

# Synthesis, Structural and Thermal Studies of Titanium(IV) Complexes of N-Alkyl Phenothiazines

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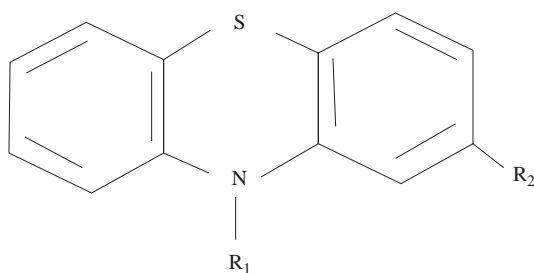
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Received 11.08.1998

New coordination compounds of the type  $[\text{Ti}(\text{C}_2\text{O}_4)_2\text{L}]\cdot 2\text{H}_2\text{O}$  where L=N-alkyl phenothiazines (NAPs) were synthesised and characterised by elemental analyses, molar conductance, magnetic, thermal and spectral data. The spectral data suggest the bidentate nature of NAPs in the complexes. An octahedral structure is proposed for all the complexes. Thermal studies were used to evaluate the kinetic and thermodynamic parameters.

## Introduction

N-Alkyl phenothiazines are biologically active heterocyclic compounds which find extensive applications in the fields of medicine and chemical analysis. In the pharmaceutical industry they are used as psychotherapeutic, antiemetic and antihistamine drugs<sup>1-2</sup> whilst elsewhere some are employed as chromogens in the spectrophotometric determination of transition metals in solution<sup>3-5</sup>. The synthesis and characterisation of coordination compounds of phenothiazines with transition metals such as molybdenum(IV)<sup>6</sup>, tungsten(IV)<sup>7</sup>, zirconium(IV)<sup>8</sup>, dioxouranium(VI)<sup>9</sup>, polynuclear iridium<sup>10</sup>, copper(II)<sup>11</sup>, palladium(II)<sup>12</sup>, platinum(IV)<sup>13</sup> and rhenium(VII)<sup>14</sup> have been reported. In a continuation of our work on metal-ion interactions with phenothiazine drugs, we report the synthesis and structural studies of titanium(IV) complexes of three selected NAP ligands, the structures of which are shown in Figure 1.



**Figure 1.** General structure of the N-Alkyl phenothiazines

Trifluoperazine (TEP):  $R_1 = (\text{CH}_2)_3\text{NC}_4\text{H}_8\text{NCH}_3$  ;  $R_2 = \text{CF}_3$

Prochlorperazine (PCP):  $R_1 = (\text{CH}_2)_3\text{NC}_4\text{H}_8\text{NCH}_3$  ;  $R_2 = \text{Cl}$

Methdilazine (MD):  $R_1 = \text{CH}_2\text{C}_4\text{H}_7\text{NCH}_3$  ;  $R_2 = \text{H}$

## Experimental

### Starting Materials

The prochlorperazine maleate and methdilazine hydrochloride and trifluoperazine dihydrochloride were obtained as gift samples from Rhone-poulenc, Glaxo (Ind) Ltd. and Smithkline Beecham Pharmaceuticals, India and were used as received. Potassium titanyl oxalate, dimethyl formamide (DMF) and dimethyl sulphoxide (DMSO) were BDH AnalaR Products.

### Analytical procedures

Elemental analyses were performed at the Bio-Organic Chemistry division, Bhaba Atomic Research Centre, Mumbai, India. Titanium was determined as  $\text{TiO}_2$  gravimetrically.

### Physical measurements

The magnetic measurements were obtained by the Gouy method at room temperature using  $\text{Hg}[(\text{Co}(\text{SCN})_4)]$  as the calibrant. The IR spectra of samples in KBr pellets were recorded on a FTIR spectrophotometer model Impact 410, Nicolet. Far IR spectra were recorded using polythene discs on a polytech far IR spectrophotometer model 30. The electronic spectra of the complex in DMF were measured on a HITACHI UV-Visible spectrophotometer model 150-20. The molar conductance of the complexes was measured on  $10^{-3}$  M DMF solutions using a Philips PR 9500 conductivity bridge. Thermal analysis was carried out on a Rigaku Thermoflex model TG 8110 with a heating rate of  $10^\circ\text{C min}^{-1}$  in air in the temperature range ambient to  $800^\circ\text{C}$ . The kinetic and thermodynamic parameters of the degradation processes were evaluated by Briodo's method<sup>15</sup>. X-ray diffraction data was obtained with a Jeol X-ray diffractometer model JDX 8P with a monochromatic  $\text{Fe K}_\alpha$  ( $\lambda = 1.934 \text{ \AA}$ ) as the source.

