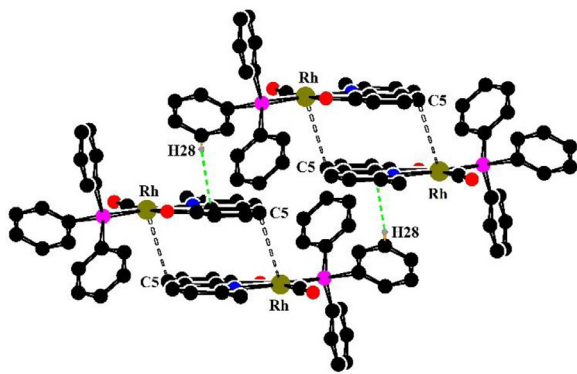


Fig. 2. The packing diagram of Rh(2-Me-8-Oxq)(CO)(PPh₃) (2).

same plane as expected for square planar coordination of the rhodium atom. The bond lengths and angles in 2 and 3 are close to each other (Table 2). However, one can detect the shortening of Rh-P and Rh-N bond lengths in complex 3 compared to the same bonds in 2 (by 0.084 and 0.027 Å, respectively). This shortening is apparently attributed to the better π -acceptor ability of the P(OPh)₃ ligand with respect to PPh₃ in 2. The Rh-CO distance in 3 is by 0.013 Å longer than in 2. Similar correlations in geometric parameters were observed for the analogous 8-quinolinolato rhodium (I) complexes Rh(8-Oxq)(CO)(PPh₃) [17,18] and Rh(8-Oxq)(CO)[P(OPh)₃] [19]. Moreover, a comparison of these complexes with 2 and 3 indicates that there are negligible structural differences between them. Only lengthening of Rh-N bond distances in 2 and 3 by ca. 0.04 Å should be noted, compared to 8-quinolinolato rhodium (I) complexes.

Square planar 16-electron rhodium (I) complexes are known to be prone to stack, producing continuous one-dimensional chains or dimers in the solid state [20–22]. These aggregation properties were showed to control by metallophilic rhodium-rhodium interactions caused by the sigma-sigma interaction of d_{z^2} molecular orbitals [23]. In the crystals of 2, no metallophilic Rh(I)⋯Rh(I) interaction are observed. The shortest rhodium-rhodium distances are 6.846 Å. However, more detailed study of crystal packing showed that molecules of Rh(2-Me-8-Oxq)(CO)(PPh₃) (2) form centrosymmetric dimers due to π -stacking interactions between rhodium 2-methyl-8-quinolinolato fragments [Rh(2-Me-8-Oxq)] with interplanar distance of 3.481 Å and the shortest interatomic Rh⋯C5 (2-x, 1-y, 2-z) distance of 3.682(4) Å (Fig. 2). In these dimers the Rh(2-Me-8-oxq)(CO)(PPh₃) molecules are related by an inversion center. Beside, weak interactions of the C-H⋯C type between dimers were detected in the crystal of 2. The shortest one of 2.782(5) Å was found between the meta hydrogen H28(1+x, y, z) of PPh₃ ligand and C7 atom of 2-methyl-8-quinolinolato unit (C28-H28⋯C7 angle is equal to 143°). The interplanar distance be-

tween the two nearest molecules of neighboring dimers of Rh(2-Me-8-Oxq)(CO)(PPh₃) (2) is 1.697 Å (Fig. 2). In contrast to 2, complex Rh(2-Me-8-Oxq)(CO)[P(OPh)₃] (3) exists as a monomer in the solid state with no intermolecular contacts. The shortest intermolecular distance observed in 3 between the oxygen of CO ligand and hydrogen of P(OPh)₃ is 3.255 Å and cannot be defined as an interaction. The absence of any intermolecular contacts between molecules in the crystal of 3 can be attributed to the larger steric size of OPh substituents vs. Ph. Thus, despite the similarity of the geometric parameters of molecules of both complexes, their crystal packing is very different.

