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DISTORTION OF PLANARITY IN QUINONE LIGANDS. CRYSTAL AND MOLECULAR STRUCTURES OF THREE DUROQUINONE RHODIUM π-COMPLEXES

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SUMMARY

In the three duroquinone π-complexes of rhodium studied the coordinated quinone molecule acquires a boat-like conformation. However, the degree of planarity distortion is not sensitive to the second ligand and to steric hindrance in a quinone molecule.

INTRODUCTION

X-ray study of π-cyclopentadienyl-π-(2,6-di-tert-butyl-1,4-benzoquinone)-rhodium (IV) has shown[1] a large distortion of quinone ligand planarity. This ligand acquires a boat-like conformation with the dihedral angles $\alpha \approx 23°$ between the plane of four olefinic carbon atoms C(2), C(3), C(5) and C(6) and the planes of the bent-out triangles C(6), C(1), C(2) and C(3), C(4), C(5) going through the carbonylic and two adjoining carbon atoms (Fig. 1). Previously a planarity distortion of the duroquinone (DQ) molecule on coordination by a metal atom was assumed on the basis of the IR spectroscopic study[2] of complexes of the general formula $(\pi\text{-}C_5H_5)M$ (π-DQ) where M = Co, Rh, Ir. Such distortion, though not very large ($\alpha = 6°$) was first observed[3] by

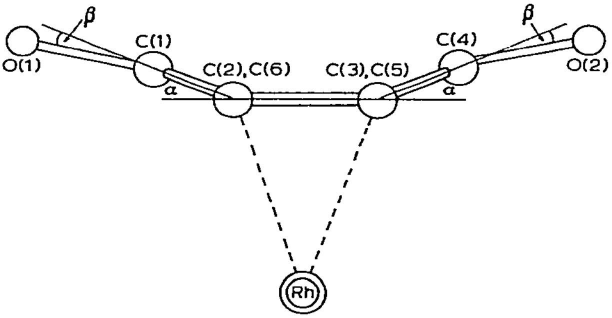

Fig. 1. The molecular projection on the plane going through the Rh atom parallel to the double bonds C(2)=C(3) and C(5)=C(6).

the X-ray study of π-1,5-cyclooctadiene-π-duroquinonenickel (V). Thus the greater distortion of quinone ligand in (IV) might be caused by steric hindrance due to bulky tert-butyl groups. Therefore we believed it of interest to study the rhodium π-complexes with duroquinone since its non-coordinated molecule is known[4] to be planar and thus is not sterically hindered to any significant degree.

The polarographic investigation[5] of duroquinone rhodium π-complexes (π-C_5H_5)Rh(π-DQ) (I), (π-C_9H_7)Rh(π-DQ) (II)[6] and ($C_5H_7O_2$)Rh(π-DQ) (III)[6] (C_5H_5=cyclopentadienyl, C_9H_7=indenyl, $C_5H_7O_2$=acetylacetonate) has shown a strong dependence of the reactivity of coordinated quinones on the electronic properties of the second ligand. This dependence does not permit to rule out the possibility that a duroquinone ligand conformation is somewhat affected by an alteration of the metal atom effective charge caused by replacement of the second ligand. To find out effects of steric hindrance and of the nature of the second ligand on a quinone ligand conformation we have undertaken the X-ray investigation of the three complexes (I), (II) and (III).

X-RAY DATA

Intensities of ca. 1400, 1000 and 1200 reflexions [for (I), (II) and (III) respectively] were estimated visually disregarding absorption correction (equi-inclination Weissenberg goniometer, unfiltered copper radiation). The structures were resolved by the heavy-atom technique and refined by the least-squares method (full matrix, isotropic temperature factors, Cruickshank's weighing scheme[7]). Standard deviations in bond lengths are 0.01–0.03 Å, in bond angles 1–3° depending on atomic numbers.

(I) is monoclinic, $a=10.18\pm0.01$, $b=16.36\pm0.02$, $c=8.82\pm0.01$ Å, $\gamma=98.5°\pm0.3°$, $D_m=1.52$, $D_c=1.53$ g/cm^3 for $Z=4$, space group $P2_1/b$, discrepancy index $R_F=0.121$, overall temperature factor $B=1.6$ Å^2.

(II) is monoclinic, $a=7.84\pm0.01$, $b=17.76\pm0.02$, $c=10.94\pm0.01$ Å, $\beta=97.1\pm0.3°$, $D_m=1.68$, $D_c=1.69$ g/cm^3 for $Z=4$, space group $P2_1/c$, $R_F=0.090$, $B=1.6$ Å^2.

(III) is triclinic, $a=8.80\pm0.01$, $b=11.92\pm0.01$, $c=8.21\pm0.01$ Å, $\alpha=96.3\pm0.3°$, $\beta=118.1\pm0.3°$, $\gamma=98.7\pm0.3°$, $D_m=1.63$, $D_c=1.66$ g/cm^3 for $Z=2$, space group $P\bar{1}$, $R_F=0.100$, $B=2.7$ Å^2.

