



Synthesis, spectral studies, crystal structures and TDDFT studies of the rhenium(I) complexes of 2,4-dihydroxy-*N'*-(4-hydroxybenzilidene) benzohydrazide

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ABSTRACT

The rhenium(I) carbonyl bromide complex, $[\text{ReBr}(\text{CO})_3(\text{HL})]$, of the ligand derived from 2,4-dihydroxybenzaldehyde and 4-hydroxybenzoic acid hydrazide (HL), has been prepared. HL and its complex have been characterized by elemental analysis, MS, IR, UV–Vis and ^1H NMR spectroscopic methods. The structure of HL and the aqua-complex $[\text{Re}(\text{OH}_2)(\text{CO})_3(\text{L})]$ where the ligands are monodeprotonated have been elucidated by X-ray diffraction. The structure of $[\text{ReBr}(\text{CO})_3(\text{HL})]$ has been calculated from conformational parameters found in the aqua-complex. DFT and TDDFT calculations have been performed to obtain the IR spectra and UV–Vis absorption and emission spectra. The calculated spectra agree with the experimental results.

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1. Introduction

Rhenium(I) complexes containing fragments $\text{fac-}\{\text{Re}(\text{CO})_3\}^+$ have recently aroused attention because of the advantage of conjugating this fragment for labeling of targeting biomolecules.

Information obtained with the rhenium complex may be used as a hypothesis in the design of the analogs $^{99\text{m}}\text{Tc}$ to explore its application in nuclear medicine. Furthermore, the luminescent properties of rhenium(I) tricarbonyl complexes [1] have been demonstrated to have applications in biological imaging as fluorochromes in fluorescence microscopy [1,2]. The large Stokes shifts, long life times and good quantum yields allow easy differentiation of their emission from interfering autofluorescence [2].

A great deal of this work has focused on hydrazone derivatives containing N-heterocycles because of the high stability of $\{\text{M}(\text{CO})_3\}^+$ ($\text{M} = \text{Re}, \text{Tc}$) complexes, particularly pyridine, and their antitumor and antiviral activities [3]. Less interest has been received by acyl-hydrazone derivatives designed to O,N-coordination, in spite of preliminary results that suggest a closer affinity of rhenium(I) for N,O-chelate than N,N'-chelate [4].

Comparable stability may permit the formation of several complexes in the reaction medium used to prepare the radiopharm. From this point of view, linkage isomerism is a not desirable phenomenon in radiopharmaceuticals based on $^{99\text{m}}\text{Tc}$ because it may

result in a biodistribution of unpredictable characteristics. Furthermore, differentiation of multiple coordination modes in samples of Re^I/Tc^I complexes may be not possible by HPLC routine analysis [5,6]. Thus, spectroscopic tools may be suitable for coordinative diagnosis and detection of the isomers.

In the present paper, we report the study of a hydrazone derived from 2,4-dihydroxybenzoic and 4-hydroxycarbaldehyde (Scheme 1). The resulting hydrazone maintains structural relationship with diethylstilbestrol [7] and genistein [8] which are antagonists of the estrogen receptor (ER) α and β , respectively (Scheme 1). The two divergent –OH phenol groups are a pattern which is present in other ER targeting molecules such as raloxifene [9], while the acyl-hydrazone group may be used to anchor the metal to obtain radioimager of this receptor. Both the chelate ring and that formed by the intramolecular hydrogen bond (see HL in Scheme 1) should contribute to achieving the quasi planar conformation of estradiol.

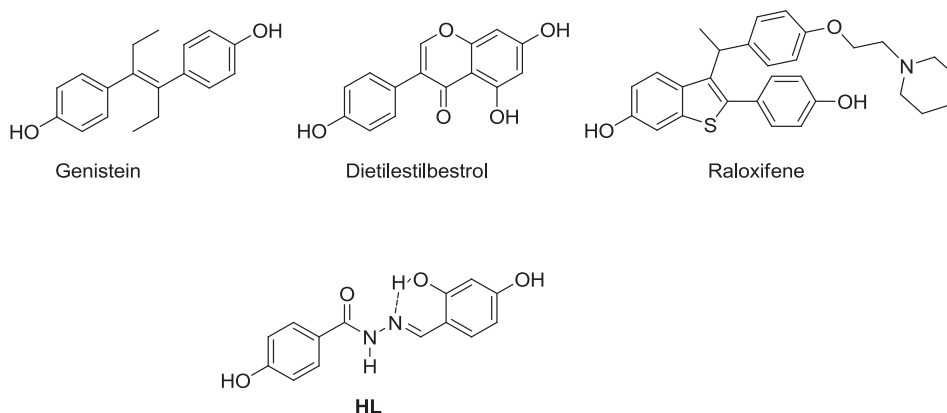
2. Results and discussion

2.1. Synthesis and spectroscopic characterization

The ligand HL was synthesized by Schiff base condensation using 4-hydroxybenzohydrazide and 2,4-dihydroxybenzaldehyde. Although the reaction of this ligand with $\text{fac-}\{\text{ReX}(\text{CO})_3(\text{CH}_3\text{CN})_2\}$ ($\text{X} = \text{Cl}, \text{Br}$) were tried, only the bromide derivative was isolated as a solid. The last complex was isolated as an air stable solid

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Scheme 1.