3.3. NMR and IR parameters

The ¹H, ¹³C, ³¹P NMR and the IR data for the complexes 2 and 3 were obtained (see Table 1S and Experimental part). The structure of these complexes in solution can be deduced from the combined NMR and IR data, which are similar to those of previously described Rh(2-Me-8-Oxq)(CO)₂ (1) and 8-quinolinolato rhodium complexes [9,16,19,24]. The ¹H and ¹³C resonances of 2-methyl-8-quinolinolato ligand of 2 and 3 were assigned on the basis of the published data of relative rhodium (I) complexes with 8-quinolinolato ligand. Overall, chemical shifts of this ligand of 2 and 3 ¹H and ¹³C NMR spectra are comparable with those of 1 and only minor differences are observed [9]. For example, the carbon atom of phenolic function in the ¹³C NMR spectra of 2 (164.4 ppm) are upfield shifted by ~ 2.5 ppm in comparison to those of 1 (167.0 ppm) and 3 (168.0 ppm) containing better π -acceptor CO and P(OPh)₃ groups. The signals of PPh₃ and P(OPh)₃ ligands in the ¹H, ¹³C, ³¹P NMR spectra of 2 and 3 are found in regions that are typical for these ligands coordinated to the metal center.

The IR spectra of 2 and 3 in KBr pellets contain intense carbonyl group stretching bands at 1950 and 1983 cm⁻¹, respectively. Carbonyl carbon resonance in the ¹³C NMR spectra of these complexes in CDCl₃ solutions appears as doublet of doublets at 191.3 ppm ($J_{\text{RhC}} = 70.1$ Hz) and 188.6 ppm ($J_{\text{RhC}} = 69.0$ Hz), respectively. Comparison of IR data of 1–3 revealed a decrease of $\nu(\text{CO})$ frequencies in order of decreasing π -acceptor and increasing σ -donor ability of ligands from CO to P(OPh)₃ and PPh₃. The downfield shift of carbon resonances of CO group is also observed in the ¹³C NMR spectra of 1–3 in the same order. The same tendencies in changes of $\nu(\text{CO})$ values and carbonyl δ ¹³C shifts was detected for the series of the analogous 8-quinolinolato rhodium (I) complexes Rh(8-Oxq)(CO)L (L = CO, PPh₃, P(OPh)₃) [16,24]. It is worth noting that the differences in the IR and NMR parameters of carbonyl groups between the 2-methyl-8-quinolinolato rhodium (I) complexes (1–3) and their 8-quinolinolato analogues are minor. For example, an upfield shift of δ ¹³C carbon resonances of CO ligands by ~ 1 ppm can be noted for 1–3 in comparison to Rh(8-Oxq)(CO)L (L = CO, PPh₃, P(OPh)₃).

Table 3

UV/vis spectroscopic data of 2-methyl-8-quinolinolato rhodium (I) complexes 1–3 ($C = 0.5$ mM, $L = 2$ mm), 2-Me-8-OxqH, its protonated and deprotonated forms in acetonitrile solutions ($C = 1$ mM, $L = 2$ mm).

Compound	λ , nm	ϵ , L·mol ⁻¹ ·cm ⁻¹	$\Delta H_{1/2}$, cm ⁻¹
2-Me-8-OxqH	303	1500	3700
	243	19700	2500
[2-Me-8-OxqH ₂] ⁺	361	700	4200
	324	1500	2600
[2-Me-8-Oxq] ⁻	258	19000	2400
	396	2160	3800
	349	3820	1500
	266	15000	2500
Rh(2-Me-8-Oxq)(CO) ₂ (1)	430	3300	3300
	369	2800	2600
	273	28800	2400
Rh(2-Me-8-Oxq)(CO)(PPh ₃) (2)	415	3500	3400
	343	4400	2800
	271	20400	2300
Rh(2-Me-8-Oxq)(CO)[P(OPh) ₃] (3)	428	3300	3100
	385	3200	3000
	270	24500	2300