MOLECULAR STRUCTURES

All the three crystal structures studied consist of discrete molecules. Figs. 2, 3 and 4 show projections of the molecules (I), (II) and (III) respectively onto the planes C(2), C(3), C(5), C(6) of two double C=C bonds of the DQ ligand; the deviations (in Å) of the DQ ligand atoms from these planes are also given. Main geometrical molecular parameters of all quinonic π-complexes studied and of the non-coordinated DQ are listed in Table 1.

In (I) all five Rh–C (cyclopentadienyl) distances are practically equivalent (2.17–2.21 Å, average, 2.19 Å); they agree well with those found in (IV) (2.19 Å) and in (π-C_5H_5)Rh[$C_6(CF_3)_6$] (2.18 Å)[8] and are very close to the single-bonded covalent radii sum 2.23 Å (1.46 Å for Rh[9], 0.77 Å for C). The deviation of molecular symmetry from ideal C_s is due to mutual shift and turn of ligands, probably caused by crystal packing forces. However, such lowering of molecular symmetry, at least in crystals, is

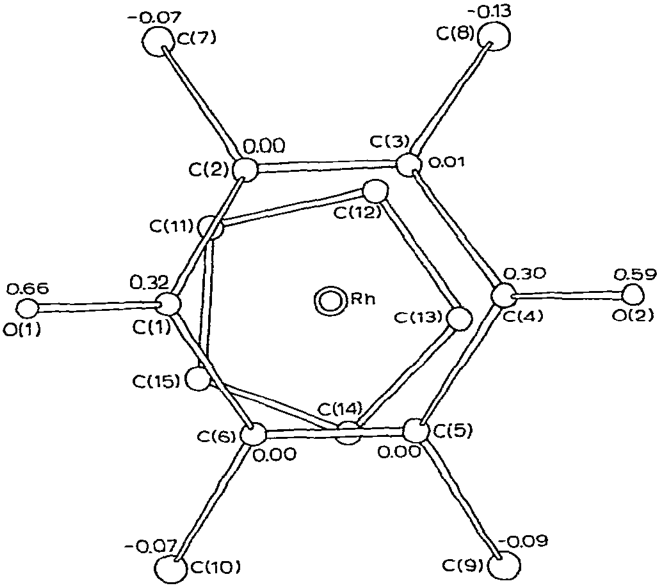

Fig. 2. The (π-C_5H_5)Rh(π-DQ) molecule projected on the plane going through C(2), C(3), C(5) and C(6).

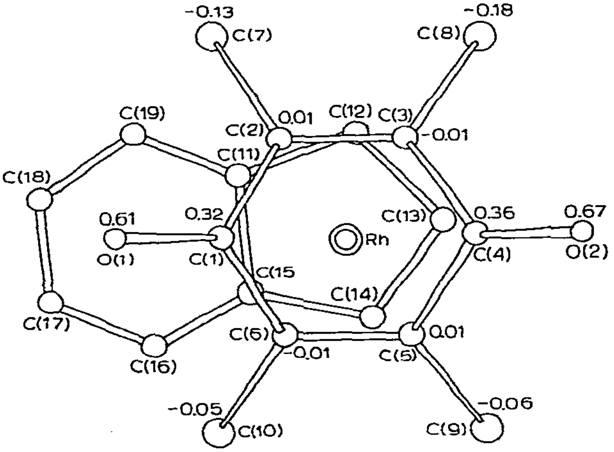

Fig. 3. The (π-C_9H_7)Rh(π-DQ) molecule in the same projection.

rather usual for π-complexes in general.

In (II) distances between the Rh atom and carbons of the five-membered cycle (average 2.21 Å) increase from 2.17 Å for Rh–C(13) to 2.23 Å for Rh–C(11) and Rh–C(15). The planar indenyl ligand is almost parallel to the plane of four olefinic carbon atoms C(2), C(3), C(5), C(6) making with it an angle of 3°. The own molecular symmetry approximates C_s.

In (III) the planar acetylacetonate ligand is almost normal to the C(2), C(3), C(5), C(6) plane (dihedral angle 88°) and the molecular symmetry is very close to C_{2v}. The Rh–O bonds (average length 1.98 Å) are considerably shortened in comparison

