

## Oxotitanium(IV) Complexes of *ortho*-substituted Benzalidene Thiosemicarbazones

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Oxotitanium(IV) complexes of *ortho*-substituted benzaldehyde thiosemicarbazones of composition  $[\text{TiOL}_2(\text{H}_2\text{O})]$  (HL = thiosemicarbazones of 4,4-dimethyl-N-thiosemicarbazide, 4,4-diethyl-N-thiosemicarbazide and 4,4-dibutyl-N-thiosemicarbazide of *ortho*-Cl, -Br, -NO<sub>2</sub> and -OCH<sub>3</sub> benzaldehyde) have been prepared and characterized by UV, IR, electrical conductance and magnetic susceptibility measurements.

**Key Words:** Oxotitanium(IV) complexes, *ortho*-substituted benzaldehyde thiosemicarbazones, UV and IR.

### INTRODUCTION

Thiosemicarbazide and thiosemicarbazones have physiological activity against viruses, protozoa smallpox, tuberculosis and certain kinds of tumours<sup>1,2</sup>. In view of enhanced physiological activities of metal chelates of various thiosemicarbazones<sup>3,4</sup>, oxotitanium(IV) complexes have been prepared and characterized with a number of thiosemicarbazone derivatives.

### EXPERIMENTAL

All the chemicals used were of AnalaR grade reagents. *Ortho*-substituted benzalidene thiosemicarbazones and related ligands were prepared by methods reported in literature<sup>5</sup>. The abbreviated symbols of ligands prepared and studied are given below:

<i>o</i> -chloro benzalidene thiosemicarbazone	(HL-I)
<i>o</i> -bromo benzalidene thiosemicarbazone	(HL-II)
<i>o</i> -nitro benzalidene thiosemicarbazone	(HL-III)
<i>o</i> -methoxy benzalidene thiosemicarbazone	(HL-IV)
<i>o</i> -chloro benzalidene-4,4-dimethyl-N-thiosemicarbazone	(HL'-I)
<i>o</i> -bromo benzalidene-4,4-dimethyl-N-thiosemicarbazone	(HL'-II)
<i>o</i> -nitro benzalidene-4,4-dimethyl-N-thiosemicarbazone	(HL'-III)
<i>o</i> -methoxy-benzalidene-4,4-dimethyl-N-thiosemicarbazone	(HL'-IV)

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<i>o</i> -chloro benzalidene-4,4-diethyl-N-thiosemicarbazone	(HL''-I)
<i>o</i> -bromo benzalidene-4,4-diethyl-N-thiosemicarbazone	(HL''-II)
<i>o</i> -nitro benzalidene-4,4-diethyl-N-thiosemicarbazone	(HL''-III)
<i>o</i> -methoxy benzalidene-4,4-diethyl-N-thiosemicarbazone	(HL''-VI)
<i>o</i> -chloro benzalidene-4,4-dibutyl-N-thiosemicarbazone	(HL'''-I)
<i>o</i> -bromo benzalidene-4,4-dibutyl-N-thiosemicarbazone	(HL'''-II)
<i>o</i> -nitro benzalidene-4,4-dibutyl-N-thiosemicarbazone	(HL'''-III)
<i>o</i> -methoxybenzalidene-4,4-dibutyl-N-thiosemicarbazone	(HL'''-IV)

### Preparation of Oxotitanium(IV) complexes [TiOL<sub>2</sub>(H<sub>2</sub>O)]

Potassium titanyl oxalate (BDH) was used as starting material<sup>6</sup>. An aqueous solution of metal salt (0.005 mol) containing 2.5 g of sodium acetate was heated with required quantity of ligand (1 : 2 mol) in absolute alcohol. The whole solution was refluxed for about 2 h and precipitate was digested in a beaker on a steam bath. The product was collected on filter, washed with hot water, alcohol and dried in vacuum. The analytical results and diagnostic IR bands of ligands are shown in Table-1. The analytical results, magnetic susceptibility, partial infrared data and electronic absorption bands of complexes are shown in Table-2. The physical measurements were made as reported earlier<sup>7</sup>.

