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Diastereoselectivity and molecular recognition of mercury(II) ions

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ABSTRACT

Two diastereoisomers of a new heteroleptic ruthenium cis-dithiocyanate dicarboxy-bipyridyl phenanthrolyl complex have been synthesized and characterized. This type of complexes can selectively bind mercury ions through the sulphur atoms on the thiocyanate groups. The properties of these complexes as chemosensor towards Hg^{2+} in solution and anchored onto a mesoporous Al_2O_3 film have been studied and analysed. A different level of sensitivity versus mercury ions in aqueous solutions was observed for each stereoisomer.

One of the important research topics in chemistry is the design of cheap and easy-to-use molecular receptors for highly toxic substances such as mercury [1]. During the last years, molecular receptors allowing simple visual discrimination of mercury have attracted much attention. Several different strategies have been described on the literature in order to detect metal ions, ranging from the use of organic molecules [2] and synthetically modified mesoporous materials [3] to the use of biological molecules [4]. In all cases, the control over the molecular receptor design was critical. We would like to illustrate that such control is important to the extent that molecular diastereoisomers have different sensitivities towards the presence of inorganic mercury.

Following our research on the synthesis of selective colorimetric molecular receptors for mercury ions [5], we have designed, synthesized and characterized new heteroleptic ruthenium cis-dithiocyanate complexes of the type cis-$[Ru(NCS)_2LL']$ (L = 4,4′-dicarboxy-2,2′-bipyridine, L′ = 5-amino-1,10-phenanthroline). This kind of ruthenium molecules, with two thiocyanates in a cis-conformation, among other metal-coordinated complexes [6], are particularly attractive molecular receptors for the selective optical detection of mercury ions. In spite of this, we decided to move a step forward and obtain a series of heteroleptic ruthenium diastereoisomers which contain the cis-dithiocyanate moiety. This ligand does in fact act as a mercury binding unit due to the presence of the sulfur atoms. Moreover, the presence of the thiocyanate ligands, coordinated axially to the Ruthenium atom, shifts the Highest Occupied Molecular Orbital (HOMO) from the central ruthenium atom towards the thiocyanate ligands and it is responsible for the strong light absorption of the ruthenium complex in the visible region of the light spectra ($\lambda_{abs} = 511$ nm). This observation is further is confirmed by theoretical calculations using Gaussian'03 (level and data basis B3LYP/6-31G(d)/SDD(Ru)) (Fig. 1).

The AR24 diastereoisomers were synthesized using the previously described procedures [7] that involve a series of straightforward steps: firstly the insertion of a phenanthroline, subsequent anchoring of a 4,4′-dicarboxy-bipyridine and the final introduction of thiocyanate ligands. Proton NMR analysis confirmed the presence of both diastereoisomers, as evidenced by the protons corresponding to the bipyridine moiety, which had the same chemical shift for both molecules resulting in an integration value of two protons for each signal. Moreover, proton signals corresponding to the phenanthroline moiety had different chemical shifts depending on their position respect to the thiocyanate ligands, resulting in an integration value of one proton for each signal. The purification of the diastereoisomers was carried out using reverse-phase semipreparative high performance liquid chromatography using acetonirile (0.1% trifluoroacetic acid (TFA)):water (0.1%TFA) (30:70) as mobile phase. Again, proton NMR analysis was utilized to confirm the separation of both stereoisomers and, furthermore, mass spectroscopy confirmed the molecular weight for both molecular receptors.

Our interest was to study how the binding of mercury ions to the thiocyanate ligands could affect the visual response in a different manner for the two diastereoisomers and, thus, we could identify the key parameters to increase the sensitivity of our molecular sensor towards mercury ions. To test our hypothesis either AR24α or AR24β was dissolved in ethanol to give a coloured solution (10^{-4} M), having an absorption band at $\lambda_{AR24\alpha} = 511$ nm

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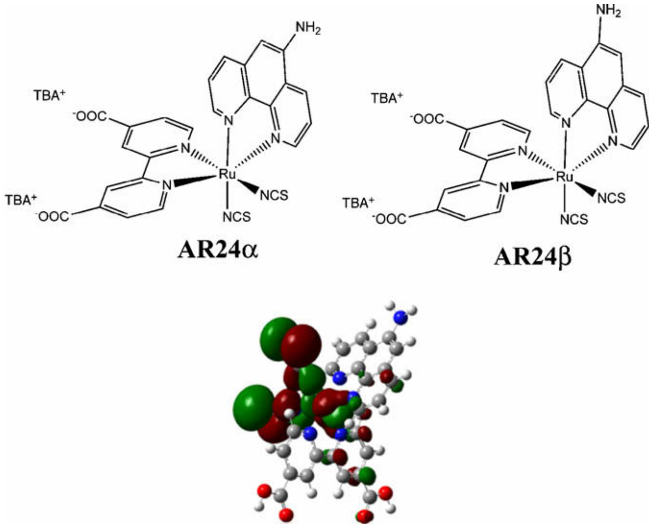

Fig. 1. Molecular structures of both AR24 diastereoisomers (top) and graphical representation of the HOMO orbital for AR24α that sites on the –NCS groups (bottom).