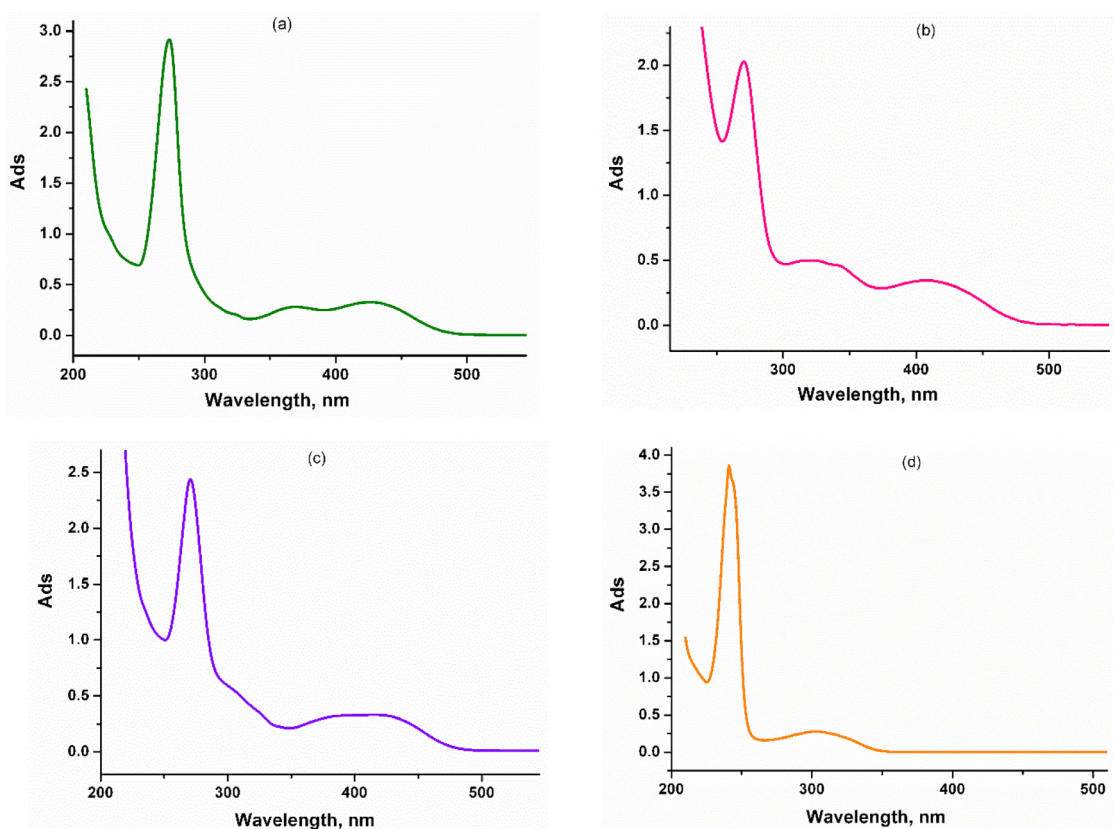


Fig. 3. UV/vis spectra of: (a) – Rh(2-Me-8-Oxq)(CO)₂ (1), (b) – Rh(2-Me-8-Oxq)(CO)(PPh₃) (2), (c) – Rh(2-Me-8-Oxq)(CO)[P(OPh)₃] (3), (d) – 2-Me-8-OxqH in MeCN.

3.4. UV/vis absorption spectra

The UV/vis-absorption spectra of the complexes 1–3, as well as 2-methyl-8-hydroxyquinoline, its protonated and deprotonated forms, were obtained in CH₃CN solutions. The UV data obtained are given in Table 3, the spectra of 1–3 are shown in Fig. 3. The spectrum of 2-methyl-8-hydroxyquinoline shows two intense absorption bands at $\lambda_1 = 303$ nm ($\epsilon = 1630$) and $\lambda_2 = 243$ nm ($\epsilon = 23,000$). In the spectra of protonated [2-Me-8-OxqH₂]⁺ and deprotonated (2-Me-8-Oxq⁻) forms of the ligand, a red shift of electronic transitions is observed, together with an appearance of new low-lying bands at 363 [2-Me-8-OxqH₂]⁺ and 400 [2-Me-8-

