

Monohalogenbenzoylhydrazones II. Synthesis and Study of Ti(IV) Complexes with Monochlorobenzoylhydrazones of 2-Furaldehyde, 2-Thiophenylaldehyde, 2-Pyrrolaldehyde and Di-2-pyridylketone as Ligands

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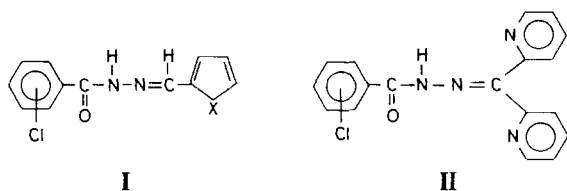
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Abstract

Sixteen new titanium(IV) complexes of the general formulae L_2TiCl_2 [L^- = benzoyl and monochlorobenzoylhydrazones of 2-furaldehyde(FBH-H and FCIBH-H), 2-thiophenylaldehyde(TBH-H and TCIBH-H), 2-pyrrolaldehyde(PBH-H and PCIBH-H)] and $L'TiCl_3$ [L' = benzoyl and monochlorobenzoylhydrazones of di-2-pyridylketone (DBH-H and DCIBH-H)] have been prepared and characterised by various physicochemical methods. All ligands appear to be coordinated to the titanium through the carbonyl and azomethine groups in a bidentate fashion, with the exception of the DBH and DCIBH molecules, which act as tridentate ligands involving the nitrogen atom of the pyridyl group in their coordination.

Introduction

In previous communications [1–4] we reported our preliminary results on the preparation and study of Co, Ni, Cu, Sn, Zn, Cd and Hg complexes employing as ligands halogenbenzoylhydrazones of 2-furaldehyde, 2-thiophenylaldehyde, 2-pyrrolaldehyde and di-2-pyridylketone. Herein we report the preparation and study of Ti(IV) complexes with the following ligands:



where X = O, S, NH

In general one would expect the hydrazones of type I to be coordinated in a bidentate fashion with the coordination sites being the oxygen atom of carbonyl and the nitrogen atom of amino group [5–9], whereas those of type II would be expected to be coordinated in a tridentate fashion offering one more possible coordination site [10–13] (the nitrogen atom of pyridyl group). The characterization of the new compounds was done by elemental analysis, infrared and UV–Vis spectroscopy, as well as by conductivity and magnetic susceptibility measurements. For two of the investigated compounds thermal studies (DTA/TG) have also been carried out.

Experimental

Reagents and General Techniques

Benzoyl and chlorobenzoylhydrazones were prepared according to the published methods [14–20]. The reagents were used without further purification. Microanalyses of carbon, hydrogen and nitrogen were carried out using a Perkin-Elmer 240 elemental analyser. Titanium and chlorine were determined spectrophotometrically and by Volhard's method respectively [21].

IR spectra were recorded in 'KBr pellets' in the region 4000–250 cm^{-1} on a Perkin-Elmer 467 spectrophotometer. Electronic absorption spectra were measured on a Perkin-Elmer Hitachi 200 spectrophotometer. Magnetic measurements were carried out by Gouy's method using mercury tetrathiocyanato-cobaltate(II) as a calibrant. The molar conductivities were measured in 10^{-3} M DMF or methanol solutions with an Industrial Instruments, Inc. Model RC 216 B2 conductivity bridge. The thermodiagrams were recorded with a thermobalance Linseis L81-22 with 20 mg samples in platinum crucibles in nitrogen atmosphere.

