The Crystal Structure of 8-Hydroxyquinolinato(1,5-cyclooctadiene)rhodium(I)

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8-Hydroxyquinolinato(1,5-cyclooctadiene)rhodium(I), [Rh(oxine)(COD)], was synthesized by the reaction between $[RhCl(COD)]_2$ and the sodium salt of 8-hydroxyquinoline. This compound crystallizes in the triclinic space group $P\bar{1}$ with a = 7.701 Å, b = 10.062 Å, c = 9.802 Å, $\alpha = 72.82°$, $\beta = 108.03°$ and $\gamma = 99.42°$ and with 2 molecules per unit cell. The crystal structure was determined from 2917 observed reflections obtained with a computer-automated diffractometer. The final R-value was 0.062. The Rh–S(1) and Rh–S(2) bond distances (S(1) and S(2) are the centres of the double bonds of 1,5-cyclooctadiene), as well as the carbon–carbon double bond lengths of 1,5-cyclooctadiene, indicate that the nitrogen atom of the chelate ring has a larger trans *influence than the oxygen atom.*

Introduction

The fact that only one of the CO groups in complexes of the type $[Rh(LL')(CO)_2]$ (where LL' = singly charged bidentate ligands such as β-diketones, tropolone and 8-hydroxyquinoline) can be substituted by neutral ligands like triphenylphosphine [1, 2] was used to determine the relative thermodynamic *trans* effect of the two atoms of LL' which are bonded to the rhodium atom in the case where LL' = thenoyltrifluoroacetone (TTA) [3], N-benzoyl-N-phenylhydroxylamine (BPHA) [4], and 8-hydroxyquinoline(oxine) [5]. This was achieved by means of the crystal structure determination of $[RhTTA(CO)(PPh_3)]$, $[Rh(oxine)(CO)(PPh_3)]$ and $[Rh(BPHA)(CO)(PPh_3)]$ (which were prepared according to the following reaction: $[RhLL'(CO)_2] + PPh_3 \rightarrow [RhLL'(CO)(PPh_3)] + CO$), as it can be assumed that the carbonyl group which is situated *trans* to the atom which has the largest *trans* influence will be displaced by PPh_3. The results obtained by means of these structure determinations indicate that the most electronegative atom of the chelate ring has the smallest *trans* influence. In the case of two identical atoms (like the oxygen atoms of β-diketones) the atom nearest to the strongest electron attracting group (like a CF_3 group) has the smallest *trans* influence. These results are in agreement with the polarization theory [6] and the σ-*trans* effect [7] since the most electronegative atom (or in the case of β-diketones the oxygen atom nearest to the most electronegative group) will be the least polarizable and also a weaker σ-donor.

Another obvious way to distinguish between the thermodynamic *trans* effect of two bonded atoms is to determine the bond distance of the atoms *trans* to these atoms. When the chelating ligand LL' is symmetrical like acetylacetone (acac), the bonds *trans* to the LL' group should be chemically equivalent as was confirmed by the structure determination of $[Rh(acac)(CO)_2]$ where the two Rh–O and the two Rh–C bond lengths were the same, within experimental error: 2.044(4) and 2.040(4) in the case of the Rh–O and 1.831(7) and 1.831(7) in the case of the Rh–C bond distances [8]. The two Rh–S distances (S is the centre of the carbon–carbon double bonds in 1,5-cyclooctadiene) in [Rh(acac)(COD)] were also the same within the experimental error, 1.982(8) Å and 1.982(7) Å [9]. It is, however, reasonable to expect that the rhodium–ligand bond lengths *trans* to the bonded atoms of a non-symmetrical chelating ligand LL' may differ as a result of the difference in the *trans* influence of L and L'. The relative thermodynamic *trans* effect of the oxygen atoms of trifluorobenzoylacetone (TFBA) was established by means of the crystal structure determination of [Rh(TFBA)(COD)] [10]. All the bond distances (Rh–O, Rh–S and the C–C double bond) indicate that the oxygen atom nearest to the more electron attracting CF_3 group has the smallest *trans* effect. This result is also in agreement with the polarization theory [6] and the σ-*trans* effect [7].

