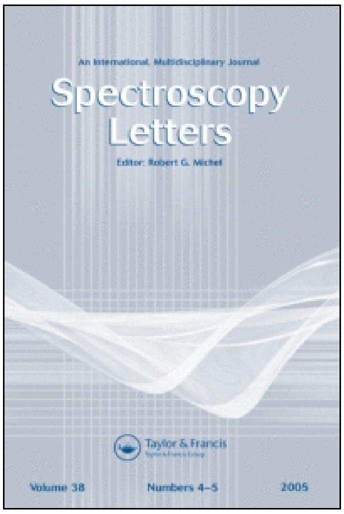

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Preparation and Characterization of New ^{99}Tc and Re-Complexes in Colloidal State

S. A. El-Shatoury[a]; R. M. Hassan[a]; R. M. Mahfouz[a]
[a] Chemistry Department, Faculty of Science, Assiut University, Assiut, Egypt

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PREPARATION AND CHARACTERIZATION OF NEW ^{99}Tc AND Re-COMPLEXES IN COLLOIDAL STATE

S.A. El-Shatoury, R.M. Hassan and R.M. Mahfouz

Chemistry Department, Faculty of Science, Assiut University, Assiut 71516 Egypt.

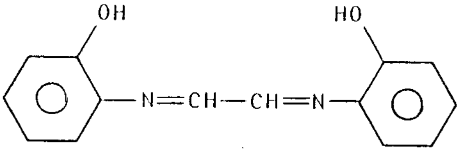
Summary:

New ^{99}Tc and Re-complexes in colloidal state were prepared by the direct reduction of TcO_4^- and ReO_4^- with $NaBH_4$ in presence of a new synthezied ligand: 2,2'(ethan diylidene dinitrilo) diphenol. The two complexes were precipitated in colloidal forms and characterized by spectroscopy and HPL chromatography. The complexes are H_2O soluble.

Introduction:

The development of fundamental coordination chemistry of technetium and rhenium continue to make significant impact in the discovery of new radiopharmaceuticals in nuclear medicine due to ideal nuclear properties of both ^{99m}Tc and ^{186}Re(1,2). New ligand systems are being extensively used to produce complexes of Tc and ^{186}Re of potential use as radiopharmaceuticals. It is of great importance in clinical studies to produce such radiopharmaceuticals in heigh yeild, high radiochemical purity, and in a simple manner by mixing of

$^{99m}TcO_4^-$ or $^{186}ReO_4^-$ with ligand solution in presence of a simple reducing agent such as $NaBH_4$(3). The nature of most ^{99m}Tc imaging agent is, however, speculative because only nanomolar amounts of ^{99m}Tc are used in diagnostic imaging procedures. By working with long-lived ^{99}Tc, 0.3MeVβ emitter with a half-life of 2.12 x 10^5 years, macroscopic amounts of technetium compounds can be isolated and characterized by conventional chemical and spectroscopic methods. In the present work we selected a new synthesized ligand 2,2'(ethan diylidene dinitrilo)diphenol (EDOP).



For complexation with technetium and rhenium with aim to find informations about the mechanism of complexes formation and to prepare new Tc and Re complexes of potential use in nuclear medicine.

Experimental:

Chemicals and Reagent:

^{99}Tc as NH_4TcO_4 (Amersham), Re as NH_4ReO_4 (Aldrich) and $NaBH_4$ (Aldrich) were obtained as gifts from KFA (Julich FRG). All other chemicals and solvents used were of analytical and HPLC grades. 2,2'(ethane diylidene dinitrilo) diphenol was prepared according to the following chemical method:

A mixture of 0.2 mol O-aminophenol and 0.1 mol glyoxal (40 wt% solution in H_2O) was dissolved in 100 ml acetone. The reaction mixture was refluxed for couple of hours where a pale buff needles separated. The product was filtered off washed with ethanol, dried and recrystallized from acetone as pale buff needles crystals. The found microchemical analysis data was in good agreement with the values calculated for $C_{14}H_{12}N_2O_2$.