moderately soluble in alcohols and other organic solvents, although with a lower solubility in chloroform. Elemental analysis and mass spectrometry (FAB) allow the establishment of the 1:1 stoichiometry. The mass spectrum contains signals with different intensity being the heaviest peak that corresponds to the $[M-Br]^+$. This specie is also observed in the spectra of all hydrazone complexes as the metallated peak with highest intensity. *Fac*- geometry around the rhenium atom is suggested by the three strong $\nu(\text{CO})$ IR bands in the range $2030\text{--}1900\text{ cm}^{-1}$. The group of bands in the range $1650\text{--}1600\text{ cm}^{-1}$, assigned to the carbonyl hydrazone group, is shifted to lower energy with the formation of the complex, which suggest that the hydrazone oxygen atom is involved in the coordination of the metal, as observed in the rhenium(I) complexes of the ferrocenyl carbaldehyde derivatives of 2-hydroxybenzoic acid hydrazide [10]. These bands are hardly modified when the carbonyl group is not involved in the coordination [11].

The ^1H NMR spectra of the rhenium(I) complex and ligand in acetone- d_6 were acquired and the assignments (see Fig. 1 for atom numbering scheme) are included in Section 3 for comparison.

The ^{15}N -HSQC experiments on HL and its complex allowed the assignment of the N-H signal. The O(3)-H proton is the most deshielded in the spectrum of HL and the next signal, at 10.94 ppm, is due to the N-H group. It was observed that, in general, the C-H proton signals in the rhenium complexes are shifted downfield with respect to those in the free ligand in hydrazone [10–12] and thiosemicarbazone [13–17] derivatives. In contrast, the hydrazine proton singlet is strongly shifted (about 2 ppm) when the N-H group is a member of the chelate ring [10,13] or by around 1 ppm when the N-H group does not form part of the ring [10,16]. The ^1H NMR spectrum of the complex shows substantial deshielding of the proton signals apart from the N-H group. On coordination, the N(1)-H proton gives rise to the most deshielded signal in the spectrum and the signal is shifted by 1.7 ppm with respect to that in the free ligand in agreement with the N,O-coordination of the ligand.

Furthermore, the rhenium(I) coordination breaks the intramolecular hydrogen bond O(3)-H...N(2) and, consequently, the magnetic behavior of this proton should be similar to the other O-H groups of the ligand. Thus, the three signals in the 9.5–9.3 ppm range are assigned to the corresponding O-H groups. Computational studies and the nature of the complex $[\text{Re}(\text{OH}_2)(\text{CO})_3(\text{L})]$, as revealed by X-ray diffraction (*vide infra*), suggest that the O(3)-H group establishes an intramolecular interaction as acceptor with the N(1)-H group. Consequently, a change of the configuration around the C(8)=N(1) is required: i.e. the *Z* configuration of the free ligand has to change to *E* (Scheme 2).

2.2. X-ray studies

2.2.1. The molecular structure of the compounds

The molecular structures and the numbering scheme of the free ligand and the rhenium(I) complex included in the present paper are shown in Fig. 1. Selected bond distances and angles are included in Table 1. Details about the data collection and refinements are included in Section 3.

The two aromatic rings in the structure of HL are almost coplanar. The configuration of the bonds involved in the hydrazone group are probably dominated by the hydrogen bonding between the O(3)-H group and N(2) atom. This interaction forms a six-membered ring that is also coplanar with the molecule plane and fixes the *E* configuration of the C(1)=N(1) bond. As in other acylhydrazone derived from aldehydes, the configuration of the bonds in the fragment C(1)-N(1)-N(2)-C(8) is *Z*, *E*, and *E*, respectively. The C-N and N-N distances in this fragment suggest mainly a double-bond character for the C(8)-N(2) link although some π -delocalization along the hydrazone chain is also possible.

Attempts to obtain single crystals of $[\text{ReBr}(\text{CO})_3(\text{HL})]$ were unsuccessful, but we have obtained single crystals of the deprotonated compound $[\text{Re}(\text{OH}_2)(\text{CO})_3(\text{L})]$. The formation of the rhenium(I) aqua complex by recrystallization of the halide complex is not without precedent. In fact, the formation of the aqua-complexes from the hydrazone precursor has been reported before [4,10]. This compound crystallized as a monohydrate compound $[\text{Re}(\text{OH}_2)(\text{CO})_3(\text{L})]\cdot\text{H}_2\text{O}$.

The rhenium atom is coordinated to N(2) and O(1) hydrazone atoms, by three carbon carbonyl atoms and by the oxygen of a water molecule. The resulting coordination geometry may be described as distorted octahedral, the main distortion being the N(2)-Re-O(1) angle. The Re-O(1) and Re-N(2) distances are very close to those found in the ferrocenylcarbaldehyde hydrazone complexes where we have observed O,N-coordination mode [10,12], in spite of the deprotonated nature of the hydrazone ligand in the last complexes. The poor sensitivity of the Re-L distances to the deprotonated nature of the ligand have been also observed in the rhenium(I) thiosemicarbazone complexes [13–15]. The distance Re(1)-O(1 W) is similar to those found in other hydrazone complexes [4,10], as well as phosphinite and phosphonite complexes [18].

Comparison of the distances in the hydrazone chain between the free ligand and the complex is difficult due to the high values of the esd's usually associated with the rhenium X-ray structures. Thus, the differences in the values of the distances N(1)-C(1) and N(8)-C(8) are statistically insignificant and they are not conclusive in the distances C(1)-O(1).

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