The results of the structure determination of $[Rh(oxine)(CO)(PPh_3)]$ [5] showed that the nitrogen atom of the chelating ring has a larger *trans* effect than the oxygen atom as the CO group *trans* to the nitrogen atom was displaced by PPh_3 during the reaction $[Rh(oxine)(CO)_2] + PPh_3 \rightarrow [Rh(oxine)(CO)(PPh_3)] + CO$. The crystal structure of [Rh(oxine)(COD)] was determined in order to establish to what extent the rhodium–ligand bond lengths may be used to determine the *trans* influence of different atoms and if the results that are obtained in

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TABLE I. Fractional Atomic Coordinates and Thermal Parameters with Estimated Standard Deviations in Parentheses. Positional Parameters (× 10^4) and Thermal Parameters (× 10^3).

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rh	3084,8(9)	2570,6(7)	1469,4(8)	20(1)	19(1)	20(1)	5(1)	−5(1)	−11(1)
O	1402(10)	3096(7)	−658(8)	37(4)	30(4)	26(4)	7(3)	−7(3)	−13(3)
N	2963(11)	696(8)	905(9)	26(4)	23(4)	30(4)	2(3)	4(3)	−13(3)
C(1)	3724(16)	−498(11)	1736(13)	49(6)	20(5)	45(6)	13(4)	5(5)	−13(4)
C(2)	3489(19)	−1656(12)	1155(15)	61(8)	31(6)	57(8)	10(5)	15(6)	−21(6)
C(3)	2489(18)	−1589(12)	−271(15)	53(7)	34(6)	55(7)	1(5)	22(6)	−25(5)
C(4)	1663(14)	−332(11)	−1184(12)	31(5)	37(6)	41(6)	−10(4)	17(4)	−26(5)
C(5)	608(16)	−149(14)	−2676(13)	39(6)	61(8)	40(6)	−12(6)	12(5)	−35(6)
C(6)	−138(17)	1100(14)	−3449(13)	45(7)	59(8)	35(6)	−10(6)	6(5)	−29(6)
C(7)	121(16)	2235(14)	−2797(12)	41(6)	55(7)	28(5)	1(5)	−2(5)	−20(5)
C(8)	1130(13)	2092(11)	−1334(11)	23(5)	32(5)	28(5)	−1(4)	2(4)	−14(4)
C(9)	1941(13)	788(10)	−528(11)	22(4)	27(5)	27(5)	−5(4)	7(4)	−15(4)
C(10)	2130(16)	3782(13)	3594(13)	33(6)	54(7)	43(6)	15(5)	6(5)	−24(6)
C(11)	2166(14)	4211(11)	1991(12)	31(5)	29(5)	38(5)	12(4)	−1(4)	−19(4)
C(12)	3789(15)	4716(10)	1504(12)	38(6)	19(4)	35(5)	5(4)	1(4)	−13(4)
C(13)	5671(15)	4935(11)	2582(13)	32(5)	31(5)	47(6)	−6(4)	0(5)	−24(5)
C(14)	6788(13)	3650(12)	3100(13)	20(5)	45(6)	46(6)	−1(4)	−3(4)	−26(5)
C(15)	5603(13)	2268(11)	3160(11)	18(4)	38(5)	27(5)	9(4)	−9(4)	−13(4)
C(16)	4074(14)	1870(11)	3826(11)	30(5)	35(5)	23(5)	7(4)	1(4)	−9(4)
C(17)	3592(16)	2757(13)	4645(12)	42(6)	49(7)	27(5)	11(5)	7(5)	−15(5)

this way are in agreement with the results of the structure determination of [Rh(oxine)(CO)(PPh_3)].

TABLE II. Interatomic Distances (Å) with Estimated Standard Deviations in Parentheses.

Rh–O	2.051(6)	C(4)–C(5)	1.409(15)
Rh–N	2.098(9)	C(5)–C(6)	1.373(18)
Rh–S_1	2.020(11)	C(6)–C(7)	1.425(22)
Rh–S_2	1.996(8)	C(7)–C(8)	1.381(14)
O–C(8)	1.321(15)	C(10)–C(11)	1.510(18)
C(8)–C(9)	1.444(13)	C(11)–C(12)	1.438(17)
C(9)–N	1.365(12)	C(12)–C(13)	1.533(14)
N–C(1)	1.344(13)	C(13)–C(14)	1.541(17)
C(1)–C(2)	1.405(20)	C(14)–C(15)	1.530(15)
C(2)–C(3)	1.359(18)	C(15)–C(16)	1.463(16)
C(3)–C(4)	1.431(15)	C(16)–C(17)	1.515(20)
C(4)–C(9)	1.412(17)	C(17)–C(10)	1.558(16)