### RESULTS AND DISCUSSION

The analytical results of complexes with thiosemicarbazones obtained by *ortho*-substituted benzaldehyde and thiosemicarbazide, 4,4-dimethyl-N-thiosemicarbazide, 4,4-diethyl-N-thiosemicarbazide and 4,4-dibutyl-N-thiosemicarbazide correspond to formula [TiOL<sub>2</sub>(H<sub>2</sub>O)] (HL = thiosemicarbazones). The complexes are almost insoluble in water and sparingly soluble in methanol, ethanol, benzene and chloroform but dissolve appreciably in pyridine and diethyl formamide. However, the complexes of 4,4-disubstituted-N-thiosemicarbazones are relatively more soluble in organic solvents. It may be attributed to organic substituents at N-atoms. The DMF solutions of complexes show negligible electrical conductance at room temperature (30–35°C) indicating their non-ionic nature. Complexes are stable in air and do not lose weight up to 150°C. This suggests that H<sub>2</sub>O is either coordinated or strongly held up in crystal lattices. The complexes are diamagnetic supporting d<sup>0</sup> configuration of titanium in (+IV) oxidation state, complexes are cream coloured. The IR spectra of ligand (Table-1) obtained from thiosemicarbazide (NH<sub>2</sub>-CS-NH-NH<sub>2</sub>) and *ortho*-substituted benzaldehyde display two or three IR bands in the region 3110–3340 cm<sup>-1</sup> assignable to  $\nu_{\text{sym}}(\text{NH}_2)(\text{NH}_2)$ ,  $\nu_{\text{asym}}(\text{NH}_2)$  and  $\nu(\text{NH})$  vibrations.

The thioamide band I [ $\nu(\text{CN}) + \delta(\text{NH})$ ] was observed in the region 1525–1485 cm<sup>-1</sup>, thioamide band II near 1310–1340 cm<sup>-1</sup>, thioamide band III at 1280–1230 cm<sup>-1</sup> and thioamide band IV which is mainly due to  $\nu(\text{C}=\text{S})$  vibration was observed at 890–860 cm<sup>-1</sup> in free ligand. In complexes, it has been observed that IR band at 3220–3170 cm<sup>-1</sup> is absent but band around 3320 cm<sup>-1</sup> is retained. It indicates that —CSNH— proton is deprotonated in complex formation. The thioamide bands I, II and III of ligands are raised to higher frequencies by 20–40 cm<sup>-1</sup> which is characteristic of coordinated thioamide group<sup>8–10</sup>. The thioamide

band IV of ligand shifts to lower frequency at around 720–700  $\text{cm}^{-1}$ . This supports coordination of thioamide group through deprotonated thiol sulphur. The  $\nu(\text{C}=\text{N})$  (1630–1600  $\text{cm}^{-1}$ ) of ligand is shifted to lower frequencies in complexes supporting the coordination of aldimine ( $\text{C}=\text{N}$ ) nitrogen with metal atom. Thus IR studies indicate coordination through deprotonated thiol sulphur and aldimine nitrogen as bidentate chelate. A broad weak band at 3400  $\text{cm}^{-1}$  in complexes

TABLE-I  
ANALYTICAL AND KEY IR BANDS ( $\text{cm}^{-1}$ ) OF LIGANDS

Ligands	% of N Found (Calcd.)	$\nu(\text{C}=\text{N})$	Thioamide bands				$\nu(\text{NH}_2)+$ $\nu(\text{NH})$
			I	II	III	IV	
HL-I	19.43 (19.67)	1625	1512	1338	1262	878	3344, 3215
HL-II	16.20 (16.27)	1628	1505	1342	1256	882	3312, 3195
HL-III	24.78 (25.00)	1615	1486	1312	1264	890	3340, 3208
HL-IV	19.73 (20.09)	1612	1524	1340	1272	872	3340, 3195
HL'-I	17.20 (17.39)	1630	1516	1342	1250	870	3218
HL'-II	14.50 (14.68)	1622	1510	1315	1230	884	3242
HL'-III	22.10 (22.22)	1612	1492	1328	1255	895	3208
HL'-IV	17.60 (17.72)	1628	1516	1332	1245	875	3225
HL''-I	15.40 (15.54)	1620	1510	1330	1260	880	3230
HL''-II	13.30 (13.37)	1625	1505	1340	1255	874	3232
HL''-III	15.42 (15.55)	1620	1490	1342	1260	870	3240
HL''-IV	15.70 (15.84)	1610	1520	1328	1270	890	3234
HL'''-I	13.00 (12.90)	1622	1525	1340	1245	868	3192
HL'''-II	11.40 (11.35)	1615	1518	1332	1238	872	3184
HL'''-III	16.41 (16.66)	1608	1510	1312	1250	880	3172
HL'''-IV	12.80 (13.08)	1625	1520	1335	1242	865	3208

% of C and H of ligands corresponds to their calculated values.

