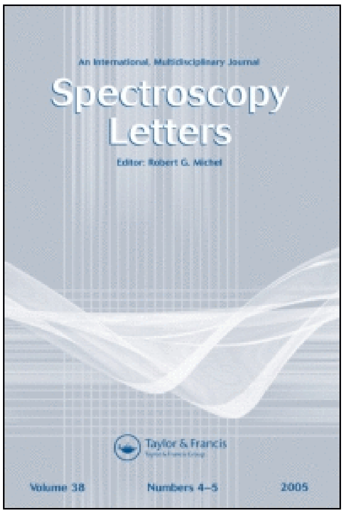

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SYNTHESIS AND CHARACTERIZATION OF NEW In(III), Re(III), Re(V), Pd(II), AND Rh(III) COMPLEXES OF TOLUENE-3,4-DITHIOL

Abdulaziz I. Al-Wassil[a]; Khalid A. Al-Farhan[a]; Saad M. Alsheri[a]; Mohsen H. Mukhalalati[a]; Refaat M. Mahfouz[a]
[a] Department of Chemistry, College of Sciences, King Saud University, Riyadh, Saudi Arabia

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SYNTHESIS AND CHARACTERIZATION OF NEW In(III), Re(III), Re(V), Pd(II), AND Rh(III) COMPLEXES OF TOLUENE-3,4-DITHIOL

**Abdulaziz I. Al-Wassil, Khalid A. Al-Farhan,
Saad M. Alsheri, Mohsen H. Mukhalalati, and
Refaat M. Mahfouz***

Department of Chemistry, College of Sciences, King
Saud University, P.O. Box 2455 Riyadh 11451,
Saudi Arabia

ABSTRACT

New In(III), Re(III), Re(V), Pd(II) and Rh(III) Complexes of Toluene-3,4-Dithiol with 2:1 ligand : metal ratio have been prepared and characterized in the solid state. Microanalytical data of the investigated complexes correspond to the general formula [M(TDT)*x* (H2O)m] where *M* refers to the metal ion, x, m are the numbers of the coordinated $TDT^{=}$ and H_2O respectively. The solid complexes have been characterized using conventional chemical and physical methods of analysis.

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*Corresponding author.

Key Words: In(III); Re(III); Re(V); Pd(II); Rh(III); Complexes; Toluene-3,4-Dithiol; Metal ions

INTRODUCTION

Coordination compounds of transition metal complexes have a wide applications in life science and technology. A number of chelate compounds of In^{111} and Re^{186} are characterized as diagnostic and therapeutic agents in nuclear medicine[1,2]. New ligand systems are being extensively used to synthesize complexes of In^{111} and Re^{186} of potential use as radiopharmaceuticals[3,4]. The preparation of these radiopharmaceuticals in cold reactions using inactive In and Re metal ions are necessary to deduce their chemical structures before being applicable in biosystems. In recent years it has became apparent that same metal ions including Rh and Pd have serious biological consequences for humans and therefore metal chelators are important for their bio extraction[5].

The present work deals with preparation of new In(III), Re(III), Re(V), Pd(II) and Rh(III) complexes containing toluene 3,4 dithiol as ligand with 2:1 ligand:metal ratio and characterization of the investigated complexes using conventional physical and chemical methods of analysis. No previous work concerning synthesis of these complexes has been described before in chemical literature.

EXPERIMENTAL

Abbreviation H_2TDT = Toluene-3,4-dithiol

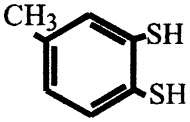
All chemical used were of analytical grade. IR spectra were recorded in KBr pellets on a Perkin Elmer spectrophotometer model 599-B. UV-Vis. Spectra in 10^{-3}M ethanolic solution were record on A CECIL 599 spectrophotometer usinig 1 cm matched silica cells[1]. ^1H NMR were measured in DMSO on a Jeol Fx 100 FT- NMR. Elemental analysis were carried out on Perkin Elmer 2400 CHNSO elemental analyzer.