Experimental

An equivalent amount of the sodium salt of 8-hydroxyquinoline was added to a solution of 0.05 g [RhCl(COD)]$_2$ (obtained by the reaction of $RhCl_3 \cdot 3H_2O$ with cyclooctadiene in methyl alcohol [11]) in acetone. Red prismatic crystals of [Rh(oxine)(COD)] which were suitable for X-ray analysis were obtained by slow evaporation of the solution. Crystal data: $a = 7.701$ Å, $b = 10.062$ Å, $c = 9.802$ Å, $\alpha = 72.82°$, $\beta = 108.03°$, $\gamma = 99.42°$, $z = 2$ and $\mu(MoK\alpha) = 12.08$ cm^{-1}. Graphite monochromated MoKα radiation ($\lambda = 0.7107$ Å) was used for the collection of the three dimensional intensity data on a Philips four circle single crystal X-ray diffractometer. Three reflections were used as standards and were re-measured after every 60 reflections. No decomposition of the crystal was detectable in this way during the data collection. A total of 2992 independent reflections were measured for θ values between 3° and 27° of which 2917 were considered as observed. A crystal with dimensions 0.7 × 0.5 × 0.5 mm^3 was used for the data collection. Only Lorentz and polarization corrections were applied. The rhodium atom was located from a three dimensional Patterson map. A subsequent Fourier map (phased by the rhodium atom) gave the positions of all the remaining non-hydrogen atoms. A full matrix least squares refinement using all the observed reflections and anisotropic temperature parameters for all the atoms resulted in the residual factor $R = \Sigma//F_0/-/F_c// \div \Sigma/F_0/$ of 6.2%. The atomic scattering factors were those tabulated by Cromer and Waber [12]. A list of the observed and calculated structure factors may be obtained from the authors. The final positional and thermal parameters are listed in Table I. The estimated standard deviations of these parameters are given in parentheses.

Results and Discussion

The crystal structure of [Rh(oxine)(COD)] consists of well-separated discrete molecular units. The bond lengths and angles, with their standard deviations are given in Table II and III respectively, while

TABLE III. Bond Angles (degrees) with Estimated Standard Deviations in Parentheses.

N–Rh–O	80.9(3)	C(9)–C(4)–C(5)	118.7(10)
O–Rh–S_1	91.9(4)	C(4)–C(5)–C(6)	119.6(13)
S_2–Rh–S_1	88.9(4)	C(5)–C(6)–C(7)	122.2(11)
S_2–Rh–N	98.5(4)	C(6)–C(7)–C(8)	119.9(11)
Rh–O–C(8)	112.6(6)	C(7)–C(8)–C(9)	117.9(11)
O–C(8)–C(9)	119.2(8)	C(8)–C(9)–C(4)	121.6(8)
C(8)–C(9)–N	116.2(10)	C(10)–C(11)–C(12)	124.5(9)
C(9)–N–Rh	111.0(6)	C(11)–C(12)–C(13)	122.6(10)
C(9)–N–C(1)	119.6(10)	C(12)–C(13)–C(14)	112.2(10)
N–C(1)–C(2)	121.1(10)	C(13)–C(14)–C(15)	113.5(8)
C(1)–C(2)–C(3)	120.4(11)	C(14)–C(15)–C(16)	124.7(11)
C(2)–C(3)–C(4)	119.7(13)	C(15)–C(16)–C(17)	122.7(9)
C(3)–C(4)–C(9)	116.9(10)	C(16)–C(17)–C(10)	111.8(9)
C(4)–C(9)–N	122.1(8)	C(17)–C(10)–C(11)	114.0(12)

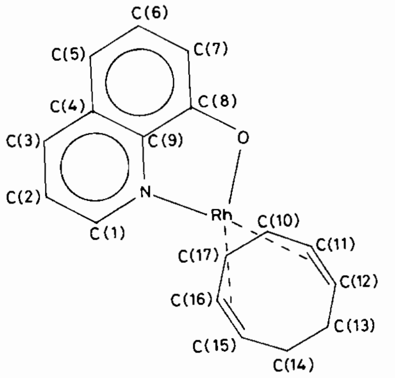

Fig. 1. The system of numbering of atoms in the molecule.

the system of numbering of the atoms in the molecule is shown in Fig. 1.

