New semiquinone-catecholate rhodium complex with 2,2'-dipyridyl

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A new semiquinone rhodium complex, *viz.*, (2,2'-dipyridyl)(3,6-di-*tert*-butyl-*o*-benzosemiquinone)(3,6-di-*tert*-butylcatecholate)rhodium(III) (1), which is a structural analog of the known redox-isomeric cobalt complex, was prepared, isolated in the individual state. and characterized by X-ray analysis. magnetochemistry, and IR and ESR spectroscopy. At room temperature. compound 1, unlike the cobalt analog, is a complex of trivalent low-spin rhodium with one catecholate and one semiquinone ligand. However, broadening of the lines in the ESR spectra both of a solution and a powder of complex 1 with increasing temperature indicates that the redox-isomeric transformation occurs in this case as well. The equilibrium of this transformation is virtually completely shifted toward the low-spin semiquinone-catecholate isomer.

Key words: rhodium(III), *o*-semiquinone, redox isomerism, X-ray diffraction study, ESR spectra.

Redox isomerism (or valence tautomerism) is one of the most intriguing phenomena observed for *o*-semiquinone transition metal complexes.[1−3] The unique ability of these complexes to undergo reversible isomerization both in solutions and in the solid state *via* electron transfer from the metal atom to the ligand and in the opposite direction is determined by the "variable valence" (redox activity) of the *o*-semiquinone ligand.[4,5]
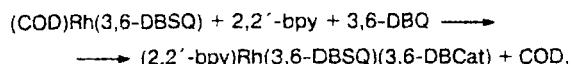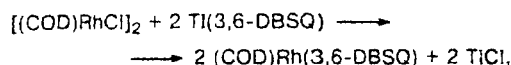
Redox isomerism has received the most detailed and in-depth study for six-coordinate cobalt complexes, whose coordination spheres contain a bidentate nitrogen-donor ligand, for example, dipyridyl, along with two *o*-semiquinone ligands.[6] The valence tautomerism of (2,2'-dipyridyl)(3,5-di-*tert*-butyl-*o*-benzosemiquinone)(3,5-di-*tert*-butylcatecholate)cobalt in solution was first reported in 1980.[1] More recently, redox-isomeric transformations were observed for (2,2'-dipyridyl)(3,6-di-*tert*-butyl-*o*-benzosemiquinone)(3,6-di-*tert*-butylcatecholate)cobalt in the crystalline phase.[5] Prerequisites to the occurrence of this phenomenon were found[7] and its thermodynamic[8,9] and kinetic parameters[7,9] were determined.

As well as being of interest by itself, redox isomerism is of great importance for understanding another unique property of *o*-semiquinone transition metal complexes, *viz.*, the photo(thermo)mechanical effect (the reversible bending of thin molecular crystals of the complex in responce to light or under the action of heating).[10,11] It was suggested that there is a possible association between the above-mentioned two phenomena.[5,12]

Since the photo(thermo)mechanical effect is most pronounced in rhodium complexes,[10,11] the aim of this work is to prepare the rhodium analog of the above-mentioned complexes and to study its structure and properties.

(2,2'-Dipyridyl)(3,6-di-*tert*-butyl-*o*-benzosemiquinone)(3,6-di-*tert*-butylcatecholate)rhodium(III) (1) was prepared from the cyclooctadiene-1,5-semiquinone rhodium(I) complex. which, in turn, was synthesized by exchange reaction from (cyclooctadiene)rhodium chloride and thallium semiquinolate[13]:

$$[(COD)RhCl]_2 + 2\ Tl(3,6\text{-}DBSQ) \longrightarrow$$
$$\longrightarrow 2\ (COD)Rh(3,6\text{-}DBSQ) + 2\ TlCl,$$

$$(COD)Rh(3,6\text{-}DBSQ) + 2,2'\text{-}bpy + 3,6\text{-}DBQ \longrightarrow$$
$$\longrightarrow (2,2'\text{-}bpy)Rh(3,6\text{-}DBSQ)(3,6\text{-}DBCat) + COD,$$

where COD is cycloocta-1,5-diene and 3,6-DBQ, 3,6-DBSQ, and 3,6-DBCat are 3,6-di-*tert*-butyl-*o*-benzoquinone, 3,6-di-*tert*-butyl-2-benzosemiquinone, and 3,6-di-*tert*-butylcatecholate, respectively.

