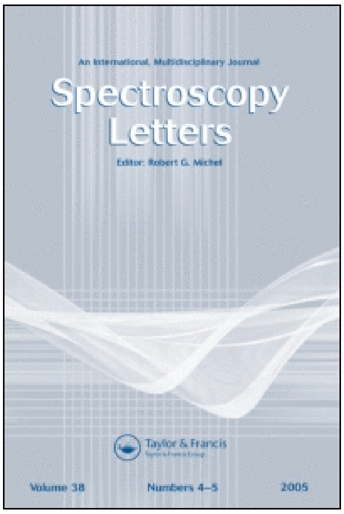

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New Technetium (V) and Rhenium (V)-N-Acetyl Anthranilic Acid (NAA) Complexes

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New Technetium (V) and Rhenium (V)-N-acetyl Anthranilic Acid (NAA) Complexes.

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Summary

New N-acetyl anthranilic acid (NAA) -Tc(V) and -Re(V) complexes were prepared by the direct reduction of TcO_4^- and ReO_4^- with alkaline and acidic $NaBH_4$ respectively and in the presence of an excess of ligand. The complexes were characterized by spectroscopy and elemental analysis. Reversed phase HPLC on Lichrosorb-Rp-18 was used to isolate Tc(V)-NAA complex. Electrophoresis measurements showed them having negative charges. The complexes were H_2O soluble.

Introduction

Stimulated by the wide use of ^{99m}Tc radiopharmaceuticals (^{99m}Tc; γ-emitter with E_γ= 140 KeV, half-life time $t_{1/2}$=6h) in diagnostic nuclear medicine also the coordination chemistry of this man made element entered the center of interest. The present status of technetium research has been described in several excellent reviews$^{(1-4)}$.

Several complexes of technetium and rhenium with hydroxy carboxylic acids have been studied, but little work has been done about complexes of technetium with phenolcarboxylic acids(5).

We report here, synthesis and characterization of oxotechnetium and oxorhenium complexes of N-acetyl-anthranilic acid. The complexes have been investigated by spectroscopy, HPLC, and elemental analysis.

Experimental

Unless otherwise noted all chemicals were of reagent grade. Solvent used in HPLC were of HPLC grade. Tc as NH_4TcO_4 was obtained as a gift from KFA (Jülich, Germany). N-acetyl-anthranilic acid (NAA) was purchased from Aldrich and used without further purifications.

I.R. spectra were recorded as KBr pellets on a shimadzu 408 spectrophotometer. The U.v. Vis. spectra of the complexes were recorded using a shimadzu double beam 200 spectrophotometer.

HPLC was performed on a Merck-Hitachi (Tokyo) chromatograph fitted with an L-6000 pump, L-4200 UV Vis. detector and controlled by data processor. Separations were effected using $5x10^{-3}$ mole NaCl in H_2O (solvent A) and in MeOH mixture (solvent B). Initial conditions were A:B=40:60. Upon injection of the sample a 10 min linear gradient to a ratio A:B=80:20 was performed Electrophoresis experiments were performed with a thin layer electrophoresis cell in a mixture of 1.0 M HCl/1.0 M Na_2BO_4 at 600 V for 20 min. On whatman No. 1 paper. Elemental analysis for C,N and H was carried out using a perkin-Elmer 240 C instruments.

Tc content in Tc-NAA complex was determined by radioactivity measurements on dilute solutions of the complex using a liquid scintillation counter. A dilute solution of NH_4TcO_4 of known concentration was used for calibration.

^{99}Tc is a weak β emitter (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 some elementary precautions are taken. For more details concerning the handling of Tc, see reference (6).

Synthesis of the Complex

(i) Tc-NAA Complex

≃ 18 mg of NH_4TcO_4 were dissolved in 5 ml bidistilled water. 5 ml of NAA solution in methanol containing ≃ 180 mg of NAA was added to NH_4TcO_4 solution. 30 mg of $NaBH_4$ was dissolved in a minimum volume of 0.1 M NaOH and added dropwise to the reaction mixture. The resultant deep brown solution of Tc-NAA was rotary evaporated untill the volume was reduced to quarter of the original. The complex was isolated as brown solid product.