TABLE-2  
ANALYTICAL AND KEY IR BANDS ( $\text{cm}^{-1}$ ) OF Ti(IV) COMPLEXES

Complexes	% Found (Calcd.)		IR spectral bands	
	Ti	N	$\nu(\text{Ti}=\text{O})$	$\nu(\text{C}-\text{S})$
[TiO(L-I) <sub>2</sub> (H <sub>2</sub> O)]	9.10 (9.46)	19.54 (19.76)	1050	718
[TiO(L-II) <sub>2</sub> (H <sub>2</sub> O)]	7.95 (8.06)	13.88 (14.09)	1040	712
[TiO(L-III) <sub>2</sub> (H <sub>2</sub> O)]	8.90 (9.09)	15.85 (15.90)	1045	710
[TiO(L-IV) <sub>2</sub> (H <sub>2</sub> O)]	9.50 (9.63)	16.10 (16.44)	1040	708
[TiO(L'-I) <sub>2</sub> (H <sub>2</sub> O)]	8.40 (8.52)	14.80 (14.95)	1030	705
[TiO(L'-II) <sub>2</sub> (H <sub>2</sub> O)]	7.28 (7.36)	12.70 (12.88)	1020	700
[TiO(L'-III) <sub>2</sub> (H <sub>2</sub> O)]	7.10 (8.21)	14.12 (14.38)	1012	700
[TiO(L'-IV) <sub>2</sub> (H <sub>2</sub> O)]	8.46 (8.68)	14.95 (15.16)	1015	710
[TiO(L''-I) <sub>2</sub> (H <sub>2</sub> O)]	8.05 (8.12)	14.12 (14.21)	1030	715
[TiO(L''-II) <sub>2</sub> (H <sub>2</sub> O)]	6.92 (7.05)	12.15 (12.35)	1022	702
[TiO(L''-III) <sub>2</sub> (H <sub>2</sub> O)]	7.68 (7.84)	13.60 (13.72)	1025	712
[TiO(L''-IV) <sub>2</sub> (H <sub>2</sub> O)]	8.15 (8.26)	14.20 (14.43)	1010	705
[TiO(L'''-I) <sub>2</sub> (H <sub>2</sub> O)]	7.32 (7.42)	12.85 (12.98)	1020	715
[TiO(L'''-II) <sub>2</sub> (H <sub>2</sub> O)]	6.40 (6.52)	11.28 (11.41)	1012	710
[TiO(L'''-III) <sub>2</sub> (H <sub>2</sub> O)]	6.98 (7.18)	12.42 (12.55)	1016	712
[TiO(L'''-IV) <sub>2</sub> (H <sub>2</sub> O)]	7.40 (7.52)	12.95 (13.14)	1022	718

indicates the presence of water in the complex. A strong broad band in 1050–1000  $\text{cm}^{-1}$  suggests the presence of Ti=O in complexes (Table-2).

The position of  $\nu(\text{Ti}=\text{O})$  vibration decreases from  $\text{CH}_3\text{O} > \text{Cl} > \text{Br} > \text{NO}_2$ . The decrease in  $\nu(\text{Ti}=\text{O})$  is in increasing order of steric volume of substituent at *ortho* position of aldehyde. The IR of N,N-disubstituted thiosemicarbazones displays one band at 3250–3100  $\text{cm}^{-1}$  attributed to  $\nu(\text{N}-\text{H})$  vibration. The strong and sharp bands between 2980–2860  $\text{cm}^{-1}$  observed in ligands as retained in their complexes are attributed to  $\nu(\text{CH}_2)$  and  $\nu(\text{CH}_3)$  vibrations of methyl, ethyl and butyl substituents in the ligands. The thioamide bands I, II, III and IV of ligands (Table-1) are also affected on coordination. The substantial decrease in thioamide band IV by 130–150  $\text{cm}^{-1}$  clearly indicates coordination through deprotonated thiol sulphur. The decrease of  $\nu(\text{C}=\text{N})$  of ligand (Table-1) by 15–20  $\text{cm}^{-1}$  in oxotitanium (IV) complexes suggests coordination of these ligands through aldimine nitrogen. The IR spectral pattern shows the mode of coordination of N,N-disubstituted thiosemicarbazone complexes similar to unsubstituted thiosemicarbazones. Thus from the above discussions, six coordinated pseudo octahedral structure is suggested to almost all oxotitanium complexes derived from *ortho*-substituted benzaldehyde thiosemicarbazones.

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