Attempts to prepare complex 1 directly from the salt $RhCl_3 \cdot 4H_2O$ by exchange reactions with equimolar amounts of Tl(3,6-DBSQ), Tl_2(3,6-DBCat), and 2,2'-dipyridyl have not met with success.

Complex 1 was isolated in the individual state and characterized by IR and ESR spectroscopy, magnetochemistry, and X-ray analysis.

The IR spectrum of compound 1 has bands corresponding to fundamental vibrations of the dipyridyl and quinone fragments. The presence of the dipyridyl ligand is evidenced by the bands at 1620 and 775 cm^{-1} belonging to skeletal C—C vibrations and out-of-plane
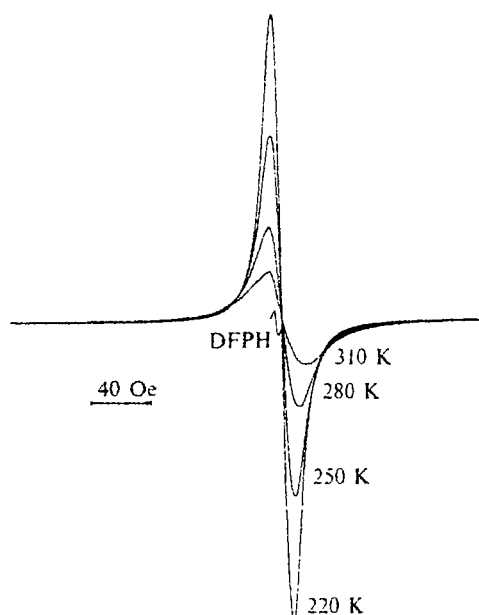
Fig. 1. ESR spectra of a solution of complex 1 in methyl-tetrahydrofuran.

Fig. 2. ESR spectra of a powder of complex 1.

C—H vibrations, respectively. The semiquinone fragment is characterized by the stretching vibration band of the C—O bond (one-and-a-half order bond) at 1565 cm^{-1}. The catecholate fragment is characterized by the C—O stretching vibration band at 1325 cm^{-1}. The bands at 1395, 1360, 1225, 1205, and 1165 cm^{-1} correspond to the *tert*-butyl groups. The distinguishing features of the IR spectrum are the presence of the broad band with v_{max} ~970 cm^{-1} and the long-wave-lengths wing, which begins at ~5000 cm^{-1} and extends to the near IR region. These bands ($\lambda \approx$ 1500 nm) belonging to electron transitions are typical of most of the known redox-isomeric *o*-semiquinone metal complexes. The origin of these bands was associated with catecholate—semiquinone charge transfer.[14—17] The band at 970 cm^{-1} remains to be identified.

The ESR spectrum of a solution of complex 1 in methyltetrahydrofuran is a single line (Fig. 1) whose integral intensity decreases and the width increases as the temperature increases (ΔH = 30 Oe at 220 K and 63 Oe at 310 K); g_{iso} = 2.0013. At a temperature lower than 200 K, the anisotropic spectrum with axial symme-

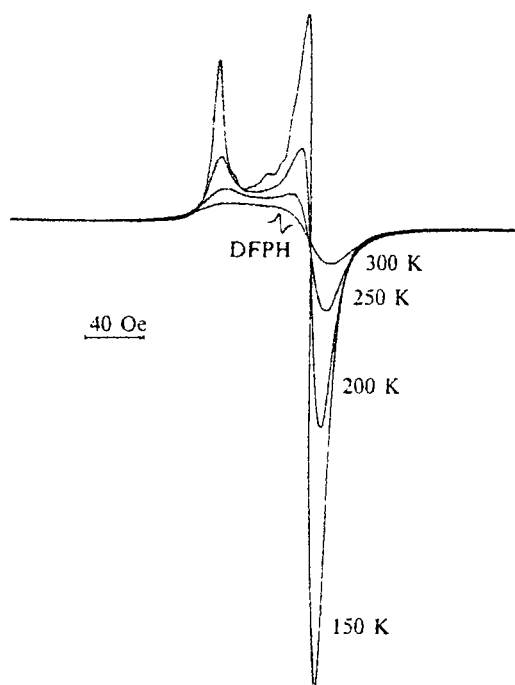try of the g tensor is observed: $g_\perp$ = 1.990, $g_\parallel$ = 2.030. The hyperfine interaction constant with the ^{14}N nucleus (a 1 : 1 : 1 triplet, $A_\perp$ = 7.5 Oe) is observed in the perpendicular component. Judging from the value of this constant, the ^{14}N nucleus is in the apical position with respect to the plane of the semiquinone ligand. The ESR spectrum of a powder of the complex is anisotropic throughout the temperature range under study: $g_\perp$ = 1.988 and $g_\parallel$ = 2.030. The line widths increase as the temperature increases (Fig. 2).