Instruments:

I.R spectra were recorded as KBr pellets on a shimadzu 408 spectro-photometer. The U.V vis. spectra of aqueous solutions of the complexes were recorded using a schimadzu double beem 200 spectro-photometer. HPLC was performed on a Merck - Hitachi (Tokyo) apparatus filted with L-600 pump, L-4200 U.V. vis detector and Lichrosorb Rp-18 (7μm) column using 60-40 MeOH: H_20 as the mobile phase and a flow rate of 2 m/min. The detector frequency was 254 nm. ^{99}Tc is a β weak emilter (E_{max} = 0.29 MeV) and β emission is not accompanied by γ-radiation, the handling of ^{99}Tc on a small scale (<20 mg) is not dangerous, provided elementary precautions are taken. For more details concerning the handling of Tc, see reference(4).

Synthesis of the complexes:

20 ml (0.2 mol) of non-aqueous solution of ligand in MeOH was added to aqueous solution of each NH_4TcO_4 and NH_4ReO_4 (0.2 mol each). An alkaline solution of $NaBH_4$ (0.04 mol) was added dropwise to the reaction mixture in case of NH_4TcO_4 whilist an acidic solution of this reducing agent was added to NH_4ReO_4. The brown solution of the complex formed were evaporated and precipitatated in colloidal state.

Results and Discussion:

Complexation reactions with Tc and Re have been carried out using the following ligand:

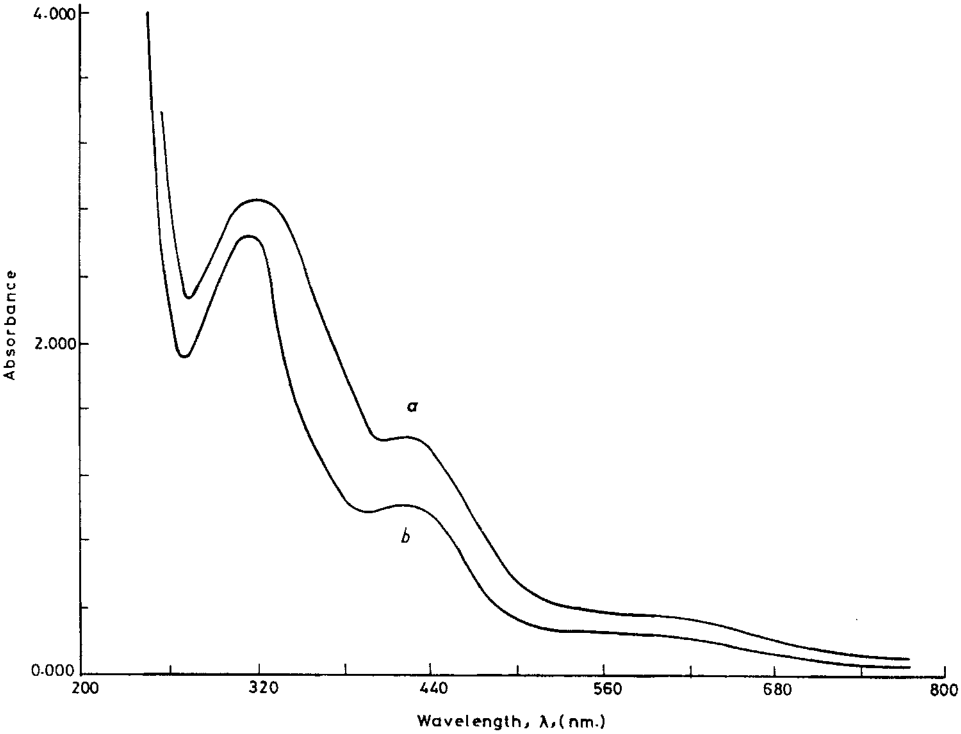
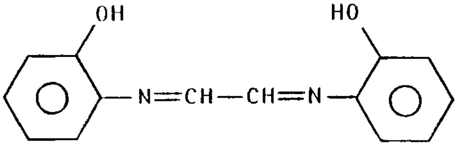


Fig. 1. The electronic absorption spectra of: a: Tc-EDOP and b: Re-EDOP Complexes in H_2O (25°C).



