Inorganica Chimica Acta, 45 (1980) L255–L256
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Crystal and Molecular Structures of (N-*o*-Tolyl Salicylideneiminato)(1,5-Cyclooctadiene)Iridium(I) and of a Novel Binuclear (1,5-cyclooctadiene) Rhodium(I) with Bridging N,N′-(1,2-phenylene)bis(salicylideneiminato) Ligand

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Received July 16, 1980

Introduction

Both di-μ-methoxo bis(η-1,5-cyclooctadiene)dirhodium(I) and iridium(I) compounds react easily with Schiff bases formed from salicylaldehyde and primary amines, giving complexes: $[(M(cod))_2(sb)]$ or [M(sb)(cod)] [1] (where M = Rh(I), Ir(I); cod = 1,5-cyclooctadiene and sb = Schiff base ligand).

We report here the principal structural features of two series of compounds: a mononuclear complex of iridium(I) with formula [Ir(sal*o*tol)(cod)] (where Hsal*o*tol = N-*o*-tolylsalicylideneimine) and a binuclear complex of rhodium(I): $[(Rh(cod))_2(\text{sal}o\text{phen})]$ (where H_2sal*o*phen = N,N′-(1,2-phenylene)bis(salicylideneimine).

Experimental

All operations were carried out under nitrogen atmosphere. All solvents and materials were reagent grade. The Schiff base ligands and the complexes $[(M(OCH_3)(cod))_2]$ were prepared by published procedures.

The products were obtained by dissolving $[(M(OCH_3)(cod))_2]$ and the appropriate ligand in dichloromethane. The dichloromethane was boiled off and replaced by pentane and the reaction mixture was cooled until a precipitate was formed.

Crystals suitable for X-ray diffraction were prepared by slow diffusion at low temperature of methanol into a concentrated dichloromethane solution.

Results and Discussion

[Ir(sal*o*tol)(cod)].

Crystal Data

$IrC_{22}H_{24}ON$, M = 510,6, monoclinic, a = 10.776(4), b = 9.882(2), c = 19.554(5) Å, β = 118.06(3)°, V = 1837.5 Å^3, D_{ex} = 1.82 g cm^{-3} (by flotation), D_c = 1.84, Z = 4, space group $P2_1/c$, μ(Mo-Kα) = 41.8 cm^{-1}.

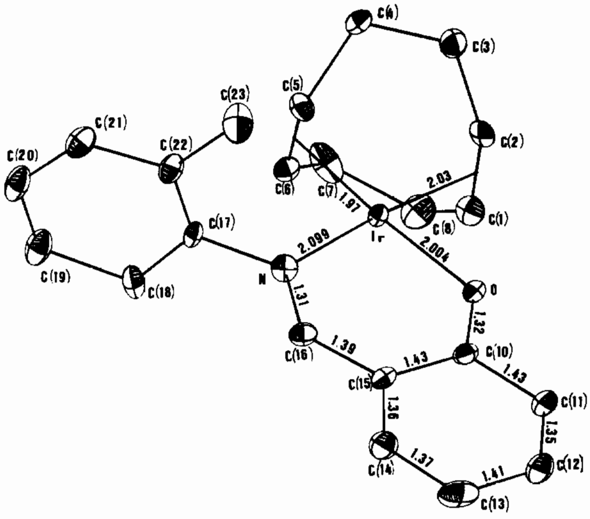

Fig. 1. Perspective drawing of [Ir(sal*o*tol)(cod)].

Intensity data were recorded on a NONIUS C.A.D. 4 diffractometer with graphite monochromated MoKα radiation. The 3417 independent reflections measured above zero and $\theta \leqslant 30°$ were corrected for absorption. The structure was solved by the heavy atom method. Positional and anisotropic thermal parameters for all non hydrogen atoms were refined by full matrix least-squares. The hydrogen atoms located on a difference Fourier synthesis were included in the F_c calculations with an idealized position (except the methyl hydrogens which were allowed to refine) and a fixed isotropic thermal parameter. Final reliability factors are R = 0.043 and R_w = 0.044.

A perspective view of the structure is given in Fig. 1. The geometry around iridium is approximately square-planar with the coordination plane defined by O,N,M(1) and M(2)**. We can discuss the present compound on the light of the structural analysis made on the 2-chloro-N-salicylideneaniline molecule [2], which we assume to be close of the sal*o*tol ligand concerning the salicylaldimine residue.

Upon coordination, distances such as O–C(10) and C(16)–C(15) shrink by about 0.05 and 0.06 Å respectively, a lengthening of N–C(16) (iminium bond) is also observed. These variations drive the residue toward a resonance scheme in which the contribu-

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**M(1) is the midpoint of C(1)–C(2), M(2) the midpoint of C(5)–C(6).

