

Preliminary communication

Synthesis and characterization of [pyRh(salen)adam], an adamantyl Rh^{III} complex containing bis(salicylaldehyde)ethylenediimine as equatorial ligand

Renata Dreos-Garlatti ^a, Silvano Geremia ^b, Lucio Randaccio ^{a,*}, Stefano Ruffini ^a, Giovanni Tazher ^a^a Dipartimento di Scienze Chimiche, Università di Trieste, 34127 Trieste, Italy^b Dipartimento di Scienze dei Materiali e della Terra, Università di Ancona, 60131 Ancona, Italy

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Abstract

The determination of the X-ray structure and formation constant of a Rh^{III} organometallic complex containing bis(salicylaldehyde)ethylenediimine [(pyridine)Rh(salen)(adamantyl)], revealed a *cis*-influence on the axial metal–nitrogen bond significantly greater than that found in the analogous dimethylglyoximate. Comparison of the formation constants suggests that the stability of the hexacoordinate species with respect to the pentacoordinate species in Rh complexes is greater than that for Co complexes.

Keywords: Rhodium; Schiff base; *cis*-influence; X-ray structure

Octahedral Co^{III} complexes, [LCo(chel)R], where L is a Lewis base, R an alkyl group and (chel) is either (Hdmg)₂ (alkylcobaloximes) [1] or a tetradentate Schiff base such as salen or saloph [2], have been studied as both models of the vitamin B₁₂ system [3] and convenient sources of carbon radicals [4]. The (chel) influences the coordination of the axial ligands, especially L, and the Schiff bases stabilize noticeably five-coordinate species [RCo(chel)] compared with cobaloximes [2]. The observation [5] that the Rh analogue of 5'-deoxyadenosylcobalamin, 5'-deoxyadenosylrhodamin, is a vitamin B₁₂ inhibitor in *E. Coli* has prompted studies on the rhodoximes, [LRh(Hdmg)₂R] [6–8], which have suggested that the Rh–C bond should be influenced by steric interactions with the equatorial ligand less than the corresponding Co–C bond. Many years ago, the synthesis of the [LRh(salen)R] with several different R groups was reported [9]. However, the lack of structural and solution characterization does not allow the analysis of the influence of the equatorial ligand on the axial L–Rh–C fragment. Therefore, the study of organometallic Rh(salen) complexes with bulky R groups has been undertaken. The synthesis [10] of

[pyRh(salen)adam] (**1**) and [Rh(salen)adam] (**2**) (adam = adamantyl) complexes and the X-ray structure of **1** are reported. The formation constants of **1** and of its analogous Co complex were measured.

Two crystalline forms of **1**, **a** and **b**, were obtained and structurally characterized. The ORTEP drawings [11] of **1a** (which applies also to **1b**) is shown in Fig. 1. The molecules of **1a** and **1b** are very similar. The equatorial moiety in both **1a** and **1b** deviates from planarity in a step conformation [12]. The equatorial coordination bond lengths, very similar in **1a** and **1b**, are given in Fig. 1. The Rh–C distances are 2.125(3) (**1a**) and 2.116(4) Å (**1b**) and the Rh–N(axial) distances are 2.347(3) (**1a**) and 2.351(4) Å (**1b**), respectively. The comparison of **1a** and **1b** with the analogous rhodoxime, [(1-MeIm)Rh(Hdmg)₂(adam)] (**3**) [8] (1-MeIm = 1-methylimidazole) with Rh–C and Rh–N(axial) distances of 2.148(2) and 2.195(2) Å, respectively, indicates that the Rh–C distances are hardly affected by the change of the equatorial ligand, the salen derivative being slightly shorter. The Rh–adam bonds are even shorter than the Co–adam bonds in [LCo(Hdmg)₂(adam)] [13] with L = 4-Me₂NC₅H₄N (2.160(4) Å) and L = 1-MeIm (2.154(5) Å), despite the larger ionic radius of Rh^{III}, supporting the hypothesis that the Rh–C bond is stronger than the Co–C bond

* Corresponding author.

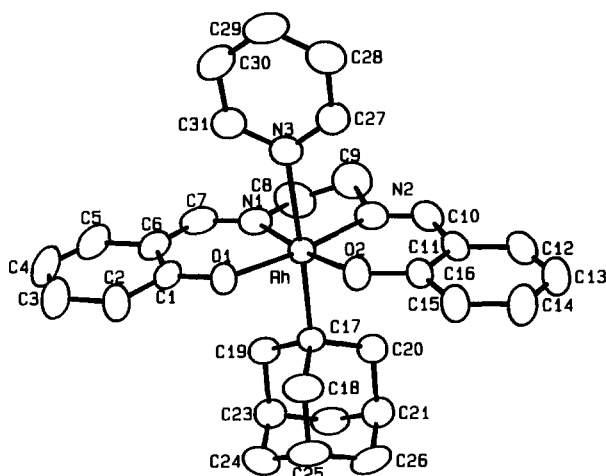
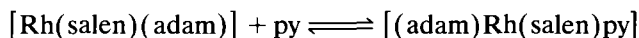


Fig. 1. ORTEP drawing (50% probability thermal ellipsoids) and labelling scheme for non-hydrogen atoms of molecule **1a**. The same scheme applies also for **1b**. Equatorial coordination distances: Rh–O(1) 2.026(3) [2.024(2)]; Rh–O(2) 2.037(2) [2.037(2)]; Rh–N(1) 1.964(3) [1.956(3)]; Rh–N(2) 1.978(3) [1.980(3)] Å. Values in square bracket refer to **1b**.