Preparation of Complexes

The reactants titanium tetrachloride and the corresponding hydrazone were added in chloro-

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TABLE I. Analytical and Physical Data of Titanium(IV) Complexes

Compound	Yield (%)	Colour	Melting point (°C) ^a	Molar conductance (ohms ⁻¹ cm ² mol ⁻¹) at 25 °C (Solvent)	%C	%H		%N		%Ti		%Cl	
						found	calc.	found	calc.	found	calc.	found	calc.
TiCl ₂ (FBH-H) ₂ (I)	90	yellow	166	125 (DMF)	52.87	3.33	3.71	10.27	10.42	8.78	8.60	13.00	13.18
TiCl ₂ (FcCIBH-H) ₂ (II)	50	yellow	160	126 (DMF)	46.94	2.63	2.85	9.12	8.81	7.80	8.10	23.09	22.65
TiCl ₂ (FmCIBH-H) ₂ (III)	49	yellow	176	130 (DMF)	46.94	2.63	2.83	9.12	8.95	7.80	7.65	23.09	22.80
TiCl ₂ (FpCIBH-H) ₂ (IV)	90	yellow	190	135 (DMF)	46.94	2.63	2.91	9.12	9.01	7.80	7.50	23.09	22.60
TiCl ₂ (TBH-H) ₂ (V)	40	red	160	155 (MeOH)	49.93	3.14	3.33	9.70	9.94	8.30	9.17	12.28	11.95
TiCl ₂ (ToCIBH-H) ₂ (VI)	90	red	155	157 (MeOH)	44.61	2.50	2.88	8.67	8.84	7.41	7.60	21.94	22.10
TiCl ₂ (TmCIBH-H) ₂ (VII)	60	red	105	160 (MeOH)	44.61	2.50	2.65	8.67	8.52	7.41	7.20	21.94	21.55
TiCl ₂ (TpCIBH-H) ₂ (VIII)	70	red	150	165 (MeOH)	44.61	2.50	2.72	8.67	7.98	7.41	7.15	21.94	21.45
TiCl ₂ (PBH-H) ₂ (IX)	35	brown	125	130 (DMF)	53.06	3.71	3.61	15.47	15.63	8.82	8.40	13.05	12.70
TiCl ₂ (FcCIBH-H) ₂ (X)	30	brown-red	118	135 (DMF)	47.09	2.96	2.78	13.73	13.90	7.82	7.60	23.17	23.00
TiCl ₂ (FmCIBH-H) ₂ (XI)	60	brown-red	140	141 (DMF)	47.09	2.96	2.81	13.73	13.28	7.82	8.10	23.17	22.55
TiCl ₂ (FpCIBH-H) ₂ (XII)	50	brown-red	135	136 (DMF)	47.09	2.96	2.67	13.73	13.91	7.82	7.45	23.17	24.03
TiCl ₃ (DBH-H) (XIII)	50	orange	225	272 (MeOH)	47.46	2.87	3.02	12.30	12.67	10.51	11.05	23.35	23.10
TiCl ₃ (DmCIBH-H) (XIV)	60	orange	205	277 (MeOH)	44.12	2.47	2.68	11.43	10.92	9.78	9.30	28.94	28.20
TiCl ₃ (DpCIBH-H) (XV)	60	orange	220	282 (MeOH)	44.12	2.47	2.39	11.43	11.73	9.78	9.45	28.94	28.45
TiCl ₃ (DpCIBH-H) (XVI)	50	orange	225	286 (MeOH)	44.12	2.47	2.61	11.43	11.62	9.78	9.35	28.94	28.15

^aThe compounds darken with apparent decomposition above the temperature cited.

form (20 ml) in molar ratio 1:2 for the hydrazones of 2-furaldehyde, 2-thiophenylaldehyde and 2-pyrrolaldehyde, and in a ratio of 1:1 for the hydrazones of di-2-pyridylketone. The resultant mixture was refluxed for 1 h usually affording a solid product. In some cases the products were soluble in the used solvent, so the resultant solution had to be evaporated to a small volume *ca.* 10 ml; then the precipitation of the complex was achieved by addition of diethyl-ether. The precipitate was removed by filtration, washed with chloroform and diethylether and dried *in vacuo*.

Results and Discussion

All the compounds studied were fairly stable in the atmosphere either in solid state or in solution; they were soluble in DMF, CH₃OH and EtOH, but only slightly soluble in dichloromethane. The analytical and some physical data along with yields for the complexes (I–XVI) are listed in Table I. The molar conductivities of the investigated complexes measured in DMF or MeOH solutions strongly suggest the 2:1 and 3:1 electrolyte type for the TiCl₂(L-H) and TiCl₃(L'-H) compounds, respectively. As was expected, all complexes were found to be diamagnetic.