Synthesis of the Solid Chelates

The following general procedure has been adopted for the preparation of metal chelates. The required amount of ligand was dissolved in the least amount of ethanol and treated with the approprite amount of the solution of $In_2(SO_4)_3.H_2O$, $ReCl_3$, $ReCl_5$, $PdCl_2$, and $RhCl_3$ in the molar ratio ligand:metal (2:1). The reaction mixture was stirred for 60 min and was then rotary evaporated to small volume and left to cool where by the solid chelates separated. The deposited solids were filtered off, washed with diethylether and dried in vacuo over P_2O_5. Syntheses were carried out in an nitrogen atmosphere. For Re (V) complex the preparation was preformed in air. Microanalytical data of the prepared chelates together with their color, decomposition temperature are listed in Table 1.

RESULTS AND DISCUSSION

Toluene-3,4-dithiol (H_2TDT) has the following structure:



The solid complexes of In(III), Re(III), Re(V), Pd(II) and Rh(III) with H_2TDT were characterized using conventional physical and chemical methods of analysis. The microanalytical data are tabulated in Table 1. The analytical data are consistent with the general formulation $[M(TDT)_x(H_2O)_m]^{n-x}$ where M = In(III), Re(III), Re(V), Pd(II) and Rh(III), x is the number of coordinated $TDT^=$, m number of coordinated water, n is the oxidation state of metal ion investigated. For Re(V) the chemical formula is $ReO(TDT)_2H_2O$.

Infrared Spectra

Relevant IR bands which provide structural evidence for the mode of attachment of the ligand to the metal ions are reported in Table 2. The strong band appearing at 2535 cm^{-1} in the spectrum of the free ligand can be assigned to the S-H stretching vibration. This band disappeared in the spectra of the investigated complexes, a behavior that is convincing evidence for coordination of the metal ion investigated with H_2TDT ligand via sulfur atoms. The band due to M-S stretching vibration was observed at (440–460 cm^{-1}). In some of the investigated complexes a sharp and spilt band at higher frequencies (3400–3430 cm^{-1}) was appeared. Which is ascribed to the presence of coordinated water molecules in the complexes. For

Table 1. Analytical Data of the Investigated Complexes

Compound	Empirical Formula	Formula Weight	Yield	Mp℃	Color	Found / (Calc)%			
						C	H	O	S
$[In(TDT)_2(H_2O)_2]^-$	$C_{14}H_{16}S_4O_2In$	458.91	91%	> 300	Yellow	36.11 (36.61)	3.49 (3.51)	6.85 (6.97)	27.81 (27.87)
$[Re(TDT)_2\ (H_2O)_2]^-$	$C_{14}H_{16}S_4O_2Re$	530.96	85%	> 200	Yellow	31.11 (31.68)	3.12 (3.04)	6.12 (6.03)	24.08 (24.16)
$[Rh(TDT)_2\ (H_2O)_2]^-$	$C_{14}H_{16}S_4O_2Rh$	446.91	82%	> 300	Yellow	37.48 (37.59)	3.58 (3.61)	7.10 (7.16)	28.51 (28.62)
$[Pd(TDT)_2]^=$	$C_{14}H_{12}S_4Pd$	413.89	80%	> 300	Yellow	40.41 (40.59)	2.81 (2.92)	—	30.87 (30.90)
$[ReO(TDT)_2\ (H_2O)_2]^-$	$C_{14}H_{14}S_4O_3Re$	544.94	85%	> 200	Yellow	30.75 (30.83)	2.41 (2.59)	8.91 (8.81)	23.45 (23.47)

Table 2. IR, ^{1}HNMR and UV-Vis. Spectroscopic Data of the Investigated Complexes

Compound	IR (cm^{-1})			UV-Vis Data (nm) (ξ cm^{-1}mol^{-1})	^{1}HNMR δ (ppm)
	$\nu_{S\text{-}H}$	$\nu_{M\text{-}S}$	ν_{OH}		
Free ligand H_2TDT	2535	—	—	261(1800), 300(3900)	7.35(m, 3H, C_6H_3), 2.88(s, 3H, CH_3) (m, 2H, SH)
$[In(TDT)_2\ (H_2O)_2]^-$	—	440	3450	270(1700), 420(3600)	7.38(m, 6H, C_6H_3), 2.89(s, 6H, CH_3)
$[Re(TDT)_2\ (H_2O)_2]^-$	—	450	3460	267(1730), 422(3600)	7.31(m, 3H, C_6H_3), 2.85(s, 6H, CH_3)
$[Rh(TDT)_2\ (H_2O)_2]^-$	—	453	3420	265(1720), 425(3500)	7.33(m, 3H, C_6H_3), 2.81(s, 6H, CH_3)
$[Pd(TDT)_2]^{=}$	—	442	—	260(1710), 420(3700)	7.32(m, 3H, C_6H_3), 2.88(s, 6H, CH_3)
$[ReO(TDT)_2\ (H_2O)_2]^-$	—	455	3400	310(1720), 425(3500)	7.32(m, 3H, C_6H_3), 2.85(s, 6H, CH_3)