[6,7]. In contrast the Rh–N (axial) distance in **1** is longer than that found in **3** [14] and that of 2.225(3) Å found in [(4-Bu⁺C₅H₄N)Rh(Hdmg)₂(Bu⁺)] [6]. The *cis*-influence of the salen on the Rh–N(axial) bond is larger than that of (Hdmg)₂, consistent with the observation that the five coordinate [Rh(salen)(adam)] (**2**) species is easily isolated, whereas only the corresponding hexacoordinate [pyRh(Hdmg)₂(adam)] has been obtained.

Species **2** has been characterized by elemental analyses and spectroscopy. The IR spectrum of a solid sample of **2** shows no absorption ascribable to coordinated water. The above data are consistent with the formulations corresponding to the five coordinate **2** and to the dimer [(adam)Rh(salen)]₂. Unfortunately, its poor solubility did not allow us to determine the molecular weight in non-coordinating solvents. However, the presence of well defined isosbestic points in the spectrophotometric titration with py in CH₂Cl₂ and the excellent fit of the absorbance at various py concentrations with the Benesi-Hildebrand equation indicate that the reaction follows the simple scheme



involving exclusively monomeric species. The values of the equilibrium constant for the reaction at 25°C are 78 M⁻¹ in CH₂Cl₂ and 25 M⁻¹ in DMF and indicate the reluctance of the complex to bind even a strong donor ligand such as py.

The equilibrium constant for [Co(salen)(adam)] [15] at 25°C in DMF is 0.15 M⁻¹, the lowest value found in [alkylCo(salen)] series, where the values range from 83 M⁻¹ for alkyl = Me to 17 M⁻¹ for alkyl = Prⁿ[16], consistent with the greater donating ability of adam ligand.

The present results suggest that organometallic five coordinate Rh species are more stable than rhodoximes when (chel) = salen. Furthermore, they confirm [8] that the axial bonds should be more stable in Rh than in Co derivatives, indicating that in these systems Rh is a better Lewis acid than Co. This stabilization could be responsible of the lack of biological activity of 5'-deoxyadenosylrhodamin [5].

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References and notes

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- [10] The synthesis of **2** was carried out by modifying one of the procedure previously reported [9] for obtaining hexacoordinate [pyRh(salen)R]. Complex **2** is obtained by reduction under dinitrogen of [pyRh(salen)Cl] with NaBH₄/PdCl₂ in a 0.01 M solution of NaOH in methanol/water (10:1), followed by addition of solid adamantyl iodide. Single crystals of **1** suitable for X-ray analysis were obtained by vapour diffusion of diethyl ether into a methanol solution of **2** containing 1% py. Elemental analyses of **1** and **2** are consistent with the above formulations.
- [11] X-ray diffraction data were collected on a CAD4 Enraf-Nonius diffractometer at 296 K. Structures were solved by standard procedures; semiempirical absorption corrections were applied

for **a**. Crystallographic data are as follows: *a*, *b*, *c*, β ; space group, 2θ range, unique observed reflections $I > 3\sigma(I)$, $R(R_w)$. **1a**: 6.742(1), 19.483(3), 20.939(4) Å; 98.52(1)°; *Cc*, 4–60°, 3403, 2.5 (2.8). **1b**: 9.999(1), 24.378(3), 12.020(2) Å; 113.340(6)°; $P2_1/c$, 4–60°, 3746, 3.9 (4.1). Tables of complete crystal data, anisotropic thermal parameters, atom coordinates, bond lengths and angles for **1a** and **1b** have been deposited at the Cambridge Crystallographic Data Centre.

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- [14] The large difference of 0.152 Å between **1** and **3** can be attributed only in part to the different axial *N*-ligand. In fact, in a series of cobaloximes with different R group, the Co–py distance is only about 0.05 Å longer than the Co–MeIm distance [1].
- [15] This complex was obtained by reduction of $[H_2OCo(salen)]OH$ with $NaBH_4$ under dinitrogen in methanol containing 2% py, followed by addition of solid adamantyl iodide. The elemental analyses are consistent with the formula $[Co(salen)(adam)]$. The electronic spectrum of the compound shows absorption bands at 350, 410 sh, 510 sh and 755 nm, very similar to those of other five coordinate $[Co(salen)R]$ derivatives (G. Costa, G. Mestroni and L. Stefani, *J. Organometal. Chem.*, 7 (1967) 493).
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