Oxq]⁻ nm (Table 3). These results correlate with published data on the UV spectroscopy study of 8-hydroxyquinoline [25,26]. The UV/vis-spectra of the complexes 1–3 are quite similar to that of the deprotonated form of 2-methyl-8-hydroxyquinoline. However, the absorption bands of 1–3 are red-shifted to a different extent relatively the [2-Me-8-Oxq]⁻ form indicative of chelation of rhodium (I) center with 2-methyl-8-quinolinolato ligand. Thus, the observed maximum of absorptions of complexes 1–3 are ligand centered (assigned to the ILCT $\pi \rightarrow \pi^*$ transition [26] and O \rightarrow N charge-transfer) but perturbed to a different extent by the rhodium and its ligand environment. For example, a sequential blue shift of the λ_3 band on going from 1 (430 nm) to 3 (428 nm) and 2 (415 nm)

Table 4
Electrochemical characteristics of 2-methyl-8-quinolinolato rhodium (I) complexes and 2-Me-8-OxqH (MeCN, 0.1 M Et₄NBF₄, 1 mM, Ag/ 0.1 M AgNO₃ in MeCN).

Compounds	E _{1/2} , V (n)				
	Pt		GC		DME
	Ox	Red	Ox	Red	Red
Rh(2-Me-8-Oxq)(CO) ₂ (1)	0.53(2)	-1.86(1)	0.60(2)	-1.93(1) ^a	-1.96(1) -2.72(<1)
Rh(2-Me-8-Oxq)(CO)(PPh ₃) (2)	0.28(2)	–	0.30(2) ^a	-2.30(1) ^a	-2.32(1) -2.72(<1) -2.95(<1)
Rh(2-Me-8-Oxq)(CO)[P(OPh) ₃] (3)	0.38(2)	–	0.40(2) ^a	-2.24(1) ^a -2.66(<1) ^a	-2.26(1) -2.70(<1)
2-Me-8-OxqH	0.58(2)	–	0.63(2)	-2.40(1) ^a	-2.41(1) -2.72(<1)

^aThe number of electrons transferred in a particular electrochemical stage (the sign “<” indicates that the wave height is smaller than the height of the one-electron wave).^aQuasi-reversible stage.

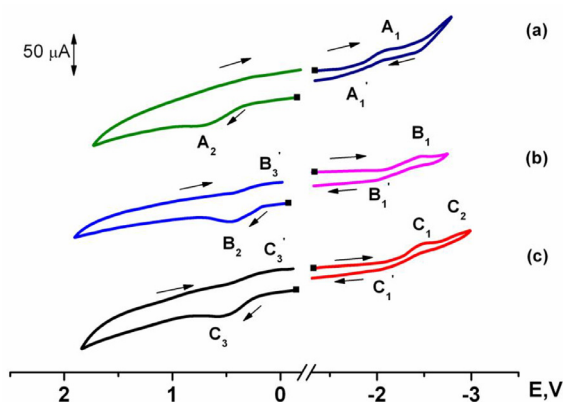


Fig. 4. Cyclic voltammograms of: (a) – Rh(2-Me-8-Oxq)(CO)₂ (1), (b) – Rh(2-Me-8-Oxq)(CO)(PPh₃) (2), (c) – Rh(2-Me-8-Oxq)(CO)[P(OPh)₃] (3) (GC, MeCN, 0.1 M Et₄NBF₄, C = 1 mM, Ag/0.1 M AgNO₃ in MeCN, scan rate is 25 mVs⁻¹).

is observed, that caused by the substitution of one CO group by σ -donor phosphorous ligands and may indicate the increase of backdonation from Rh atom to quinoline ligand.

