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Synthesis, characterization, reactivity and computational studies of new rhenium(I) complexes with thiosemicarbazone ligands derived from 4-(methylthio)benzaldehyde

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N-thioamide thiosemicarbazone derived from 4-(methylthio)benzaldehyde (R = H, HL^1; R = Me, $\mathbf{HL^2}$ and R = Ph, $\mathbf{HL^3}$) have been prepared and their reaction with *fac*-$[ReX(CO)_3(CH_3CN)_2]$ (X = Br, Cl) in methanol gave the adducts $[ReX(CO)_3(HL^n)]$ (**1a** X = Cl, *n* = 1; **1a**′ X = Br, *n* = 1; **1b** X = Cl, *n* = 2; **1b**′ X = Br, *n* = 2; **1c** X = Cl, *n* = 3; **1c**′ X = Br, *n* = 3) in good yield.

All the compounds have been characterized by elemental analysis, mass spectrometry (ESI), IR and ^1H NMR spectroscopic methods. Moreover, the structures of $\mathbf{HL^2}$, $\mathbf{HL^3}$, $\mathbf{HL^3}\cdot\mathbf{(CH_3)_2}SO$ and **1b**′$\cdot H_2O$ were also elucidated by X-ray diffraction. In **1b**′, the rhenium atom is coordinated by the sulphur and the azomethine nitrogen atoms ($\kappa S,N^3$) forming a five-membered chelate ring, as well as three carbonyl and bromide ligands. The resulting coordination polyhedron can be described as a distorted octahedron.

The structure of the dimers is based on rhenium(I) thiosemicarbazonates $[Re_2(L^1)_2(CO)_6]$ (**2a**), $[Re_2(L^2)_2(CO)_6]$ (**2b**) and $[Re_2(L^3)_2(CO)_6]$ (**2c**) as determined by X-ray studies. Methods of synthesis were optimized to obtain amounts of these thiosemicarbazonate complexes. In these compounds the dimer structures are achieved by Re–S–Re bridges, where S is the thiolate sulphur from a $\kappa S,N^3$-bidentate thiosemicarbazonate ligand.

Some single crystals isolated in the synthesis of **2b** contain $[Re(L^4)(L^2)(CO)_3]$ (**3b**) where L^4 (=2-methylamine-5-(para-methylsulfanephenyl)-1,3,4-thiadiazole) is originated in a cyclization process of the thiosemicarbazone. Furthermore, the rhenium atom is coordinate by the sulphur and the thioamidic nitrogen of the thiosemicarbazonate ($\kappa S,N^2$) affording a four-membered chelate ring.

1. Introduction

The current interest in the coordination chemistry of technetium and rhenium is due to the widespread use of the radionuclide ^{99m}Tc in diagnostic nuclear medicine and the potential of the radioisotopes ^{186}Re and ^{188}Re in radiotherapy [1–4]. The redox and configurationally stability of the fragment $\{M(CO)_3\}^+$ (M = Tc, Re), beside the photophysic/photochemistry [5–9] and catalytic properties [10], make it a suitable candidate to metal node in metallo-supramolecular architecture [11–14]. In the last years, the developing of a normal pressure preparation of $[M(H_2O)_3(CO)_3]^+$ from saline solutions of MO_4^- in high yields and purity [15] has opened the possibility of using this metallic centre in radiotherapy and radio image [16,17].

Recently, bifunctional nanoparticles were successfully constructed by encapsulating hydrophobic Re^I (phen) complexes with a novel amphiphilic block copolymer. These water soluble nanoparticles with red emission were used as biolabels for cell imaging and gene transfection [18].

On the other hand, thiosemicarbazones (TSCs) constantly attract the interest of chemist and pharmacist because of their well known and remarkable biological and pharmacological properties; that is why the sensible increase in the number of studies of their antibacterial, antiviral, antifungal and antitumour activity as Quiroga and Navarro have reported [19]. Modifications of the thiosemicarbazone framework to find new compounds have been studied, and relationships between the biological activity and chelate formation are evident in a number of cases. These ligands are very versatile; they may be neutral or anionic ligand and link metal ions by different coordinative modes [20–22].

In previous papers [23] we reported a list of thiosemicarbazone ligands and their reactions with *fac*-$[ReX(CO)_3(CH_3CN)_2]$, which is a common starting material for the synthesis of rhenium(I) complexes. We have now extended these studies to thiosemicarbazones derived 4-(methylthio)benzaldehyde. In addition, the choice of

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sulfur-containing species in the ligands is due to a strategy for the construction of molecular based devices by the self-assembly of sulphur-containing molecules onto noble metal (particularly gold) surfaces [24,25]. The –SMe group allows a variety of pendant functionality to be introduced and metal-binding domains are of particular interest as they allow the introduction of specific electronic and photophysical properties [26].

2. Results and discussion

2.1. Synthesis and spectroscopic characterization

The ligands derived from 4-(methylthio)benzaldehyde thiosemicarbazone were obtained by refluxing a mixture of 4-(methylthio)benzaldehyde and the corresponding thiosemicarbazide in methanol/water solution for 2 h (Scheme 1).

Reaction of the three ligands with *fac*-[ReX(CO)$_3$(CH$_3$CN)$_2$] afforded six adducts (Scheme 2) with general formula *fac*-[ReX(CO)$_3$(HL^n)].