The temperature dependence of the static magnetic susceptibility of complex 1 was studied in the range of 77—295 K using the Faraday method. The effective magnetic moment (μ_{eff}) is 1.65 μ_B and it remains virtually unchanged in the temperature range under study.

X-ray analysis of complex 1 demonstrated that its structure (Fig. 3, Table 1) is analogous to that of the cobalt compound studied by us previously.[5] The environment about the Rh atom is a distorted octahedron.

Table 1. Selected bond lengths (*d*) and bond angles (ω) in molecule 1

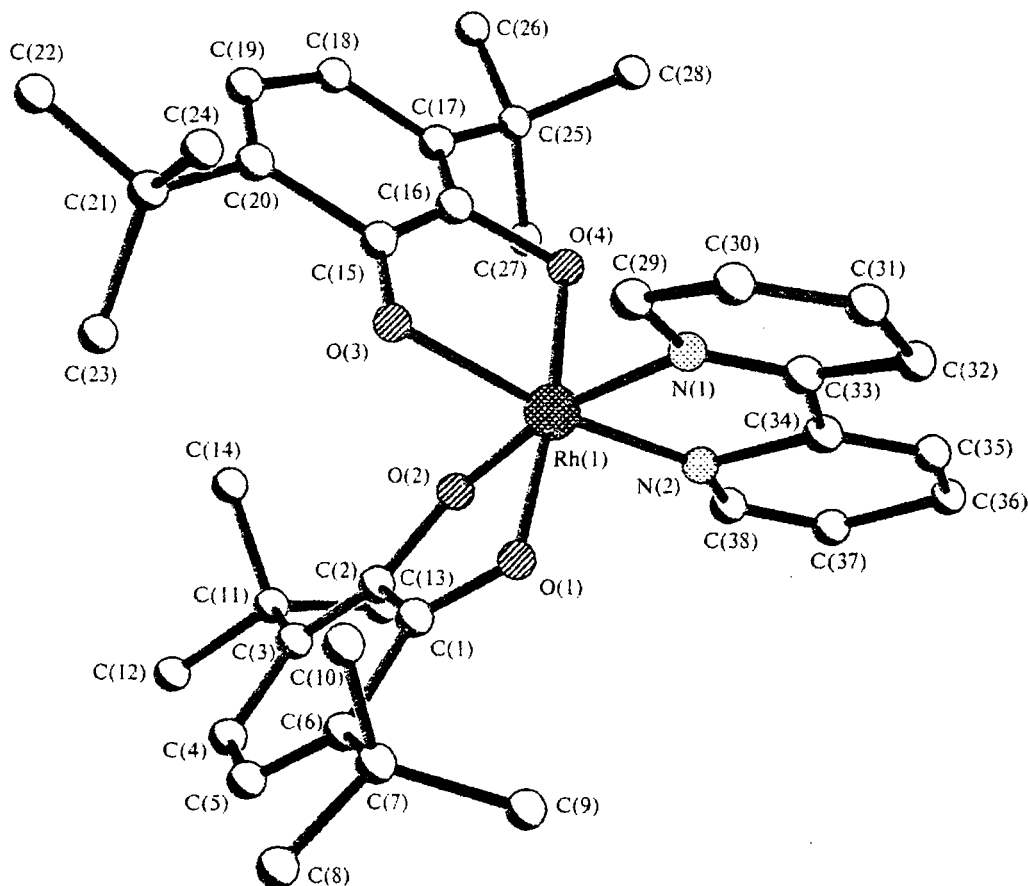| Bond	$d/Å$	Bond	$d/Å$	Angle	ω/deg
Rh(1)—O(1)	1.98(2)	O(1)—C(1)	1.34(3)	O(1)—Rh(1)—O(2)	85.4(7)
Rh(1)—O(2)	1.94(2)	O(2)—C(2)	1.39(3)	O(3)—Rh(1)—O(4)	83.0(7)
Rh(1)—O(3)	2.03(2)	O(3)—C(15)	1.29(3)	N(1)—Rh(1)—N(2)	81.5(6)
Rh(1)—O(4)	2.00(2)	O(4)—C(16)	1.35(3)	O(1)—Rh(1)—O(4)	173.3(3)
Rh(1)—N(1)	2.04(2)	C(1)—C(2)	1.45(3)	O(2)—Rh(1)—N(1)	168.1(7)
Rh(1)—N(2)	2.02(2)	C(15)—C(16)	1.40(4)	O(3)—Rh(1)—N(2)	168.4(7)