The calculation of the best plane through Rh, N, O, S(1) and S(2)(S(1) and S(2) are the centres of the C(11)–C(12) and C(15)–C(16) bonds respectively) showed that the coordination polyhedron is planar within the experimental error. The N–Rh–O bond angle of 80.9° however departs markedly from square planar geometry. This large deviation from 90° can be attributed to the small 'bite' angle of the five membered chelate ring. This angle is about the same as was found in 8-hydroxyquinolinatocarbonyltriphenylphosphinerhodium(I) ([Rh(oxine)(CO)(PPh_3)]) [5]. The Rh–N and Rh–O bond distances are also about the same as was found in [Rh(oxine)(CO)(PPh_3)]. The difference in these two bond lengths is about 0.05 Å but it can be considered as normal since the groups *trans* to the oxygen and nitrogen atoms are chemically equivalent. The calculation of the best plane through the atoms of the 8-hydroxyquinolinato ligand showed it to be planar within the experimental error. The C–C, C–N and C–O bond distances and the bond angles within the chelating ligand agree well with those found in other 8-hydroxyquinoline complexes [5, 13, 14].

The cyclooctadiene ligand has the usual 'tub' conformation. The coordinated double bonds C(11)–C(12) and C(15)–C(16) have lengths of 1.438 Å and 1.463 Å respectively compared to an uncoordinated olefinic distance of 1.34 Å [15]. The extension of the C–C double bonds corresponds to a decrease in the π-electron density as a result of the bonding to the rhodium atom. The internal geometry of the cyclooctadiene ligand is quite normal with average $C(sp^3)$–$C(sp^3)$ and $C(sp^3)$–$C(sp^2)$ distances of 1.550 Å and 1.522 Å respectively. The S(1)–Rh–S(2) angle containing the olefin bonds is 88.9°. This value agrees well with the 89.7° found in Rh[TFBA(COD)] [10]. The carbon atoms participating in the bonding are virtually in a plane. The least squares plane through these atoms (C(11), C(12), C(15) and C(16)) makes an angle of 85.7° with the plane through the coordination polyhedron. The remaining set of four atoms (C(13), C(14), C(17) and C(18) are also nearly in a plane. The C–C double bonds are nearly perpendicular to the N–Rh–O plane; they form angles of 2.5° and 6.9° with the normal of the N–Rh–O plane respectively. The carbon atoms of these two double bonds are symmetrically disposed above and below the N–Rh–O plane in contrast to what was found in [RhP(COD)] (P = 2,3-bis(diphenylphosphino) butane), where one carbon atom of the double bond was approximately twice as far out of the plane displaced than the other carbon atom [16].

The relative effect of the nitrogen and oxygen atoms of the 8-hydroxyquinoline ligand are reflected in the Rh–S(1) and Rh–S(2) bond distances. The Rh–S(1) and Rh–S(2) bond distances in [Rh(acac)(COD)] *trans* to the chemical equivalent oxygen atoms of the β-diketone are (as would be expected) the same, 1.982 Å [9]. The difference between the Rh–S(1) and Rh–S(2) bond lengths (the nitrogen and oxygen atoms of 8-hydroxyquinoline are *trans* with respect to S(1) and S(2) respectively) in the present structure (0.024 Å) can thus be considered as the effect of the difference in the *trans* influence of the nitrogen and oxygen atoms. The observation that Rh–S(1) is longer than Rh–S(2) indicates that the nitrogen atom has a larger thermodynamic *trans* effect than the oxygen atom. The longer Rh–S(1) bond length implies that less π electron density of the C(11)–C(12) double bond (than of the C(15)–C(16) double bond) is used for the bond formation with the rhodium atom. This should result in a lengthening of the C(15)–C(16) bond compared to the C(11)–C(12) bond. This is in agreement with the observed bond lengths although the difference in these bond distances (0.025 Å) is only about 1½ times the standard deviation. All the results of this structure determination thus indicate that the nitrogen atom of 8-hydroxyquinoline has a larger *trans* effect than does the oxygen atom and is also a better σ-electron donor. This conclusion is also in agreement with the results of the structure determination of [Rh(oxine)(CO)(PPh$_3$)] [5] where it was shown that the carbonyl group *trans* to the nitrogen atom was substituted by the triphenylphosphine ligand in the reaction:

$$[\mathrm{Rh(oxine)(CO)_2}] + \mathrm{PPh_3} \rightarrow [\mathrm{Rh(oxine)(CO)(PPh_3)}] + \mathrm{CO}$$

thus illustrating the larger *trans* effect of the nitrogen atom. These results thus indicate that bond lengths may be used to determine the relative *trans* influence of the different atoms in these complexes.

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