The resulting solid depends substantially on the reaction time and the R group nature. While, refluxing for 2 h affords adducts **1a**, **1a**′, **1b** and **1b**′ in good yield, the reaction time has to be shortened to avoid the formation of thiosemicarbazonate complexes (*via infra*) in **1c** and **1c**′.

Elemental analysis and mass spectrometry confirmed the stoichiometry [ReX(CO)$_3$(HL^n)]. The mass spectra of adducts show in some cases a signal corresponding to the molecular ion, although the peak due to the species [M−X]$^+$ is more intense.

Furthermore, facial geometry around the rhenium atom is suggested by the three strong bands ν(C≡O) in IR (sometimes collapsed) in the range 1895–2029 cm^{-1}. The ligand bands corresponding to the N–H groups appear between 3099 and 3422 cm^{-1} and are hardly modified by coordination (see [12] and references therein).

In general, all proton signals in the ^{1}H NMR spectra of the complexes in acetone-d$_6$ are shifted at low field (around 0.1–1 ppm) respect to the free ligands. Differently, the signal of the N(2)–H proton moves around 2 ppm. This behaviour has been previously observed in rhenium(I) complexes of arylhydrazones [27] and thiosemicarbazones [28] where the N(2)–H group is a member of the chelate ring resulting after the O/S,N-coordination. However, when the thiosemicarbazone is coordinated as a S-monodentate ligand, the N(2)–H proton signal behaves as the rest of the ligand signals [29].

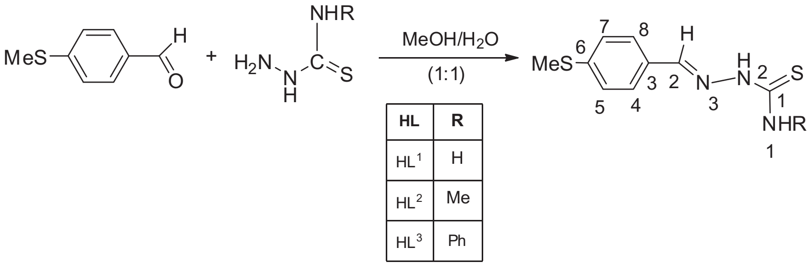
The thiosemicarbazonate complexes (**2a**–**c**) may be isolated by different ways depending of R (Scheme 3).

In all cases the X-ray study of the crystals **2a**, **2b**, **2c** (and **2c**·(CH$_3$)$_2$CO**)** showed the formation of binuclear thiosemicarbazonate complexes (*vide infra*). In a similar fashion to those observed in other rhenium(I) complexes of different thiosemicarbazone ligands [23], the deprotonation of the TSC ligand induces the labilization of the halogen in the position occupied by sulphur atom from other coordinated TSC (*vide infra*).

Thiosemicarbazonate [Re$_2$(L^3)$_2$(CO)$_6$] **2c** was identified as by-product in the reaction of *fac*-[ReX(CO)$_3$(CH$_3$CN)$_2$] and **HL^3** ligand, probably due to the easy deprotonation of this ligand in soft reaction conditions. This compound **2c** may be obtained by longer refluxing time than **1c** and **1c**′. However, to isolate the corresponding derivatives of L^1 and L^2 (**2a** and **2b**, respectively) was necessary to reflux a mixture of [ReCl(CO)$_5$] and the ligand in toluene for **2a** and the chloride adduct, **1b**, with NaOH in methanol for **2b**. In all of them, the three carbonyl IR bands are consistent with a facial geometry around rhenium atom.

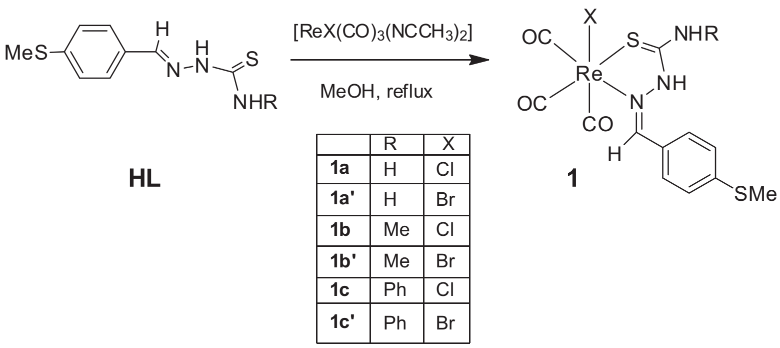
The ^{1}H NMR spectra of these compounds in acetone-d$_6$ show all the proton signals shifted at low field respect to the free ligands and, as expected, the signals for N(2)–H are absent due to the deprotonation.

The reaction in methanol of **1b**′ with NaOH in 1:2 relation yields also the compound **2b** too but, the X-ray analysis of the residual single crystals obtained after storing the filtrate solution several months showed the formation of **3b** (Scheme 4). This compound results of cyclization of a TSC yielding the thiadiazole ligand (2-methylamine-5-(para-methylsulfanephenyl)-1,3,4-thiadiazole). In



HL	R
HL^1	H
HL^2	Me
HL^3	Ph

Scheme 1. Synthesis of the thiosemicarbazone ligands.



HL

1

	R	X
1a	H	Cl
1a'	H	Br
1b	Me	Cl
1b'	Me	Br
1c	Ph	Cl
1c'	Ph	Br

Scheme 2. Synthesis of the rhenium(I) addutcs.