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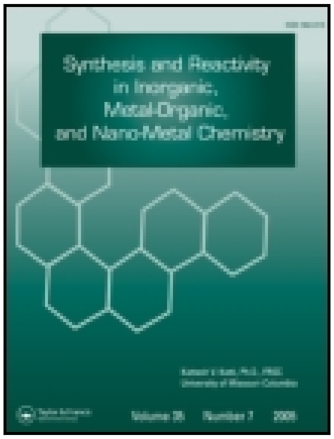

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Association Capacity of Ribose Bis(Thiosemicarbazonato)Copper(II) with Nitric Oxide

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The stability constant for copper(II) complex with ribose bis(thiosemicarbazone) (log K = 18.46 ± 0.15) was determined from UV-Vis data using LETAGROP program. Its interaction with nitric oxide was studied by spectroscopic and electrochemical techniques. This interaction was observed in the UV-Vis spectra as a shoulder around 350 nm and an isosbestic point at 420 nm. The corresponding equilibrium constant was calculated and the obtained value (log K = 8.68 ± 0.12), indicates the formation of a stable nitrosyl complex. Copper(II) bis(thiosemicarbazonato) complex was immobilized on a gold electrode, as demonstrated by cyclic voltammetric studies and used for NO recognition. The reduction of NO coordinated to the copper centre was observed at a potential around −700 mV.

Keywords bis(thiosemicarbazone), copper(II) complexes, nitric oxide, self-assembled monolayer

INTRODUCTION

Biological properties of thiosemicarbazones have been studied since 1956, when Brockman (1956) reported the antitumoral properties of 2-formylpyridine thiosemicarbazone. A series of α-(N)-heterocyclic carboxaldehyde thiosemicarbazones was later studied for their antitumoral activity (French and Blanz, 1965) and since then, this and other biological properties of thiosemicabazones have been reported (West et al., 1991). Bis(thiosemicarbazones) are tetradentate κ^4-N,N,S,S ligands that form stable and highly hydrophobic complexes with divalent first transition metals. For that reason, we studied copper(II) bis(thiosemicarbazonato) of different monosaccharide derivatives to obtain complexes with higher water solubility and potentially improved biological activity (Díaz et al., 1997, 1998a, 1999). In this sense it is important to point out that copper(II) complexes with 3-deoxy-D-erythro-hexos-2-ulose bis(thiosemicarbazones) were reported to present antitumoral activity (Horton and Nichol, 1987).

The comparison of the EPR parameters obtained in polycrystalline state and frozen DMF solution of ribose bis(thiosemicarbazonato)copper(II) (Scheme 1), Cu(RibTSC-2H), suggested a significant apical interaction with solvent molecules (Díaz et al., 1997). The obtained distortion factor (f) was around 113 cm, indicative of a slight distortion out of the relatively rigid plane of the complex. This consideration served to explain why when Cu(RibTSC-2H) was studied as a SOD mimic a very low activity was observed ($IC_{50} \sim 100\ \mu M$) (Díaz et al., 1999) as predicted before (Diaz et al., 1998a). The carbohydrate moiety apparently has no negative effect on the SOD-like activity since for copper(II) complexes with monosaccharide derived monothiosemicarbazones the corresponding activity is 100-fold higher (Díaz et al., 1998b).

The coordination of nitric oxide, a small radical with very important biological properties (Moncada et al., 1991), by copper(II) dithiocarbamate complexes (Díaz et al., 2003) stimulated us to study Cu(RibTSC-2H) as a NO scavenger. Here we report the formation constant of Cu(RibTSC-2H) and its interaction in aqueous solution with nitric oxide, NO, studied by spectroscopic and electrochemical techniques.