The structures of the complexes were evaluated from their spectroscopic (IR, UV-Vis) and thermo-analytical data. The most relevant bands of the IR spectra for the complexes and the free ligands are listed in Table II. The two absorption bands occurring in the 1690–1650 and 1620–1520 cm⁻¹ region of the spectra were attributed to $\nu(\text{C}=\text{O})$ and $\nu(\text{C}=\text{N})$ (azomethine) stretching vibrations respectively [19, 23–25]. Upon complexation these bands are shifted to lower frequencies, suggesting that the ligands are coordinated to metal via the carbonyl oxygen and azomethine nitrogen donor atoms [26, 27]. Furthermore, the presence of the characteristic $\nu(\text{NCO})$ and $\nu(\text{C}-\text{O})$ bands in the 1535–1465 and 1285–1220 cm⁻¹ regions of the spectra respectively suggest support that the ligands act with the enolic form [28].

The $\nu(\text{Ti}-\text{O})$ and $\nu(\text{Ti}-\text{N})$ bands observed in the region 600–530 cm⁻¹ are consistent with the coordination mode of the ligands [29–32]. On the other hand, the $\nu(\text{N}-\text{N})$ band around 900 cm⁻¹ occurring in the spectra of the free ligands is shifted upon complexation to higher frequencies. This shifting again suggests the involvement of at least one of the nitrogen atoms in the bonding with the metal ion [33, 34].

According to IR and conductivity data all complexes seem to be six-coordinated with a distorted octahedral stereochemistry (Scheme 1).

TABLE II. The Most Relevant Infrared Bands of the Ligands [19] and of their Corresponding Titanium(IV) Complexes as well as their Assignments