(ε_{511} = 9247 mol^{-1} cm^{-1} dm^3). Small amounts of mercury chloride dissolved in ethanol (10^{-3} M) were added to AR24α resulting in a immediate colour change, Fig. 2, from red to orange, corresponding to a hypsochromic shift of 46 nm with the concomitant decrease of the absorption band at 511 nm and the appearance of a new absorption band at 465 nm, with an isosbestic point at 485 nm, Fig. 3.

The observed blue shift (λ_{abs} = 511 nm → λ_{abs} = 465 nm) can be rationalized taking into account that the presence of the mercury linked to the thiocyanate groups implicates the formation of an electron donor-acceptor system [8] that increases the *p*-acceptor nature of the thiocyanate ligand, decreasing the electron density onto the Ru^{2+} metal atom, resulting in a decrease in the HOMO energy level, and consequently a blue shift in the maximum absorption wavelength.

When an identical experiment was carried out using AR24β, higher concentration of mercury ions (four times more concentrated) was necessary to obtain a similar optical response (Fig. 4). Analyzing the results, we can conclude that the diastereoisomers have, indeed, different sensitivities towards mercury ions.

This experimental observation has vast implications for the design of "naked eye" colorimetric ruthenium cis-dithiocyanate molecular receptors, which are, nowadays, one of the utmost selective and sensitive colorimetric molecular probes for mercury sensing (See Table 1 at the SI).

Several titrations with different metal ions of the ruthenium complexes dissolved in ethanol were studied by UV–visible spectroscopy. These complexes do not show appreciable colour change in the presence of Cd(II), Cu(II), Pb(II) or Zn (II) ions. Fig. 5 illus-

Fig. 2. Digital picture of four samples containing different stereoisomers in the presence and absence of mercury chloride (1 ppm) added from a 10^{-3} M ethanolic-based HgCl$_2$ stock solution).

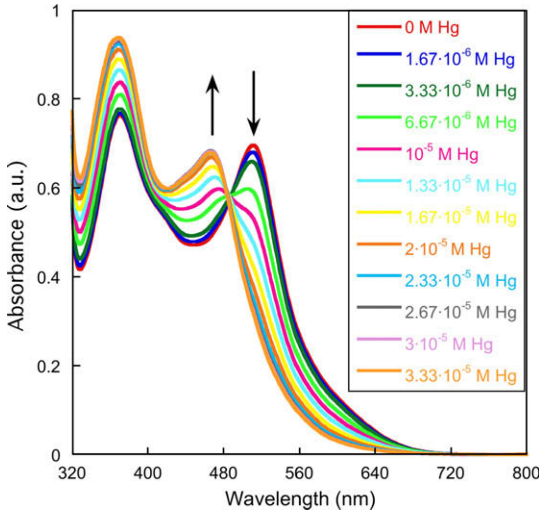

Fig. 3. Changes in the absorbance spectrum of a 10^{-4} M ethanolic AR24a solution upon the addition of increasing aliquots of mercury.

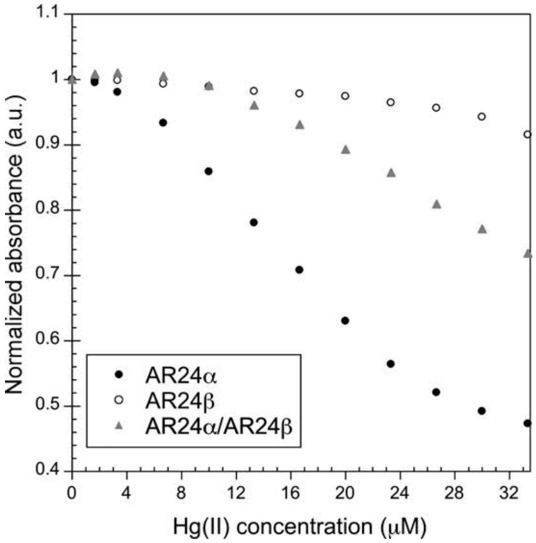

Fig. 4. Mercury titration of three 10^{-4} M solutions of AR24α, AR24β and a mixture of AR24α and AR24β in ethanol monitored at 511 nm using UV–Visible spectroscopy (total volume 3 mL). The titration with mercury chloride was carried out from a 10^{-4} M HgCl$_2$ ethanolic-based stock solution.

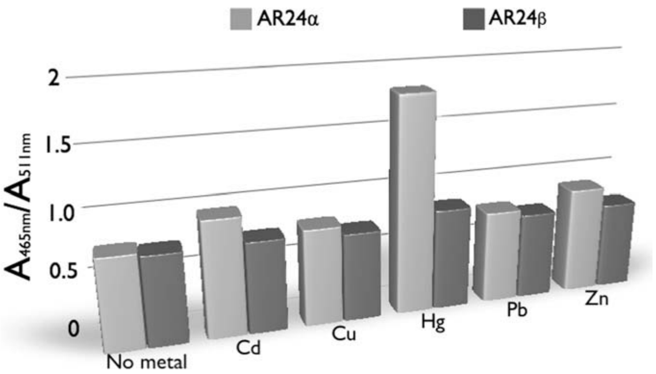

Fig. 5. Absorption ratio (A_{465nm}/A_{511nm}) of AR24α and AR24β in the presence of potential interference ions. 0.3 eq of each metal ion was added to different 10^{-3} M ethanolic solutions of the ruthenium complexes.