EXPERIMENTAL SECTION

General Procedures

All reagents were purchased from Merck (Germany) and were of analytical grade. Ribose bis(thiosemicarbazone) and its copper(II) complex were synthesized with the same procedure reported previously (Díaz et al., 1997). Saturated

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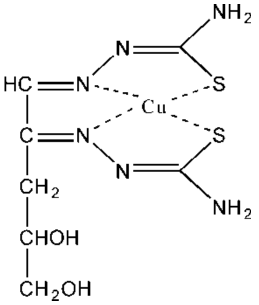

SCH. 1.

aqueous solutions of nitric oxide were obtained by generating the gas from the reaction of metallic copper with 5M nitric acid using Schlenk techniques. The reaction was performed in a Schlenk flask and the gas was purified by passing it through five traps containing 50% NaOH solutions. The purified gas was receipted in a Schlenk flask containing 20 mL of cold water, through which it was bubbled. A thin Teflon hose was connected into the NO aqueous solution through the side arm of the flask. Teflon stopcocks were used to isolate each part of the Schlenk system when necessary. The whole system, tightly isolated from air, was previously deoxygenated by passing pure nitrogen for no less than one hour. Once the NO aqueous solution was obtained the Schlenk flask was disconnected and then installed in a thermostatted bath at 293.00(5) K and the Teflon hose was connected to an Orion automatic microburette (model microBU2031) and purged.

Spectroscopy

The electronic spectra were recorded on an Ultraspec III spectrophotometer (Pharmacia) interfaced with a microcomputer for data acquisition. The temperature of the cell (293.0 K) was controlled by a Peltier controller system of Pharmacia (Autofill III) connected to the spectrophotometer and the data were processed by Origin (version 5) and SPEFO (Sillen and Warnquist, 1969; Sanchiz et al., 1997) version of the LETAGROP software (Sillén and Whiteker, 1969).

The NMR spectra were recorded on a Bruker AC 250 F spectrometer that operates at a frequency of 250.13 MHz (^{1}H) and 62.89 MHz (^{13}C).

Equilibria Studied by Electronic and NMR Spectroscopy

$KClO_4$ (0.25 M) was used as inert electrolyte. Since the RibTSC is not fairly soluble in water, the determinations were made in a mixture of DMSO (4%) in water. 0.37 mM aqueous solutions of RibTSC in excess of $HClO_4$ (0.1089 M) were prepared. NaOH (0.1 M) aliquots of 25 μL (up to 1100 μL) were added for a final volume of 25 mL. The electronic spectra were registered after each addition. The acid constant of RibTSC was obtained after processing selected data with SPEFO version of LETAGROP program.

The tautomeric equilibrium of RibTSC was studied by ^{1}H- and ^{13}C NMR. 34.6 mg of RibTSC were dissolved in 0.5 ml of DMSO-d_6 and the ^{1}H- and ^{13}C NMR spectra were recorded. This process was repeated after the addition of one and two equivalents of NaOD and followed by the neutralization of the RibTSC solution with two equivalents of CF_3OOH.

Electronic spectra were registered after different aliquots (10 μL–1100 μL) of RibTSC (52 μM) were added to an aqueous solution of $CuCl_2$ (52 μM). The absorbance at different wavelengths was introduced in the SPEFO version of LETAGROP program and the stability constant of [Cu(RibTSC-2H)] calculated.

Interaction of Cu(RibTSC-2H) with NO Studied Spectrophotometrically

Electronic spectra were made after successive additions of 10 μL aliquots of saturated aqueous solution of NO (2 mM) in 7.4 phosphate buffer solution (0.06 M) at 293.0 K to 2 mL of deoxygenated 94.9 μM aqueous solution of Cu(RibTSC-2H) at 1.5 min intervals, using Wavescan Repeat Scan facility. The recorded absorbances at different wavelengths were introduced in the SPEFO version of LETAGROP program and the stability constant of the Cu(RibTSC-2H)-NO adduct was calculated.