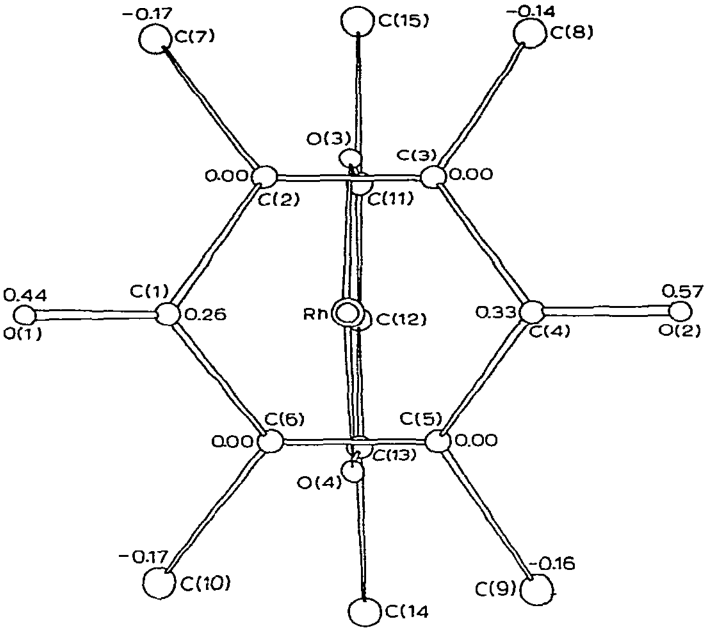

Fig. 4. The $(C_5H_9O_2)Rh(\pi\text{-}DQ)$ molecule in the same projection.

TABLE 1

MAIN GEOMETRICAL PARAMETERS OF QUINONE LIGANDS IN π-COMPLEXES

No.	Complex	C=C (Å)	C–C (Å)	C–CH_3-(C_4H_9) (Å)	C=O (Å)	M–C_{olef} (Å)	M–C_{CO} (Å)	α (°)	β (°)
(I)	$(\pi\text{-}C_5H_5)Rh(\pi\text{-}DQ)$	1.39	1.47	1.49	1.27	2.18	2.42	23	9
(II)	$(\pi\text{-}C_9H_7)Rh(\pi\text{-}DQ)$	1.38	1.47	1.52	1.22	2.16	2.44	25	11
(III)	$(C_5H_7O_2)Rh(\pi\text{-}DQ)$	1.38	1.49	1.56	1.24	2.15	2.45	20	9
(IV)	$(\pi\text{-}C_5H_5)Rh\{\pi\text{-}[C_6H_2\text{-}(C_4H_9)_2O_2]\}$	1.36	1.49		1.28	2.16	2.38	23	10
(V)	$(\pi\text{-}C_8H_{12})Ni(\pi\text{-}DQ)^3$	1.40	1.45	1.52	1.24	2.22	2.31	6	
(VI)	DQ^4	1.341	1.492	1.514	1.232			0	0

with the value 2.06 Å found[10] in $(Acac)Rh(CO)_2$; however, other bond lengths of this ligand are the same in both the compounds.

In all the three complexes studied the average distances between the Rh atom and the four olefinic carbon atoms C(2), C(3), C(5) and C(6) have very similar values [2.18, 2.16 and 2.15 Å in (I), (II) and (III), respectively], which, however, are considerably shorter than the average distance to the carbonyl carbon atoms C(1) and C(4) [2.42, 2.44 and 2.45 Å in (I), (II) and (III), respectively]. Thus, in all the three complexes, the six-membered cycle of the DQ ligand acquires a boat-like conformation (Fig. 1). Four olefinic carbon atoms C(2), C(1), C(5) and C(6) are practically coplanar and the carbonylic carbon atoms C(1) and C(4) are displaced out of this plane outwards the Rh atom by 0.31, 0.34 and 0.30 Å in (I), (II) and (III) respectively. On the contrary the methyl groups are bended towards the Rh atom by 0.05–0.18 Å (Figs. 2, 3, 4). The DQ ligand conformation is determined by angles α which have the similar values 23° (I), 25° (II) and 20° (III). It is to be noted that the oxygen atoms are not situated in the trigonal carbon atoms plane: the C=O bonds are bent from ideal directions towards the Rh atom by the angles β equal to 9° (I), 11° (II) and 9° (III). In the previously studied complex (IV) the values of these angles are very similar in the sterically unhindered half of ligand ($\alpha_1=23°$, $\beta_1=10°$) and only a little larger ($\alpha_2=27°$, $\beta_2=13°$) in the vicinity of bulky tertiary butyl groups.

Hence, steric hindrance in the quinone ligand exert only a small influence on its conformation. Furthermore a deviation from planarity is almost independent of the second nature and thus the distortion is probably caused by spacial-coordinative requirements of a central metal atom. As was already mentioned, the planarity distortion of the DQ ligand in the Ni complex (V) is much less ($\alpha=6°$) than in the Rh complexes (average $\alpha=23°$). This difference is paralleled by the fact[2] that in (V) two valence electrons are to be placed on the antibonding molecular orbitals and the shortest Ni–C (DQ) distances (2.22 Å) are longer by 0.1 Å than the single-bonded covalent radii sum[9]. On the contrary, in (I), (II) and (III) all available electrons occupy the bonding molecular orbitals[2] and the shortest Rh–C (DQ) distances (2.16 Å) are even a little shorter than the radii sum (2.23 Å).

Besides non-planarity the only, probably real, change of the DQ molecule geometry on coordination is the increase in the length of the double C=C bonds from 1.341 Å in DQ itself[4] to 1.39, 1.38, 1.38 and 1.40 Å in (I), (II), (III) and (V), respectively.

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