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SYNTHESIS AND SPECTROSCOPIC CHARACTERIZATION OF COMPLEXES OF 2-AMINOTHIOPHENOL WITH TETRACHLORIDES OF METALS

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ABSTRACT

The synthesis, characterization and structural elucidation of some bis-chelates of composition $[MCl_2(ATP)_2]$ (M = Ti (IV), Zr (IV), Pd (IV), Pt (IV) and Sn (IV); ATP = Deprotonated 2-aminothiophenol bidentate anion) are reported. The octahedral structure of metal chelates are deduced by elemental analysis, magnetic susceptibility measurements, IR, far-IR, UV-vis, and ^{1}H NMR spectral data.

Key words: Bis-chelates, Octahedral, Metal (IV)-ions, 2-Aminothiophenol anion.

INTRODUCTION

The synthesis, characterization and structural elucidation of complexes of 2-aminothiophenol are reported in literature[1-3]. Some bis-chelates of transition metals (III)[4], organo-ruthenium complexes[5] and oxo- and dioxo-metal chelates[6] are also reported in our earlier communications. The present study aims at synthesis, structural characterization of metal complexes of Ti(IV), Zr(IV), Pd(IV), Pt(IV) and Sn(IV) ions of this ligand. Metal-ligand vibrations in far-IR and structural investigations using various physico-chemical data are reported herein.

EXPERIMENTAL

All chemicals used were of AR grade or CP grade. 2-aminothio- phenol (Schuchardt, Munchen), $SnCl_4$ (Riedel), $ZrCl_4$ (Merck), and other tetra chlorides are commercial chemicals used without further purifications. The estimation of metals and chloride were done gravimetrically by Standard methods. Carbon, hydrogen and nitrogen were determined by microanalytical methods. The conductance of 10^{-3} solutions of the complexes in DMF

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were measured using Wiss-Werk-Statter Weigheim obb type LBR conductivity meter. The IR spectra were recorded on a Perkin Elmer 577 spectrometer and electronic spectra on a Beckmann DV-6 spectrometer. The ^{1}H NMR ($CDCl_3$) ona JEO_2 JMS 60011 NMR Spectrometer. Magnetic moment was measured on a Gouy balance using $Hg[Co(SCN)_4]$ as calibrant.

Preparation of complexes

S. No. 1: Dichlorobis(2-aminothiophenolato)tin(IV) : $[SnCl_2(ATP)_2]$

To a solution of $SnCl_4$ (5.7 m mol) in dry benzene (25 mL) bimolar amount of 2-aminothiophenol (11.4 m mol) dissolved separately in the same solvent was added slowly and stirred on magnetic stirrer about an hour. The reaction was further heated on reflux for about two hr. till there was no evolution of HCl gas. The resulting solution was concentrated by distilling off most of the solvent and left over night. A light yellow solid appeared in the solution, separated by filtration, washed repeatedly with petroleum ether and finally dried under vacuum (yield = 72%).

S. No. 2: Dichlorobis(2-aminothiophenolato) Palladium (IV) : $[PdCl_2(ATP)_2]$

Ethanolic solution of $PdCl_2$ having few drops of HCl and calculated quantity of chlorine obtained by heating Conc. HCl with 0.15 g of MnO_2 was passed. The deep blood-red solution of H_2PdCl_6 thus obtained was treated with an ethanolic solution of ligand. A orange yellow precipitate of the complex was formed, which was digested on a water-bath till the volume of the mixture was reduced to about ~30 mL. The precipitate was then filtered, washed thoroughly with water, cold ethanol and dried (yield = 79%).

S. No. 3: Dichlorobis(2-aminothiophenolate) Platinum (IV): $[PtCl_2(ATP)_2]$

Hexachloroplatinic acid and 2-aminothiophenol were dissolved in ethanol and mixed in molar ratio = 1:2. The solution mixture was refluxed on water-bath when yellow-brown precipitate of the complex was formed. It was further filtered, washed with water and recrystallized from ethanol (yield = 79%).