### Synthesis of the complexes

All the complexes were prepared according to the following general method. An aqueous solution (60 ml) of NAP (1m.mol) was slowly added with vigorous stirring to an aqueous solution (50 ml) of potassium titanyl oxalate (1m.mol). There was an immediate separation of a solid complex. The suspension was set aside for 1 hour, filtered, washed several times with water and finally with ethanol and dried in vacuo over fused  $\text{CaCl}_2$ .

**Table 1.** Analytical data, molar conductance and spectral data ( $\text{cm}^{-1}$ ).

Complex	Found (Calcd)%				$\Lambda_M$ ( $\text{ohm}^{-1}\text{cm}^2$ ) ( $\text{mol}^{-1}$ )	Electronic	Spectral data		
	C	H	N	Ti			$\gamma(\text{Ti-N})$	IR $\gamma(\text{Ti-S})$	$\gamma(\text{OCO})$
$[\text{Ti}(\text{C}_2\text{O}_4)_2\text{C}_{21}\text{H}_{24}\text{F}_3\text{N}_3\text{S}]2\text{H}_2\text{O}$	44.12 (44.98)	4.26 (4.19)	6.18 (6.29)	7.24 (7.17)	52.0	31948 24509	524	345	1715,1400
$[\text{Ti}(\text{C}_2\text{O}_4)_2\text{C}_{20}\text{H}_{24}\text{CIN}_3\text{S}]2\text{H}_2\text{O}$	45.92 (45.48)	4.36 (4.41)	6.58 (6.63)	7.44 (7.55)	49.5	31446 24691	522	324	1710,1380
$[\text{Ti}(\text{C}_2\text{O}_4)_2\text{C}_{18}\text{H}_{20}\text{N}_2\text{S}]2\text{H}_2\text{O}$	48.01 (47.55)	4.28 (4.31)	5.11 (5.04)	8.72 (8.61)	51.3	30769 24390	540	336	1705,1375

**Table 2.** Thermogravimetric characteristics of titanium(IV)-NAP complexes.

Complex	Transition	Temperature ( $^{\circ}\text{C}$ )	Weight %		Weight Residue %		Nature
			Calcd.	Exptl.	Calcd.	Exptl.	
$[\text{Ti}(\text{C}_2\text{O}_4)_2\text{C}_{21}\text{H}_{24}\text{F}_3\text{N}_3\text{S}]2\text{H}_2\text{O}$	I	35-108	5.39	5.28	11.97	11.78	$\text{TiO}_2$
	II	108-360	61.05	61.93			
	III	360-526	21.59	20.92			
$[\text{Ti}(\text{C}_2\text{O}_4)_2\text{C}_{20}\text{H}_{24}\text{CIN}_3\text{S}]2\text{H}_2\text{O}$	I	38-110	5.68	5.53	12.60	12.49	$\text{TiO}_2$
	II	110-375	58.98	58.40			
	III	375-520	22.73	21.58			
$[\text{Ti}(\text{C}_2\text{O}_4)_2\text{C}_{18}\text{H}_{20}\text{N}_2\text{S}]2\text{H}_2\text{O}$	I	40-105	6.47	6.26	14.36	15.03	$\text{TiO}_2$
	II	105-372	53.26	53.78			
	III	372-530	25.96	24.89			

**Table 3.** Temperature characteristics, activation energies, frequency factors and thermodynamic parameters of titanium(IV)-NAP complexes.