In the electronic spectra of previously studied complexes with 8-quinolinolato type ligands the analogous ligand-centered transitions were observed. For example, the spectrum of Cr(8-Oxq)₃ displayed one unresolved absorption band at < 300 nm and two well resolved those at 413, 319 nm [27]. Similar features were observed in the UV-absorption spectra of Al(III), Rh(III), Ir(III), Pt(II) and Fe(III) 8-quinolinolato complexes [25,26]. However, in comparison to the Cr(III) and Fe(III) species [26,27], any bands that can be assigned to metal-centered d-d transitions were not found in the absorption spectra of Rh(8-Oxq)(CO)L (L = CO, PPh₃, P(OPh)₃).

3.5. Electrochemical study

The redox properties of rhodium (I) complexes Rh(2-Me-8-oxq)(CO)(L) [L = CO (1), PPh₃ (2), P(OPh)₃ (3)] and, for comparison, of the 2-methyl-8-hydroxyquinoline were studied in acetonitrile solutions by dc polarography at a DME and cyclic voltammetry at Pt or GC electrodes. The electrochemical characteristics of 1–3 and 2-Me-8-OxqH are given in Table 4. The cyclic voltammograms at GC electrode of complexes 1–3 are shown in Fig. 4.

The CVs of complexes 1–3 at Pt and GC-electrodes demonstrate one two-electron oxidation stage. The quasi-reversible oxidation waves are observed in the CV of 2 ($I_{pa}/I_{pc} = 0.68$) and 3 ($I_{pa}/I_{pc} = 0.81$) at GC electrode (Table 4, Fig. 4 b,c). In contrast, the reduction of the complexes differs depending on the electrodes'

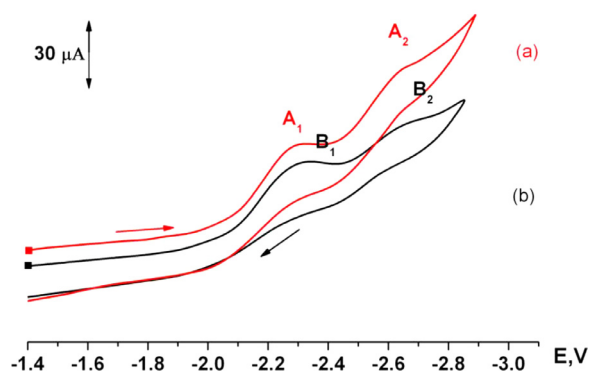
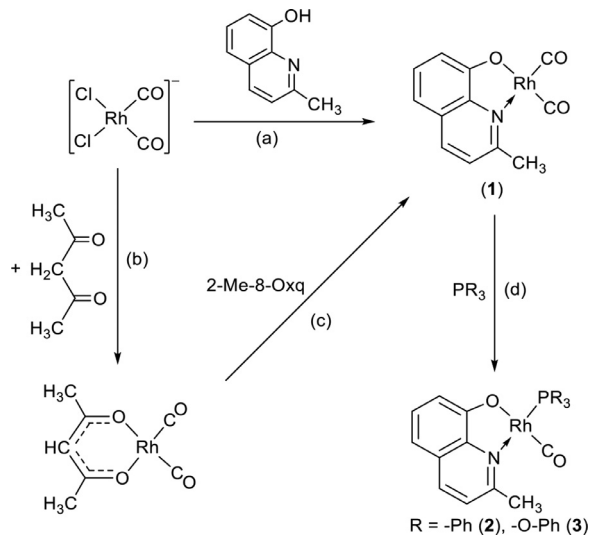
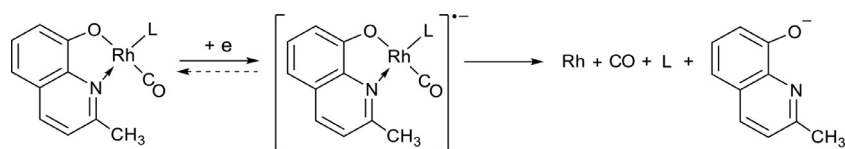


Fig. 5. Cyclic voltammograms of: (a) – Rh(2-Me-8-oxq)(CO)[P(OPh)₃] (3) with the addition of phenol at a ratio of 1:2, (b) – Rh(2-Me-8-oxq)(CO)[P(OPh)₃] (3) (GC, MeCN, 0.1 M Et₄NBF₄, C = 1 mM, Ag/0.1 M AgNO₃ in MeCN, scan rate is 25 mVs⁻¹).