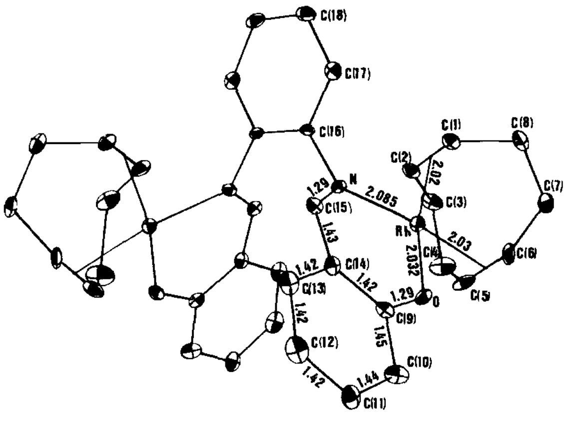

Fig. 2. Perspective drawing of [(Rh(cod))$_2$(salophen)]. The unlabelled atoms are related to the others by a binary axis.

tion of the ketamine form is as important as that of the enolamine form (free molecule). Furthermore, the benzene ring, the oxygen, the nitrogen and the C(16) carbon atoms (salicylideneimine group) are nearly coplanar allowing a π-electron delocalization on the whole planar bidentate ligand.

The salicylideneimine moiety makes an angle of 85.6° with the *o*-tolyl group as already reported in other complexes possessing a N-phenyl substituent [3, 4].

[(Rh(cod))$_2$(sal*o*phen)]

Crystal Data

$Rh_2C_{36}H_{38}O_2N_2$, M = 736.5, orthorhombic, a = 12.647(2), b = 15.964(2), c = 14.507(3) Å, V = 2928.9 Å^3, D_{ex} = 1.66 g cm^{-3} (by flotation), D_c = 1.67, Z = 4 formula units, space group P ccn.

X-ray intensity data were collected on a NONIUS C.A.D. 4 automatic diffractometer with MoKα radiation. A total of 2593 independent reflections were measured (to θ = 25°) of which 1455 were considered above zero and used for structure solution (heavy atom method) and refinement (full matrix least-squares) All atoms were treated anisotropically, the H atoms were not introduced in the refinement. The conventional R value was 0.038 (R_w = 0.047).

The molecular geometry of the dinuclear complex is shown in Fig. 2. The asymmetric unit consists of half of [(Rh(cod))$_2$(sal*o*phen)]. Thus half of the dinuclear complex, which is identified by primed atom labels is generated through a binary axis located at the midpoints of the C(16)–C(16)′ and C(18)–C(18)′ bonds.

The analysis reveals a bridging sal*o*phen molecule. Few examples of sal*o*phen ligand bridging two metals have been structurally characterised. The ligand has an extremely warped conformation, it differs from the free ligand [5] or any of its metal complexes structurally characterised to date [5, 6].

The twisted ligand conformation allows two rhodium atoms to coordinate to the potentially tetradentate Schiff base, each rhodium atom bound to one 1,5-cyclooctadiene ring. The resulting arrangement leads to a Rh–Rh separation of 5.737(1) Å. The geometry around each rhodium atom is approximately square-planar with the coordination polyhedron defined by the oxygen, the nitrogen atoms and the midpoints of the olefin bonds from the 1,5-cyclooctadiene fragment.

An accurate structural analysis of the ligand, before and after coordination to cobalt(II) was carried out by Nardin and co-workers [5]. From geometrical data, these authors establihsed the free ligand H_2salophen to have an enolamine form in the solid state. Moreover the geometry of the whole molecule is not planar, a salicylideneimine residue is removed from the plane of all the atoms of the molecule by rotation around the bond equivalent to N–C(16), the mean planes of the two residues making an angle of 56.8°.

In the present compound, the angle between the planes determined by the phenyl ring (C(16), C(17), C(18), C(16)′, C(17)′, C(18)′) and the salicylideneimine residue (N, O, C(9), C(10), C(11), C(12), C(13), C(14), C(15)) is about 85°. Furthermore distances such as C(9)–O and C(14)–C(15) are shortened by *ca.* 0.05 and 0.03 Å respectively whereas N–C(15) bond length is unchanged. These variations in bond lengths essentially single in the free ligand indicate, as suggested by Nardin, a greater contribution of a ketamine form in the complexed form.

Work is currently underway by means of NMR spectroscopy on other similar complexes with various substituted Schiff base ligands in order to confirm the proposed solid-state structures.

Acknowledgement

The authors wish to thank Professor R. Chevalier for providing facilities for X-ray measurements.

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