The deep brown complexes of Tc and Re obtained by NH_4TcO_4 and NH_4ReO_4 with $NaBH_4$ in alkaline and acidic medium respectively and in presence of the above ligand were characterized by conventional physical and

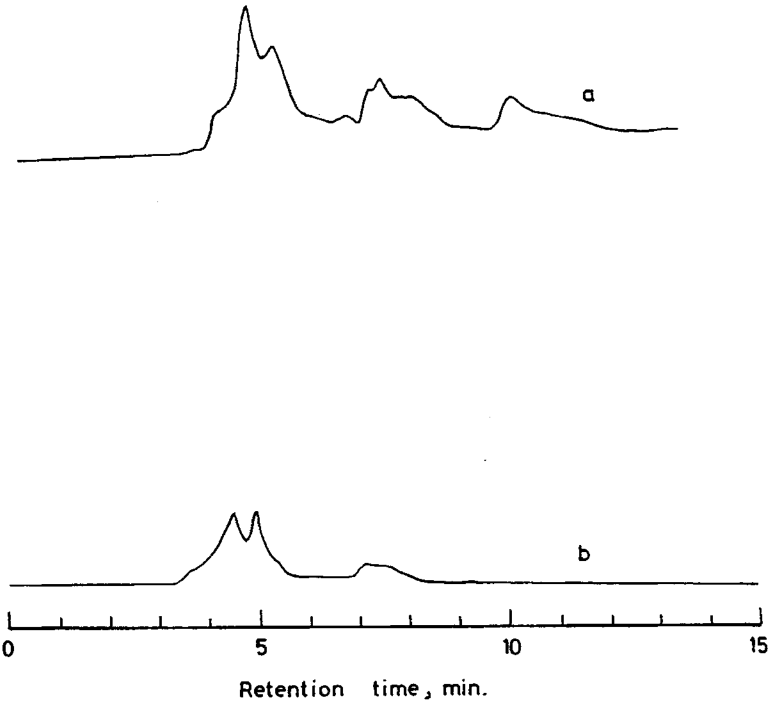


Fig. 2. The HPL Chromatograms of: a: Tc-EDOP and b: Re-EDOP Complexes, Conditions as in the text.

chemical methods of analysis and they showed resemble chemical behaviour. Their electronic spectra were recorded in H_2O at 25°C (Fig. 1). The brown solutions of both Tc-EDOP and Re-EDOP complexes exhibit two absorption maxima at 430, 420 nm and 32o, 310 nm respectively in addition to shouldars at 620 nm. The band at 450 nm may be attributed to d-d transitions; whereas the absorption at 310 nm can be assigned as a charge transfer band. Hence; from ageneral spectral point of view it can be concluded that there is resemblance in the nature of the two complexes.