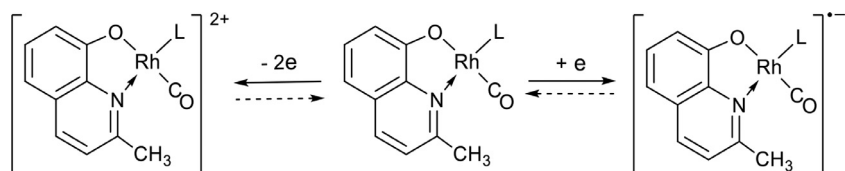


Scheme 1.

material and the nature of the ligands. However, the first reduction waves observed in the CV of 1–3 at all electrodes are one-electron and, in the case of GC electrode, quasi-reversible ($I_{pc}/I_{pa} = 0.46$ (1), 0.44 (2); 0.54 (3) [28]) (Table 4, Fig. 4). A comparison of the E_{1/2} values of the oxidation and the first reduction stages of 1–3 clearly showed that substitution of one CO group in the complex 1 by PPh₃ and P(OPh)₃ lead to a cathodic shift of the redox potentials of 2 and 3 (Table 4). The E_{1/2} values of 1–3 shifted to the



Scheme 2.



Scheme 3.

cathodic region in the order $1 < 3 < 2$ that is consistent with the electron-donating ability of the phosphorous ligands. It should be noted that the shift of $\nu(\text{CO})$ bands in the low-frequency region in the IR spectra and the blue shift of the λ_3 absorptions bands in the UV spectra also occurred in this order.

The second reduction wave is observed in the cyclic voltammogram of complex 3 at GC-electrode and polarograms of complexes 1–3 (Table 4, Fig. 4c, peak C₂). The $E_{1/2}$ of this wave almost coincides with the reduction potential value of second reduction wave ($E_{1/2} = -2.72$ V) of the free 2-Me-8-OxqH (Table 4). Thus, it may be assumed that one-electron reduction of complexes 1–3 results in the formation of the anion of this ligand. We studied the electrochemical behavior of complex 3 in the presence of phenol as a proton donor. The cyclic voltammogram in the range of potentials from 0.0 V to 2.00 V didn't change (Fig. 1S of supplementary materials) when phenol was added to the solution of 3 (in a 1:2 ratio); only a one-electron wave of phenol oxidation appeared at $E_{1/2} = 1.50$ V (Fig. 1S of Supplementary materials). However, the presence of the phenol caused an increase in the high of the second reduction wave of 3 and a slight anodic shift of its $E_{1/2}$ value (Fig. 5a, peak A₂) compared to the CVs of the initial solution of the complex (Fig. 5, peak B₂). The coincidence of the $E_{1/2}$ values between the A₂ wave of 3, observed at the addition of the proton source, and the second reduction B₂ wave of the 2-methyl-8-hydroxyquinoline indicated the formation of the identical one-electron reduction products, namely 2-methyl-8-quinolinolato anion. Therefore, the reduction of 1 and 2 should also result in the formation of [2-Me-8-Oxq][−] as a product of decomposition of their radical anions.

The half-wave reduction potential value of the third stage in the polarogram of 2 or the second reduction stage in the CV of 3 at the GC electrode coincides with the reduction potential value of PPh₃ ($E_{1/2} = -2.95$ V) or P(OPh)₃ ($E_{1/2} = -2.65$ V) at the DME. This observation demonstrates the formation of free PPh₃ or P(OPh)₃ ligands, confirming the decomposition of the radical anions of the complexes. Previously [29], the one-electron reduction of Rh(I) β -diketonate complexes were found to result in their complete decomposition. The one-electron reduction of complexes 1–3 should proceed in the same way to give a radical anion, which rapidly decomposes to rhodium (0), free CO, PPh₃ or P(OPh)₃, and the [2-Me-8-Oxq][−] anion (Scheme 2).