(ii) Re-NAA Complex:

≃ 27 mg of NH_4ReO_4 were dissolved in 5 ml bidistilled water. 5 ml of ethanolic solution of NAA containing 180 mg NAA was added to NH_4ReO_4 solution. 30 mg of $NaBH_4$ was dissolved in a minimum volume of 0.1 M HCl. and added dropwise to the reaction mixture. The reaction mixture was heated to 90°C for 30 min. The solution was extracted with diethylether to remove the excesligand and the complex was precipitated as brown solid complex.

Results and Discussion

The successful preparation of Tc, and Re-N-acetyl-anthranilic acid complexes depends on careful control of reactions parameters such as pH, temperature, time of reaction, and concentration of reductant. The brown solid products obtained by direct reduction of NH_4TcO_4 and NH_4ReO_4 solutions by $NaBH_4$ in alkaline and acidic medium respectively in the presence of an excess of ligand were characterized by standard techniques. Their electronic spectra were recorded in H_2O at ambient temperature. The electronic spectrum of Tc-NAA complex exhibits an intense CT band at 450 nm whilst the electronic spectrum of Re-NAA complex shows two absorption maxima at 490 nm, and 460 nm (Fig. 1). These bands are tentatively assigned to charge transfer transitions. The stoichiometry of the complexes formed in solutions were ascertained by appling the conventional spectrophotometric molar ratio method. The results show 1:2; M:L ratio (where M=Re,Tc and L=NAA). Electrophoresis measurements of the two complexes in a mixture containing 1.0 M HCl/1.0 M Na_2BO_3 at 540 V for 20 min. showed nucleophilic migration under the conditions applied in this work suggesting that they arenegatively charged.

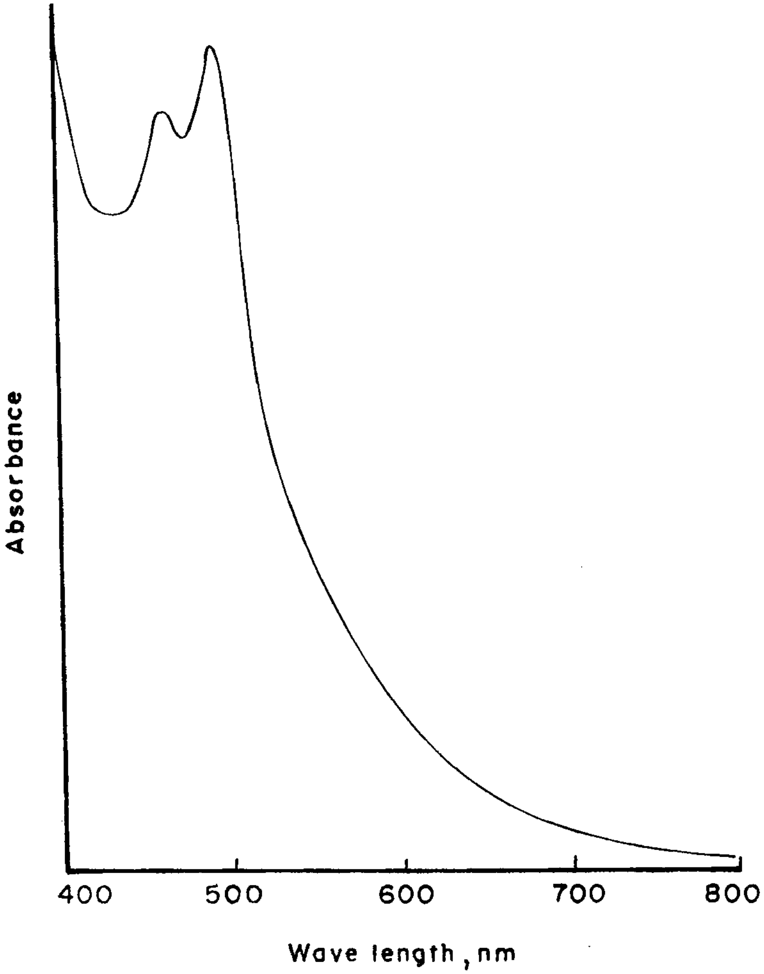


Fig. 1: Electronic absorption spectrum of Re-NAA in EtOH at 25°C.