Fig. 3. Overall view of molecule 1.

The metallocycles in the benzoquinone ligands are some-what folded along the O...O lines (by 20.4° and 17.3° along the O(1)...O(2) and O(3)...O(4) lines, respec-tively). The dipyridyl ligand is also slightly nonplanar: the maximum deviation of the atoms from the mean plane of the ligand is 0.13 Å.

The Rh—O bond lengths in the catecholate ligand (Rh(1)—O(1), 1.98(2) Å; and Rh(1)—O(2), 1.94(2) Å) are ~0.05 Å shorter than those in the semiquinone ligand (Rh(1)—O(3), 2.03 Å; and Rh(1)—O(4), 2.00 Å). An analogous difference in the M—O bond lengths was also observed in semiquinone and catecholate complexes of other metals. Thus, in the Co^{III}(o-phen)(3,5-DTBSQ)(3,5-DTBCat) and Co^{II}(o-phen)(3,5-DTBSQ)$_2$ complexes, the above-men-tioned difference is even larger (~0.16 Å: 1.861—1.918 Å as opposed to 2.040—2.074 Å).[18] The Rh—O(SQ) bond lengths in the structure of 1 are close to the analogous bond lengths (1.96—2.06 Å) in the Rh(3,6-DB-4-Cl-SQ)(CO)$_2$ complex (3,6-DB-4-Cl-SQ is 3,6-di-*tert*-butyl-4-chloro-o-benzosemiquinone).[19]

The O—C and C—C bond lengths in the metallo-cycles (in the SQ ligand, O(1)—C(1), O(2)—C(2), and C(1)—C(2) are 1.34(3), 1.39(3), and 1.45(3) Å,

respectively; and in the Cat ligand, O(3)—C(15), O(4)—C(16), and C(15)—C(16) are 1.29(3), 1.35(3), and 1.40(4) Å, respectively) are also in the ranges typi-cal of benzoquinone ligands in the SQ and Cat forms.[17]

Hence, the X-ray diffraction data (in spite of the relatively poor accuracy due to the problems associated with the preparation of high-quality crystalline samples of compound 1) indicate that at room temperature one benzoquinone ligand in molecule 1 exists in the semi-quinone form and the second ligand exists in the catecholate form.

The values of the magnetic moment and the *g* factor as well as the moderate anisotropy of the *g* tensor confirm that one unpaired electron in molecule 1 is localized on the semiquinone ligand. Unlike the cobalt analog, the Rh atom in 1 exists in the trivalent low-spin state throughout the temperature range under study, which agrees well with a regular increase in ligand field splitting in going from cobalt to rhodium. However, this interpretation leaves unexplained the changes in the ESR spectra as the temperature changes.

Analysis of the experimental data[5] demonstrates that broadening of the lines in the ESR spectrum of a powder of (2,2′-dipyridyl)(3,6-di-*tert*-butyl-o-benzosemi-

quinone)(3,6-di-*tert*-butylcatecholate)cobalt caused by an increase in the temperature occurs well before the beginning of the rise in the curve of the magnetic moment. Hence, even a low concentration of an admixture of the second redox isomer causes substantial broadening of the ESR lines.