The two-electron oxidation process of complexes 1–3 proceeds according to a scheme analogous to rhodium (I) complexes with β -diketonate ligands [30,31] and leads to the formation of dication Rh (III) species. In general, the redox conversion scheme for complexes 1–3 is given on Scheme 3.

4. Conclusion

In this article, we demonstrated that the known Rh(2-Me-8-Oxq)(CO)₂ complex (1) was easily accessible from the reaction of dicarbonyl(acetylacetonate)rhodium (I) with 2-methyl-8-hydroxyquinoline as a straightforward and solvent economic approach. The molecular structures of triphenylphosphine (2) and triphenylphosphite (3) substituted derivatives of 1 were determined. It is the first example of structurally characterized rhodium (I) complexes with the 2-methyl-8-quinolinolato ligand. The geometric parameters of both complexes are almost similar and indicate a slightly distorted square planar geometry at the rhodium center. Only differences in the Rh-P and Rh-N bond lengths of 2 and 3 should be noted. However, the crystal packing of the complexes is very different. In the crystal of 2 molecules of Rh(2-Me-8-Oxq)(CO)(PPh₃) form centrosymmetric dimers due to π -stacking interactions, whereas no intermolecular contacts in the crystal of 3 are observed at all. Complexes 2 and 3 were characterized by IR and NMR spectroscopy. For the first time, the UV spectroscopic and electrochemical study of rhodium (I) complexes with 8-quinolinolato type ligands were performed. The UV spectroscopic investigation of 1–3 and the initial 2-methyl-8-hydroxyquinoline revealed that all absorptions bands observed in the UV/vis spectra of the studied complexes belong to $\pi \rightarrow \pi^*$ transition and O \rightarrow N charge-transfer of 2-methyl-8-quinolinolato ligand. The electrochemical study established mechanisms of the complexes 1–3 redox reactions. Their two-electron oxidation leads to the formation of dication Rh (III) species. The reduction of the complexes is one-electron and leads to radical anions of 1–3, which undergoes rapid decomposition to rhodium (0), free CO, PPh₃ or P(OPh)₃, and the [2-Me-8-Oxq][−] anion.

The present study of the physical-chemical properties of the rhodium (I) complexes with 2-methyl-8-quinolinolato ligand 1–3 shows the relationship between these properties and the rhodium atom's ligand environment. The geometric, IR, NMR, UV-spectroscopic and electrochemical parameters of the complexes are the most responsive to change in the ligands' electronic properties (σ -donor/ π -acceptor ability) at the rhodium atom in Rh(2-Me-8-Oxq)(CO)(L) (L = CO, PPh₃, P(OPh)₃). At the same time, the differences in the aggregation properties of the complexes reflected in their crystal packing correlate with the steric properties of the substituents in phosphine and phosphite ligands. Thus, the obtained results on structural, spectroscopic and electrochemical properties of rhodium (I) complexes with 2-methyl-8-quinolinolato ligand would provide a piece of helpful information for further design and study of complexes of type Rh(2-Me-8-Oxq)(CO)(L).

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Victor V. Verpekin: Conceptualization, Investigation, Supervision, Writing – original draft, Writing – review & editing. **Alexander D. Vasiliev:** Data curation, Investigation. **Nikolay G. Maksimov:** Data curation, Investigation. **Galina V. Burmakina:** Data curation, Investigation, Writing – original draft. **Dmitry V. Zimonin:** Investigation, Visualization. **Tatyana S. Nedelina:** Data curation, Investigation, Methodology. **Oleg S. Chudin:** Investigation. **Anatoly I. Rubaylo:** Funding acquisition, Project administration.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2021.131557.

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