Electrochemical Studies

Electrochemical studies were carried out with a Yanaco P-900 cyclic polarograph coupled to a Graphted WX1000 X–Y recorder using a standard three-cell holder. Glassy carbon or modified gold bead, Pt and Ag/AgCl were used as working, counter and reference electrodes, respectively. All solutions were previously deoxygenated with oxygen-free nitrogen. Tetra-n-butylammonium tetrafluoroborate (0.2 M) was used as supporting electrolyte. The cyclic voltammogram of Cu(RibTSC-2H) (10 mM in DMSO) was recorded. The gold electrode was prepared by annealing the tip of a one mm diameter and 5 cm long gold wire (99.99%), previously cleaned overnight with nitric acid (68%). The gold bead was then electrochemically pre-treated in $HClO_4$ (0.1 M) at 2.1 V until gold(III) oxide formation (red colour). The electrode was cleaned with HCl (0.1 M) and thoroughly rinsed with water. The geometric area of the bead was calculated using $[Ru(NH_3)_6]Cl_3$ as previously described by Kaifer (1995). The freshly pre-treated gold surface was modified by its immersion into an oxygen-free DMSO solution of 10 mM RibTSC for 72 h, followed by its interaction with a 0.2 mM DMSO solution of $CuCl_2$ for 24 h. The double-modified electrode was thoroughly rinsed with doubly distilled water and ethanol. Its cyclic voltammograms were performed in 1 M Na_2SO_4 solution between −200 to 700 mV. The electrochemical behaviour after bubbling with NO was studied. NO was also generated ‘in situ’ from the interaction of $NaNO_2$ (10 mM) with H_2SO_4 (12.3 mM).

RESULTS AND DISCUSSION

A previous report on the spectroscopic data, particularly ^{1}H-RMN, ^{1}H-^{1}H COSY, and NOE-DIFF, and computer structure modelling indicated that the TSC moieties of the free RibTSC ligand are both in E-configuration (Díaz et al., 1997). When this ligand coordinates to copper(II) as a tetradentate NSSN ligand it adopts a Z-configuration forming a rigid and only slightly distorted square plane, as suggest by EPR spectroscopy studies in solid state and DMF solution. An apical interaction of the solvent with the copper centre was observed, probably favoured by H-bond interactions with the hydroxyl groups of the carbohydrate moiety (Diaz et al., 1997). Due to the interaction of these later groups with water, and that the sulphur atoms are oriented inwards, Cu(RibTSC-2H) is water-soluble, more than the ligand itself.

Spectrophotometric Studies

The visible spectra of RibTSC titrated with NaOH present an isosbestic point at 350 nm (Figure 1). At pH values lower than 9.2 a maximum at 331 nm is recorded, while for very basic solutions ($pH > 11$) this maximum is shifted to 368 nm. The maximum at 331 nm decreases in intensity with each addition of NaOH, while the contrary occurs for the maximum at 368 nm. The pKa calculated from these spectral data using the SPEFO version of the LETAGROP program reported a value of 11.82 ± 0.17. This result is in good agreement with those reported by Beraldo (1986) and Petering (1979) (11.50 ± 0.2 and 10.97, respectively) for 2-formylpyridine thiosemicarbazone in aqueous solutions in the presence of 0.5% DMSO, obtained by spectrophotometric methods. Signorella et al. (1999) reported pKa values (10.11 ± 0.02 and 10.23 ± 0.01) obtained by a potentiometric method in 30% v/v dioxane-water for glucose bis(thiosemicarbazone) (GluTSC), a ligand very similar to RibTSC.

When the acid-base equilibrium of RibTSC (in DMSO-d_6) was studied by NMR two signals at 10.83 and 11.68 ppm for the N2-H protons were observed. Both signals strongly decrease in intensity and become much wider upon addition of one equivalent of NaOD and completely disappear when the second equivalent of NaOD is added. The initial spectrum is restored when two equivalents of CF_3COOH are added. On the other hand, the ^{13}C NMR spectra of RibTSC did not change once the experiment was concluded indicating a high stability of the ligand under such conditions.

The high resemblance observed by NMR between both N2-H protons and the relatively high deviation in the obtained pKa value, explains why only one constant could be determined.

The addition of different aliquots of RibTSC to a $CuCl_2$ solution provoked the appearance and increase in intensity of a band at 467 nm, as depicted in Figure 2. The stability constant of Cu(RibTSC-2H) was calculated from these spectral data using the SPEFO version of the LETAGROP program. The obtained value corresponded to $\log K = 18.46 \pm 0.15$, similar to that reported for Cu(GluTSC-2H) ($\log K = 20.65 \pm 0.06$) (Signorella et al., 1999). The obtained stability constant indicates that Cu(RibTSC-2H) is highly stable, as expected, and can be submitted to study its interaction with NO.