S. No. 4: Dichlorobis(2-aminothiophenolato) Titanium (IV): $[TiCl_2(ATP)_2]$

2-aminothiophenol in 40 mL anhydrous ethanol was added dropwise to $TiCl_4$ dissolved in the same solvent in the 2:1 = L : M ratio in stirring solution on magnetic stirrer for 1 hr. The reaction mixture was further refluxed on a steam bath for two hours. The yellow-solid complexes were obtained upon crystallization and were filtered, washed with anhydrous ethanol and dried in vacuum (yield = 81%).

S. No. 5: Dichlorobis(2-aminothiophenolato) Zirconium (IV): [$ZrCl_2(ATP)_2$]

$ZrCl_4$ and ligand (1:2) in anhydrous ethanol were refluxed on water-bath for four hours and yellow solid complexes were isolated after concentration and cooling the solution mixture (yield = 85%).

RESULTS AND DISCUSSION

Analytical data indicate that the complexes have the stoichiometry [MCl_2L_2] where M = Ti (IV), Zr (IV), Pd (IV), Pt (IV) and Sn(IV) and L = Monoanionic bidentate anion. The solution of complexes in DMF (10^{-3} M) are non-conducting indicating coordinated nature of the chlorides. All complexes were found to be diamagnetic. The diamagnetic nature of Ti (IV) and Zr (IV) complexes suggest d^0-configuration and only one charge transfer band near 28940-28980 cm^{-1} are observed in electronic spectra of complexes. However, no absorption was observed above 25000 cm^{-1} indicating d^0-configuration of these complexes[7].

The diamagnetic nature of Pt (IV) complex indicate $^1A_{1g}$ ground term for d^6 system in octahedral crystal field. The ligand field transition $T_{2g}{}^6 \rightarrow T_{2g}{}^5eg^1$ give $^3T_{1g}$, $^3T_{2g}$, $^1T_{1g}$ and $^1T_{2g}$ as excited state in increasing order of energy. The spectral bands at 16690 ($^1A_{1g} \rightarrow {}^1T_{1g}$), 19910 ($^1A_{1g} \rightarrow {}^3T_{2g}$), 21400 ($^1A_{1g} \rightarrow {}^1T_{2g}$) and 29410 ($^1A_{1g} \rightarrow {}^1T_{2g}$) are due to d-d transition for octahedral structure.[8] The diamagnetic Pd (IV) complex shows bands at 33,350 cm^{-1}, 25580 cm^{-1} and 17210 cm^{-1}. The bands at 33350 cm^{-1} and 25580 cm^{-1} have very high intensity and is most probably a charge transfer band. The broad shoulders at 18820 and 17210 cm^{-1} are most probably due to d-d transition which suggest octahedral structure of [$PdCl_2(ATP)_2$] considering previous literature[9]. The [$SnCl_2(ATP)_2$] exhibits strong absorption band at 27780 cm^{-1}, which may be assigned due to charge transfer band.

IR Spectra

The IR bands of free ligand (ATP) and complexes were elaborated and elucidated for comparison to investigate mode of coordination. The characteristic ν_{SH} band of free ligand (ATP) was not found in complexes indicating deprotonation of thiol group and bonding through sulphur[10]. The $\nu_{sym}NH_2$ and $\nu_{asym}NH_2$ of free ligand are observed at 3340 cm^{-1} and 3460 cm^{-1} undergo red shift to lower frequency on comlexation about 30-45 cm^{-1} and 35-40 cm^{-1}, respectively indicate the formation of Metal-N bond and bonding through amino nitrogen atom of ligand. Thus, the ligand acts as mononegative bidentate anion and forms simultaneous Metal-N and Metal-S bond.

The far-IR spectra of complexes (Table 2) contains some new bands. New single band in $[MCl_2(ATP)_2]$ [(M = Ti (IV), Zr (IV), Pd (IV), Pt (IV)] and Sn (IV) at 370-415 cm^{-1} indicates Trans-disposition of two mutual chlorine in octahedral structure[11,12].