Complex	$T_0$	$T_{10}$	$T_{max}$	Process	$E_a \pm 2$	$\ln A \pm 2$	$\Delta H$	$\Delta S$	$\Delta G$
	$^{\circ}\text{C}$	$^{\circ}\text{C}$	$^{\circ}\text{C}$		$\text{KJ mol}^{-1}$	$\text{min}^{-1}$	$\text{KJ mol}^{-1}$	$\text{KJ mol}^{-1}$	$\text{KJ mol}^{-1}$
$[\text{Ti}(\text{C}_2\text{O}_4)_2\text{C}_{21}\text{H}_{24}\text{F}_3\text{N}_3\text{S}]2\text{H}_2\text{O}$	35	225	524	I	0.67	3.80	-2.25	-153.33	52.64
				II	27.12	13.53	22.96	-98.66	31.18
				III	39.16	14.88	33.28	-83.25	92.29
$[\text{Ti}(\text{C}_2\text{O}_4)_2\text{C}_{20}\text{H}_{24}\text{CIN}_3\text{S}]2\text{H}_2\text{O}$	38	232	518	I	0.82	3.61	-3.34	-140.34	50.51
				II	24.58	14.24	26.21	-94.36	33.72
				III	42.52	15.62	40.52	-81.72	94.36
$[\text{Ti}(\text{C}_2\text{O}_4)_2\text{C}_{18}\text{H}_{20}\text{N}_2\text{S}]2\text{H}_2\text{O}$	40	220	526	I	0.74	3.52	-2.49	-141.83	54.34
				II	26.71	13.14	24.13	-96.72	32.15
				III	33.24	15.32	31.58	-82.48	96.34

## Results and Discussion

The complexation reaction of potassium titanyl oxalate with different NAPs yields a microcrystalline product. The analytical data of the complexes shown in Table 1 correspond to the formula  $[\text{T}_i(\text{C}_2\text{O}_4)_2\text{L}]2\text{H}_2\text{O}$ , where  $\text{L}=\text{NAP}$ . All the complexes are non-hygroscopic, stable in air for long periods. They do not possess sharp melting points. The complexes are insoluble in water and soluble in chloroform, DMF and DMSO. The molar conductances in DMF are in the range 49-52  $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$  at  $10^{-3}$  M concentration indicating the non-electrolytic nature of the complexes. The magnetic susceptibility studies indicate that the complexes are diamagnetic at room temperature. In fact the titanium (IV) complexes reported in the literature are all diamagnetic and most of them are octahedral. Hence it may be reasonably assumed that all the complexes of titanium (IV)-NAP are six coordinated and octahedral. These results are consistent with the stoichiometry proposed on the basis of analytical data.

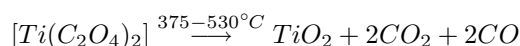
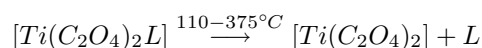
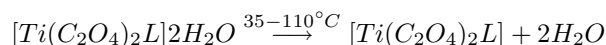
The electronic spectra of the new complexes show a band in the region 24691-24390  $\text{cm}^{-1}$  which may be assigned to charge transfer transition<sup>16</sup> in accordance with the  $(n-1)d^0 ns^0$  electronic configuration. Comparison of the spectra of the complexes which exhibit maximum absorptions in the 31948-30769  $\text{cm}^{-1}$  range with those of the corresponding free ligands shows a shift towards the higher wavelength region in each

case, attributed to the intraligand transitions of the type  $n \rightarrow \pi^*$ . This result is taken as indirect evidence for the involvement of S and/or N atoms in coordination<sup>6,8</sup>.

The selected IR frequencies of the titanium (IV)-NAP complexes are given in table 1. The existence of V=0 moiety is well established<sup>17</sup>. In contrast, solid titanium (IV) oxo complexes are rarely found to exhibit true titanyl  $T_i=0$  moiety<sup>17-19</sup>. However, some exceptions exist: TiO (porphyrin)<sup>20</sup> and TiO (edta  $H_2$ )  $H_2O$ <sup>21</sup>. The absence of a band in the 950-1050  $cm^{-1}$  region in the isolated complexes rules out the existence of Ti=O moiety in the complexes<sup>18,19</sup>. The free ligands exhibit a strong band<sup>6,9,22</sup> due to the  $CH_2NR_2H^+$  (R=Me, Et or Bu) together with chloride in the region 2250-2700  $cm^{-1}$ . In the IR spectra of the corresponding complexes, this band totally disappears indicating that the tertiary N atom of the side chain is a site of coordination. The far IR bands at 522-540  $cm^{-1}$  may be attributed to  $T_i-N$  bands<sup>23</sup>. The weak-medium C-S-C absorption bands in the region 700-725  $cm^{-1}$  of the complexes show a shift (10-25  $cm^{-1}$ ) towards lower energies compared with those in free NAPs. The frequency shift suggests that the heterocyclic S atom is coordinated to the titanium (IV) which is in agreement with previous reports<sup>10,12,13</sup>. This is further supported by the far IR bands<sup>23</sup> at 324-345  $cm^{-1}$ . The NAPs therefore behave as bidentate ligands in all the complexes studied. The coordination of bidentate oxalate is confirmed by the bands<sup>24</sup> at 1675-1715  $cm^{-1}$  due to asymmetric COO vibration and at 1375-1400  $cm^{-1}$  due to symmetric COO vibration.