The coordination of NO to a copper(II) dithiocarbamate complex was previously reported where the Cu(II)-S bond was considered to play an important role (Díaz et al., 2003). For that reason, the interaction of Cu(RibTSC-2H) with NO(aq) was considered possible. The effect of the addition of aliquots of NO saturated aqueous solutions (7.4 phosphate buffer) to Cu(RibTSC-2H)(aq) was followed spectrophotometrically. The band assigned to the ligand at 302 nm (π-π^*) increased only slightly in intensity. This variation can not be attributed to interactions of NO with the ligand, such as formation of adducts with nucleophiles (amines, sulphides

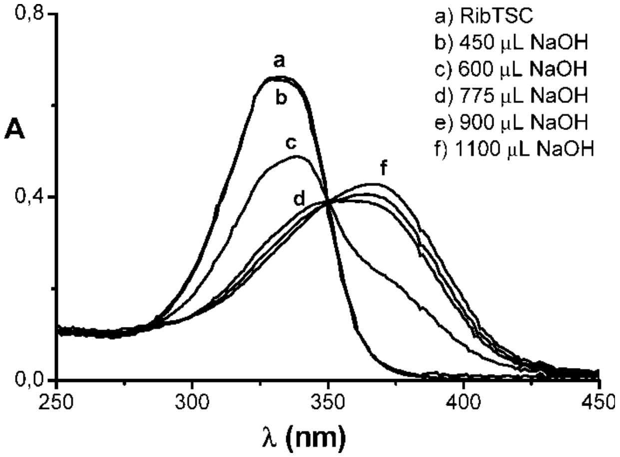

FIG. 1. Spectrophotometric titration (293.0 K) of RibTSC ($HClO_4$ in excess) with NaOH; isosbestic point at 350 nm.

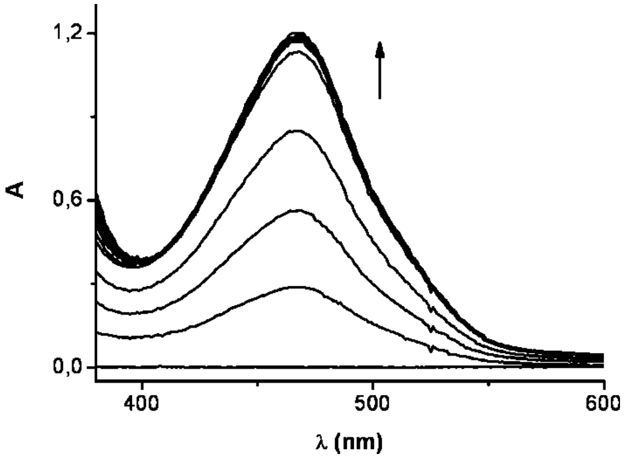

FIG. 2. Electronic spectra (293.0 K) when aliquots of RibTSC (52 μM) were added to an aqueous solution of $CuCl_2$ (52 μM).

and thiols) (Lee et al., 2002). To affirm this, the possible RibTSC-NO interaction was studied spectrophotometrically and only a partial decomposition of the ligand was observed at relatively high concentrations of NO.

A decrease in the absorbance of the band with maximum at 467 nm (d-d) was observed when NO aliquots were added to Cu(RibTSC-2H). At the same time, a shoulder around 350 nm and an isosbestic point at 420 nm were observed (Figure 3). When the Cu(RibTSC-2H)-NO system was purged with pure nitrogen gas or heated up to 333 K the spectrum corresponding to Cu(RibTSC-2H), free of NO, was recovered. The isosbestic point and these later results are indicative that a reversible NO-Cu(RibTSC-2H) interaction took place. Similar spectrophotometric results for interactions of copper(II) dithiocarbamate complexes with NO were previously reported (Díaz et al., 2003). The UV data obtained after each addition of NO were processed by the SPEFO-LETAGROP program and the stability constant of the Cu(RibTSC-2H)-NO adduct was obtained: log K = 8.68 ± 0.12. This value is in good agreements with previous reports for others nitrosyl copper complex and indicates that a stable mononitrosyl complex was formed (Díaz et al., 2003; Mederos et al., 2003).