Broadening of the lines in the ESR spectrum as the temperature increases can be associated with two processes, which act separately or together: (1) a decrease in the relaxation time due to the appearance and/or a subsequent increase in the proportion of species with a large number of unpaired electrons; (2) relatively rapid (within the ESR time scale) exchange between two forms of the complex, one of which gives an indefinitely broad ESR line, and an increase in the proportion of this form (and, correspondingly, in the rate of exchange) as the temperature increases. This exchange is known for the cobalt complex[1,5]:

$$bpyCo^{III}(Cat)(SQ) \rightleftharpoons bpyCo^{II}(SQ)_2.$$
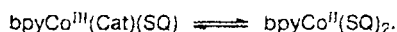
In the case of rhodium complex **1**, it can be suggested that the appearance of small amounts (several molar percent) of the bis(semiquinone) form of the complex leads to broadening of the ESR lines as a result of this exchange. At the same time, such concentrations of the "high-spin" isomer are insufficient to affect the static magnetic susceptibility.

Hence, taking into account the presence of the electron transition in the near IR region typical of semiquinone redox-isomeric complexes of cobalt and manganese and broadening of the ESR lines as the temperature changes, it can be stated that redox-isomeric transformation occurs in the case of rhodium complex **1** as well. However, the equilibrium of the redox isomerism is virtually completely shifted to the semiquinone-catecholate Rh^{III} complex.

Experimental

The ESR spectra were recorded on a Bruker ER 200D-SRC spectrometer. The IR spectra were measured on a Specord M-80 spectrometer as Nujol mulls.

The [(COD)RhCl]$_2$ complex was prepared according to a known procedure.[20]

(2,2´-Dipyridyl)(3,6-di-*tert*-butyl-*o*-benzosemiquinone)(3,6-di-*tert*-butylcatecholate)rhodium(III) (1). All operations associated with the synthesis and isolation of the complex were performed in evacuated tubes. The solvents were thoroughly dried and degassed before use. A solution of thallium semiquinolate (0.220 g, 1 mmol), which was prepared from 3,6-di-*tert*-butyl-*o*-benzoquinone,[21] in toluene (40 mL) was added to a solution of (COD)RhCl (0.246 g, 1 mmol) in toluene (50 mL). The reaction mixture was refluxed on a water bath for 1 h and then filtered. A solution of 2,2´-dipyridyl (0.156 g, 1 mmol) and 3,6-di-*tert*-butyl-*o*-benzoquinone (0.220 g, 1 mmol) in toluene (50 mL) was added to the resulting solution. Then the reaction mixture was heated at 80 °C for 30 min, concentrated to one-third of the initial volume, and kept at −10 °C for 12 h. The crystals that precipitated were

filtered off, washed with cold hexane, and dried *in vacuo*. Complex **1** was obtained as dark crystals in a yield of 0.454 g (65%). IR, v/cm^{-1}: 1620 w, 1585 s, 1480 s, 1322 s, 1300 w, 1225 v.w. 1165 s, 1000 v.s, 970 v.s, 810 w, 775 s, 670 w, 615 s, 495 s.

X-ray structural study of complex 1 was carried out on a Siemens P3/PC diffractometer at −20 °C (Mo-Kα radiation, graphite monochromator, $\theta/2\theta$ scanning technique in the range of $2° \leq 2\theta \leq 50°$, 3234 measured independent reflections of which 2350 reflections with $F > 4\sigma(F)$ were used in the refinement of the structure). Crystals of **1** are monoclinic, at 293 K $a = 10.712(5)$ Å, $b = 29.834(18)$ Å, $c = 12.108(5)$ Å, $\beta = 112.76(4)°$, $V = 3568(3)$ Å^3, $d_{calc} = 1.302$ g cm^{-3}, $\mu(Mo) = 0.519$ mm^{-1}, $Z = 4$, space group *Cc*.

The structure of **1** was solved by direct methods, which were followed by calculations of difference electron density syntheses. The positions of the H atoms were calculated from geometric considerations. The structure was refined by the full-matrix least-squares method with anisotropic thermal parameters for the Rh atom and isotropic thermal parameters for the remaining nonhydrogen atoms. The above-described mode of refinement of the structure of **1** was chosen because of the poor quality of the X-ray diffraction data due to the problems associated with the preparation of high-quality crystals of **1**. At the final stage of the refinement, the following weighting scheme was used: $w = 1/[\sigma^2(F^2) + (0.1890P)^2]$, where $P = (F_o^2 - 2F_c^2)/3$. With the aim of determining the absolute configuration of the molecule, the basic and centrosymmetrical alternatives of the structure of **1** were refined. The reported structure is characterized by the minimum value of the *R* factor $(R = 0.089)$.

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