HPL chromatogram of the Tc-NAA complex measured directly after the addition of the reactant solutions exhibits two prominent peak A, and B (t_R= 6 min, and 11 min. A small peak Cwas also shown in the chromatogram. Peak A was assignable to excess of NH_4TcO_4 remains unreacted. Peak B and C were due to complex formation. The unsymmetrical shape of Peak C indicates that it probably consist of minor overlapping components. The invitro stability of Tc-NAA complex is good even 24 h after preparation, HPLC analysis generally shows < 10% decomposition. The complex is much less stable when exposed to the conditions of chromatographic analysis, and thus these conditions must be carefully controlled in order to prevent decomposition during analysis. Attempts to separate Re-NAA by HPL chromatographic analysis were unsuccessful due to decomposition of the complex on the solid column material. Microanalysis of C,N, and H contents in both Tc-NAA, and Re-NAA are reported in table 1. further on Tc content in Tc-NAA was determined by radioactivity measurements and reported also in table 1. The values are approximately comparable with the calculated ones.

Typical i.r absorption bands assigned to the asymmetric stretch of the Tc=O, and Re=O are 980 cm^{-1} and 950 cm^{-1} respectively. Both i.r spectra of the investigated complexes show no bands associated with NH stretching modes. The $\nu_{C=O}$ in the free NAA ligand consisted of a band at $\simeq$1700 cm^{-1}. This band is shifted to lower frequency in the investigated

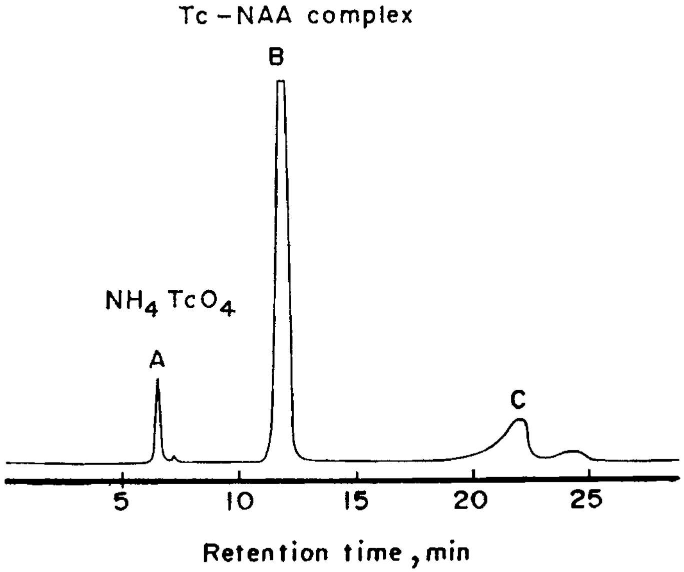


Fig. 2: Row HPL chromatogram of Tc-NAA complex, Lichrosorb Rp-18-Column, mobile phase 60:40 MeOH: H_2O, flow rate 1 ml min^{-1}.

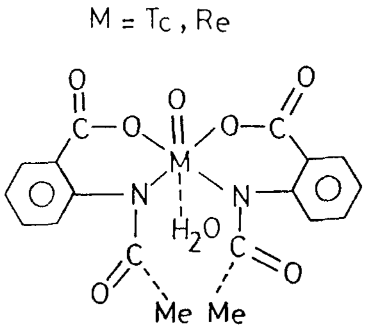
Table 1: Micro Analytical Data of the investigated complexes.

Compound	Calcd (Found) %			
	C	H	N	Tc
$[Tc\ O(CH_3CoNC_6H_4Coo)_2 \cdot H_2O]^-$	44.4	3.3	5.8	20.3
	(49.1)	(3.2)	(5.5)	(20.6)
$[Re\ O(CH_3CoNC_6H_4Coo)_2 \cdot H_2O]^-$	37.7	2.8	4.9	–
	(37.4)	(2.5)	(4.3)	–

complexes. This clearly indicates the coordination of Tc, and Re to C=O.

It should be mentioned that the oxytechnetium complexes are most conveniently categorized on the bases of their oxotechnetium cores.(7) The complexes containing TcO^{3+} core can be five, six or seven coordinate. Addition of simple monodendate ligands such as diethyl amine results in major spectral changes of the two complexes suggesting that the sixth coordination site in each complex is probably occupied by water molecule.

On the bases of the foregoing Discussion it might be deduced that N-acetyl-anthranic acid form anionic complexes with both technetium and rhenium. The following structure is plausible



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