Electrochemical Studies

The interaction of Cu(RibTSC-2H) with NO in aqueous solution was also studied by cyclic voltammetry. A thioceto-thioenolic equilibrium is present in mono- and bis(thiosemicarbazone) solutions. Taking this into consideration, the formation of a self-assembled monolayer (SAM) of RibTSC through its thioenolic groups on a gold electrode bead was studied. For this the gold bead, previously treated and cleaned, was immersed into a RibTSC solution (DMSO) for 72 h. The cyclic voltammogram (CV) of the resulting modified gold electrode in KOH ($0.5\,\mathrm{moL^{-1}}$) was recorded and an intense irreversible peak at-500 mV (vs. Ag/AgCl) was observed. This peak was assigned to the reductive desorption of RibTSC and indicates that a stable SAM was formed on the gold bead.

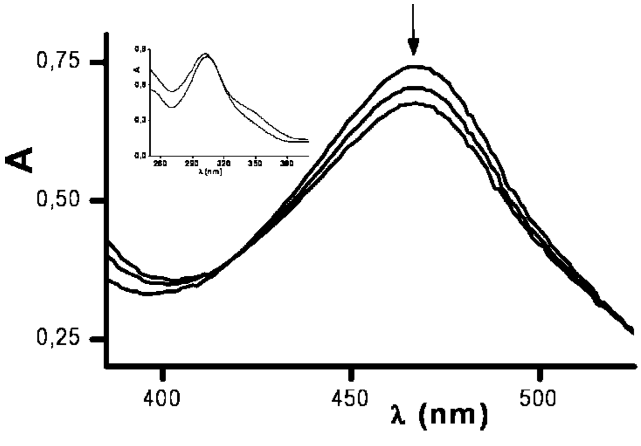

FIG 3. Electronic spectra (293.0 K) of Cu(RibTSC-2H) (94,9 μM) for different additions of NO saturated aqueous solution. Inset are the spectra for Cu(RibTSC-2H) 46.5 μM.

The CV of $[Ru(NH_3)_6]Cl_3$ with both a clean and modified (with RibTSC) gold bead, as working electrodes, were recorded. An appreciable decrease in the intensity of both anodic and cathodic waves for the Ru(III)/Ru(II) pair was observed for the modified electrode when both CV were compared. This observation confirms that the SAM was formed in the bead modified with RibTSC. Its molecular surface was determined ($\Gamma = 3\,\mathrm{nmol/cm^2}$) using the peak area of the reductive desorption curve.

Once demonstrated that RibTSC was chemisorbed on the gold electrode surface, the modified electrode was immersed into a DMSO solution of $CuCl_2$ for 24 h. The obtained double-modified electrode was then studied by cyclic voltammetry from −200 mV to 700 V in 1 M Na_2SO_4. Two redox peaks ($E_c = 180\,\mathrm{mV}$ and $E_a = 320\,\mathrm{mV}$) were observed (Figure 4a), that can be attributed to the Cu(II)/Cu(I) pair of copper(II) coordinated to the ligand self-assembled on the electrode. These values indicate the presence of Cu(II) in the double-modified electrode and areclose to those obtained for the Cu(RibTSC-2H) complex in DMSO ($E_c = 280\,\mathrm{mV}$ and $E_a = 360\,\mathrm{mV}$) using a clean gold electrode. The observed similarity between the values of the redox peaks of the Cu(RibTSC-2H) complex in DMSO and the double-modified gold electrode suggests that in the later Cu(II) is coordinated to the self-assembled ligand in a similar way as in Cu(RibTSC-2H). In the double-modified electrode both of sulphur atoms (or only one) should be associated to the gold surface forming a Au(I)-S(thioenol) bond. The association of only one sulphur atom to Au should permit a stronger π-interaction of the other one with Cu(II). On the other hand, the double interaction of each sulphur atom with Au and coordinated Cu(II), as depicted in Figure 4b, could also be possible.