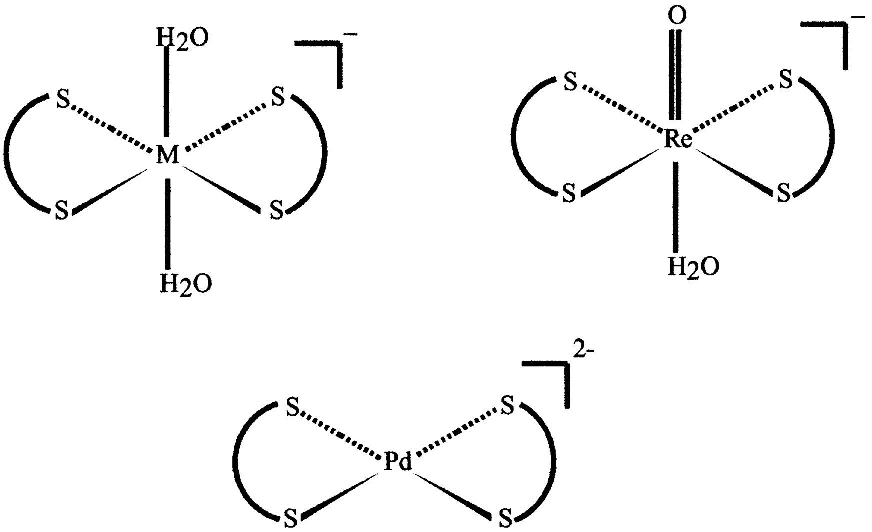


Figure 1. Proposed structures of metal complexes formulated based on experimental data. Note: M = In(III), Re(III), Rh(III).

ReO(TDT)H_2O a strong band at 1080 cm^{-1} appeared due to the $\nu(Re = O)$ vibration[6].

Electronic Spectra

The electronic spectra of complexes solutions in ethanol were recorded at ambient temperature. The λ max and ξ values of absorption bands observed are listed in Table 2. The investigated complexes exhibit a metal central ion band around (420 nm) giving rise to their yellow color and some ligand bands in the visible region.

The results of both infrared and electronic spectra of the investigated complexes were confirmed by ^{1}HNMR data (see Table 2) which confirm that two $TDT^{=}$ anions were involved in the compellation reactions and H_2TDT in this investigation act as bidenate SS donor.

On the basis of the foregoing discussion the proposed structures of metal complexes can be formulated as follows in Fig. 1.

Further studies concerning the applications of these complexes in biosystems are in progress in our laboratories.

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REFERENCES

1. Chilton, H.M.; Burchiel, S.W.; Watson. N.E., Jr. In Pharmaceuticals. In *Medical. Imaging*; Swanson, D.P., Chilton, H.M., Thrall, J.H., Eds.; MacMillan Publishing Co.: New York, 1990; pp 564–598.
2. Weiner, R.E.; Thakur, M.L. Radiochimica Acta **1995**, *70/71*, 273–287.
3. Jurisson, S.; Berning, D. Wei Jia and Dangshe Ma. Chem. Review **1993**, *93*, 1137–1156.
4. Gopal, B. Saha. *Fundamentals of Nuclear pharmacy*; 3rd Ed., Springer-Verlag: New York, Inc 1992.
5. Arthur E-Martell, Ed. Inorganic Chemistry in Biology and Medicine ACS Symposium Series 140 American Chemical Society Washington D. C. 1980.
6. Clarke, M.J.; Fackler, P.H. Structures. Bounding **1982**, 50–57.

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