Table 1: Analytical and physical data of complexes

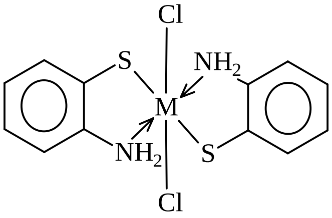
Complex/(Colour)	Analysis : Calculated/(Found) %					Molar Cond.
	C	H	N	Cl	Metal	($\wedge^{-1}cm^2mol^{-1}$)
$[TiCl_2(ATP)_2]$ (Orange-yellow)	39.24 (39.33)	3.27 (3.31)	7.63 (7.58)	22.25 (22.10)	13.05 (13.11)	5.62
$[ZrCl_2(ATP)_2]$ (Yellow)	42.45 (41.96)	3.53 (3.60)	8.25 (8.20)	20.93 (21.11)	26.89 (26.90)	5.50
$[PdCl_2(ATP)_2]$ (Orange-yellow)	40.63 (41.11)	3.38 (3.46)	7.90 (8.01)	20.03 (20.11)	30.02 (30.12)	6.60
$[PtCl_2(ATP)_2]$ (Yellow-brown)	32.50 (32.66)	2.70 (2.81)	6.32 (6.12)	16.02 (16.32)	44.01 (44.10)	8.20
$[SnCl_2(ATP)_2]$ (Yellow)	39.27 (40.01)	3.27 (3.33)	7.63 (7.62)	19.36 (19.46)	32.34 (32.12)	8.68

Table 2: Major IR and ^{1}H NMR Spectral data of ligand and complexes

Compounds	IR (cm^{-1})				^{1}H NMR (δ ppm)		
	ν_{asym} NH_2	ν_{sym} NH_2	$\nu_{M\text{-}Cl}$	$\nu_{M\text{-}S}$/ ($\nu_{M\text{-}N}$)	Amino protons	Phenyl protons	Thiol protons
ATP (ligand)	3460 m	3340 m	-	- (-)	3.68	6.64-7.23	3.66
$[TiCl_2(ATP)_2]$	3425 m	3310 m	415 m	420 w (490 m)	3.55 3.71	6.62-7.10	-
$[ZrCl_2(ATP)_2]$	3432 m	3315 m	338 m	395 w (395 m)	3.58 3.70	6.42-6.68	-
$[PdCl_2(ATP)_2]$	3430 m	3305 m	342 m	345 w (355 m)	3.66 3.78	6.42-6.56	-
$[PtCl_2(ATP)_2]$	3440 m	3315 m	302 m	340 w (370 m)	3.66 3.72	6.32-6.88	-
$[SnCl_2(ATP)_2]$	3425 m	3325 m	370 m	330 w (405 m)	3.60 3.73	6.34-6.98	-

^{1}H NMR Spectra

The ^{1}H NMR spectra of $[MCl_2(ATP)_2]$ [M = Ti (IV), Zr (IV), Pd (IV), Pt (IV) and Sn (IV)] did not display any signal at δ 3.66 PPM due to thiol group in pure ATP. Suggesting thereby the deprotonation and formation of Metal-S bond in complexes. The aromatic phenyl protons resonance at δ 6.64-7.30 ppm (multiplet) in free ligand have been observed to undergo a significant downfield shift and appeared at δ6.78 ppm on complexation. The observed downfield shift of the phenyl ring proton resonances may be rationalized in terms of deshielding of these protons due to drainage of electron density from the aromatic ring to Metal. The integration of signals due to phenyl protons supported the stoichiometric formulation of the complexes. The amino protons observed at δ3.68 ppm in free ligand (ATP) low field shifted on complexation and the integrated intensities of the signals agree well with the assigned structure of complexes (Structure I).



Trans-Oh-Str. of complexes
[M = Ti (IV), Zr (IV), Pd (IV), Pt (IV) & Sn (IV)]

(Structure I)

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