When the double-modified gold electrode was immersed into a NO aqueous solution and its CV recorded a new cathodic wave was observed at −720 mV (Figure 5), which can be assigned to the $NO + e^- \rightarrow {}^3NO^-$ reduction (Farmer

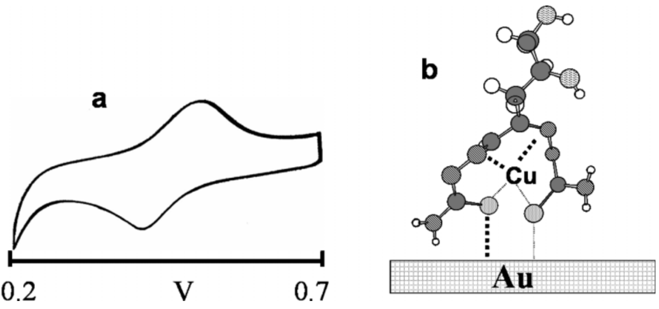

FIG. 4. Cyclic voltammogram of the double-modified gold electrode in a Na_2SO_4 (1M) solution (a); and its schematic representation (b). (● N, ● C, ● S, ● O, ○ H).

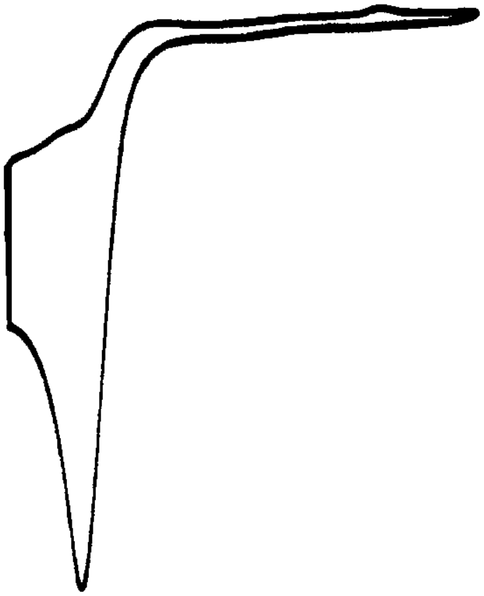

FIG. 5. Cyclic voltammogram of the double-modified gold electrode in a Na_2SO_4 (1 M) solution saturated with NO.

and Sulc, 2005), only possible when NO is coordinated to a metallic centre in one of its forms.

The double-modified electrode was also introduced in a solution containing $NaNO_2$ to which H_2SO_4 was added to generate NO (between 6 μM and 15 μM). Under such conditions the intensity of the cathodic wave at −720 mV was observed to be sensitive to the concentration of NO. Practically no shift in the Cu(II)/Cu(I) pair was observed as a consequence of the interaction with NO. Nevertheless, a small increase in the intensity of the anodic wave (Cu(I) → Cu(II)) was observed for each cycle. This observation is an indication that the coordination of NO by the Cu(II) centre could provoke its reduction with the formation of a Cu(I)-NO^+ bond, as observed before (Díaz et al., 2003; Mederos et al., 2003). The great similarity in the UV-Vis spectra of the Cu(RibTSC−2H) − NO interaction with that reported before for copper(II) dithiocarbamate complexes also supports this suggestion. The results reported here permit to suggest the possibility of using the double-modified electrode as a NO sensor. Further work in this direction is in progress at our lab.

CONCLUSIONS

The determined high stability of Cu(RibTSC-2H) in solution made possible the study of its interactions with nitric oxide by spectrophotometric and voltammometric determinations. The coordination of NO to Cu(RibTSC-2H) was expressed spectrophotometrically as a shoulder at 350 nm and an isobestic point at 420 nm and the obtained equilibrium constant indicates the formation of a stable mononitrosyl complex, [Cu(RibTSC-2H)NO].

A double-modified gold electrode was prepared by the self-assembly of RibTSC, presumably through its thioenolic groups, and the further coordination of copper(II). Electrochemically such coordination resulted to be similar to that in Cu(RibTSC-2H). Electrochemical responses of the double-modified electrode were observed when it was introduced into a NO-containing solution. An intense cathodic wave, assigned to reduction of NO was observed with double-modified electrode. The results obtained in this work permit to analyze Cu(RibTSC-2H) as a potential NO scavenger and the double-modified electrode as a NO sensor.

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