The <sup>1</sup>H NMR spectra of all the complexes recorded in deuterated chloroform exhibit chemical shifts at lower fields for N-CH<sub>3</sub> protons which appear at  $\delta$  2.70-2.90 ppm compared with the position in the free NAPs  $\delta$  2.55-2.70 ppm. This is probably due to the coordinating effect of the tertiary N atom which results in the deshielding of the protons attached to it. All the ligands show a multiplet at  $\delta$  7.30-7.48 ppm due to aromatic protons which remain the same in the complexes also.

The temperature of decomposition, the pyrolysed products, the percentage weight loss of the compounds and the percentage ash are given in Table 2. The TG curves of titanium (IV)-NAP complexes show three significant steps in the decomposition. In the first step, the loss of two water molecules occurs in the temperature range 35-110 °C with a mass loss of 5.39-6.47%. This water is not coordinated to the metal as it is lost below 120 °C and is probably lattice water. The decomposition temperature of the second stage lies in the range 110-375 °C which corresponds to the loss of the ligand moiety with a mass loss in the range 53.26-61.05%. The third step relates to the loss of oxalate followed by the formation of  $T_iO_2$  in the temperature range 375-530 °C with a mass loss in the range 21.59-25.90%. The intermediates are identified by mass loss and the end product is confirmed by X-ray diffraction data. The difference between the found and calculated mass losses lies in the range 0.15-1.15%. The decomposition scheme of  $[Ti(C_2O_4)_2L]2H_2O$  in air for each step is indicated below:



The thermograms obtained during TGA scans are analysed to give the percentage weight loss as a function of temperature.  $T_0$  (temperature of onset of decomposition),  $T_{10}$  (temperature for 10% weight loss) and  $T_{max}$  (temperature of maximum weight loss), activation energy ( $E_a$ ) and frequency factor ( $\ln A$ ) were computed and are recorded in Table 3 to know the heat stability of the complexes. The higher the

values of  $T_0$ ,  $T_{10}$  and  $T_{max}$ , the greater is the heat stability of a complex. Briodo's method was used to evaluate  $E_a$  and the order of thermal reaction ( $n$ ). In order to estimate the kinetic parameters of the thermal degradation during the analyses of thermograms, it was assumed that the reaction follows first order kinetics. In the present study the plots of  $-\ln(\ln \frac{1}{y})$  versus  $\frac{1}{T \times 10^3}$  are linear over the conversion range 0.1 to 0.9 supporting the assumption of first order kinetics. The energy of activation data are presented in Table 3. The thermodynamic parameters enthalpy ( $\Delta H$ ), entropy ( $\Delta S$ ) and free energy ( $\Delta G$ ) of activation were calculated using standard equations and the values are given in Table 3.

## Conclusion

None of the complexes gave crystals of sufficient quality to permit X-ray crystallographic analysis. Based on the above discussion, we propose the tentative structure shown below for titanium(IV)-NAP complexes where the titanium(IV) centre is surrounded by a six coordinate octahedral environment. In all the complexes, the NAP acts as a bidentate ligand using the side chain tertiary N and the heterocyclic S as the donor atoms.

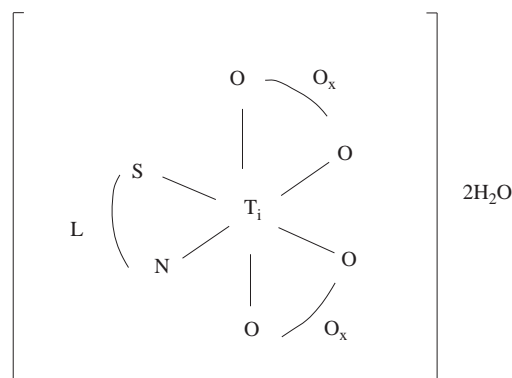


Figure 2. Structure of titanium-NAP complexes.

## Acknowledgements

The authors express their thanks to M/s Rhone-poulenc, M/s Glaxo (Ind.) Ltd. and Smithkline Beecham, India for supplying pure NAP for the study. Thanks are also due to the Chairman, Department of Chemistry, Karnatak University for providing the necessary facilities.

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