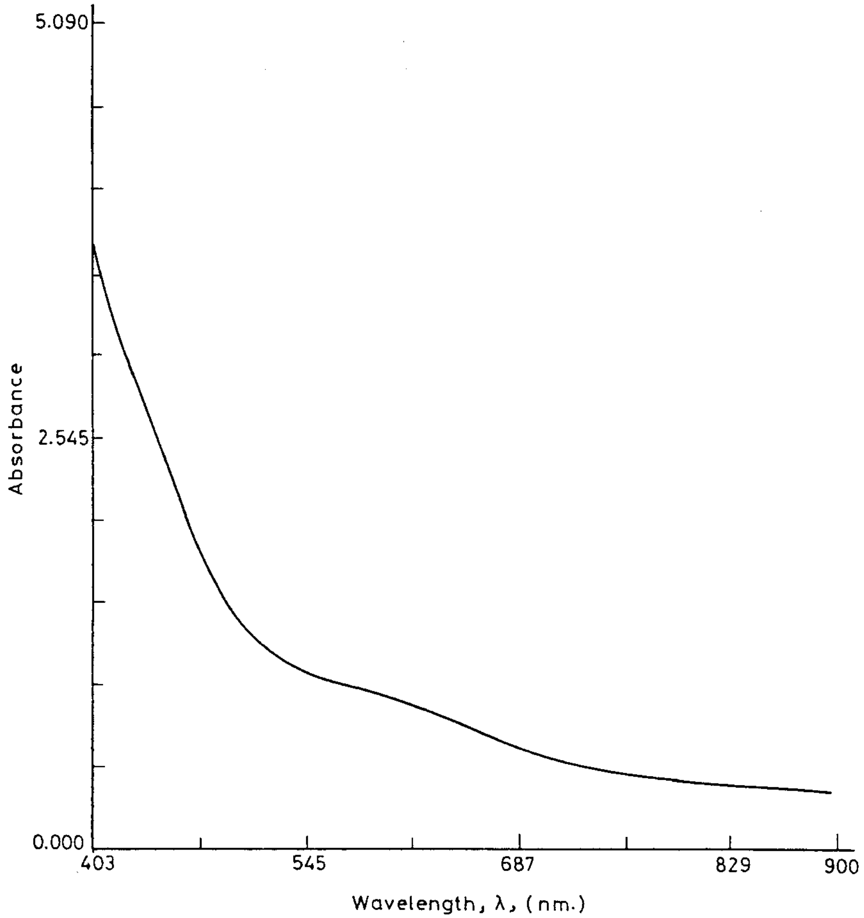


Fig. 3. The Electronic Absorption Spectra of Re-EDOP after Standing Couple of Months (in air) in H_2O (25°C).

Relevant i-r bands for free ligand which provide structural evidence for the mode of attachment of the ligand to technetium and rhenium are 1600 cm^{-1} [$^{\upsilon}$C=N] and 3400 cm^{-1} [$^{\upsilon}$OH]. The $^{\upsilon}$(C=N) band of free ligand was observed at heigher frequency (1650 cm^{-1}) in the spectra of Tc and Re complexes. The disappearance of OH band at 3300 cm^{-1} indicate that it was deprotonated. These results indicate that the coordination has been done via oxygen and nitrogen atoms. A band at 3500 cm^{-1} is consistent with the presence of water in the compounds.

The complexes were investigated by HPLC using a mixture of MeOH and H_2O (60/40 v/v) as a mobile phase. Fig. 2 shows the HpL chromatograms of Tc- and Re complexes respectively directly after complexes preparation. The chromatograms show unresolved peaks and it was very difficult to separate these peaks by changing the conditions of HPLC experiments. These chromatograms show nearly the same chromatographic profile after standing in air for couples of days. The complexes solutions were kept in air for couple of months and another HPLC experiment was carried out to test the stability of these complexes. The chromatograms of both Tc-EDOP and Re-EDOP showed different chromatographic profiles due to decomposition of these complexes. The unstability was also tested by measuring UV.-Vis. spectra of the investigated complexes. The spectra showed dissappearance of bands at (420 nm, 430 nm) and (310 nm, 320 nm) for Tc-EDOP and Re-EDOP respectively (Fig. 3). The precipitation of the complexes in colloidal state make more chemical and physical investigations on these complexes rather difficult and based on the foregoing discussion, it could be concluded that 2,2` (ethan diylidene dinitrilo) diphenol forms complexes with technetium and rhenium and coordinated via oxygen and nitrogen atoms. Although the solutions of the complexes was not indefinitely stable, the fact that it is H_20 soluble may be of potential use in clinical studies.

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