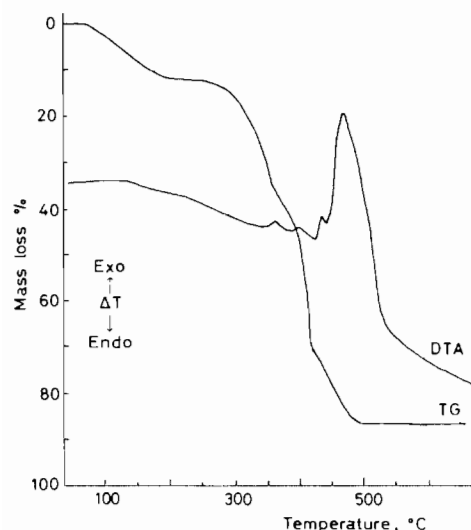
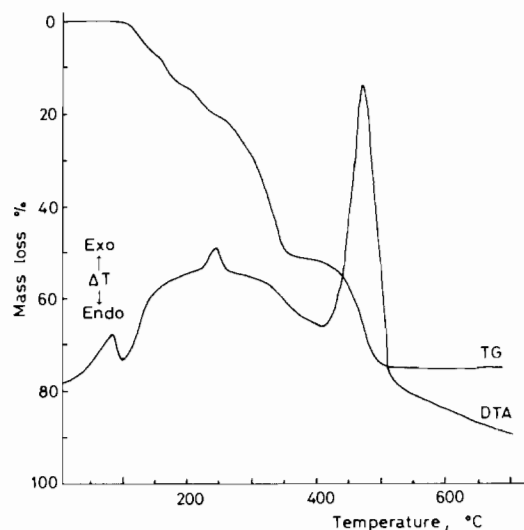
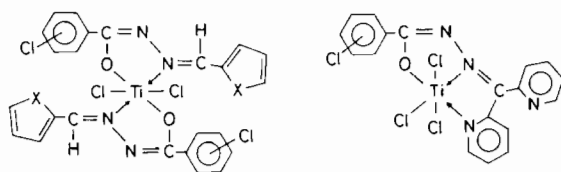
Compound	$\nu(\text{C}=\text{O})$ (cm^{-1})	Shift in $\nu(\text{C}=\text{O})$ (cm^{-1})	$\nu(\text{C}=\text{N})$ (cm^{-1})	$\nu(\text{C}=\text{C})$ (cm^{-1})	$\nu(\text{NCO})$ (cm^{-1})	$\nu(\text{C}-\text{O})$ (cm^{-1})	$\nu(\text{N}-\text{N})$ (cm^{-1})	Shift in $\nu(\text{N}-\text{N})$ (cm^{-1})	$\nu(\text{Ti}-\text{O})$ (cm^{-1})	$\nu(\text{Ti}-\text{Cl})$ (cm^{-1})
FBH	1650		1590	1540			900			
I	1620	-30	1570	1530	1470	1275	930	+30	530, 580	365
FoClBH	1665		1570	1550			905			
II	1600	-65	1550	1520	1465	1285	930	+25	560	330
FmClBH	1650		1570	1550			885			
III	1600	-50	1575	1530	1490	1270	920	+35	545, 580	345
FpClBH	1650		1585	1555			925			
IV	1600	-50	1565	1550	1490	1285	940	+15	535, 575	360
TBH	1650		1605	1555			900			
V	1610	-40	1590	1530	1495	1225	925	+25	600, 575	350
ToClBH	1670		1600	1540			910			
VI	1605	-65	1590	1530	1480	1220	940	+30	600, 570	360
TmClBH	1655		1610	1570			895			
VII	1615	-40	1600	1435	1485	1230	910	+15	600, 575	360
TpClBH	1655		1605	1565			910			
VIII	1615	-40	1605	1535	1500	1230	930	+20	610, 585	345
PBH	1660		1615	1570			885			
IX	1620	-40	1600	1550	1530	1280	910	+25	590, 570	360
PoClBH	1660		1610	1575			875			
X	1610	-50	1595	1550	1530	1280	890	+15	590, 580	370
PmClBH	1670		1625	1560			890			
XI	1620	-50	1600	1550	1530	1270	915	+25	585	365
PpClBH	1660		1625	1565			880			
XII	1620	-40	1600	1550	1530	1280	895	+15	570	390, 320
DBH	1690		1585	1560			895			
XIII	1635	-55	1600	1550	1535	1220	930	+35	575, 550	325
DoClBH	1695		1595	1570			895			
XIV	1625	-70	1600	1540	1520	1220	910	+15	575	360
DmClBH	1695		1590	1575			895			
XV	1640	-55	1595	1540	1510	1220	930	+35	570, 530	330
DpClBH	1680		1590	1565			890			
XVI	1630	-50	1595	1535	1485	1220	930	+40	580, 530	330

TABLE III. Electronic Spectral Data for Titanium(IV) Complexes at 25 °C

Compound	Solvent	Absorption bands in nm (log ϵ)				
I	methanol	230(4.68)	315(4.68)	360sh	380sh	
II	methanol	227sh	306(4.72)	350sh	380sh	
III	methanol	230(4.63)	312(4.75)	360sh	385sh	
IV	methanol	235(4.67)	313(4.77)	355sh	385sh	
V	DMF	264(4.38)	322(4.49)	375sh	405sh	
VI	DMF	264(4.62)	325(4.48)	365sh	385sh	405sh
VII	DMF	264(4.68)	325(4.50)	365sh	382sh	405sh
VIII	DMF	264(4.62)	322(4.49)	365sh	382sh	405sh
IX	methanol	225(4.48)	250sh	325(4.51)	390sh	
X	methanol	235sh	255sh	327(4.62)	385sh	
XI	methanol	230(4.53)	255sh	328(4.63)	400sh	
XII	methanol	237(4.52)	255sh	332(4.64)	400sh	
XIII	methanol	230(4.49)	255sh	318(3.91)	386(4.02)	
XIV	methanol	230(4.48)	262(4.38)	363(4.09)		
XV	methanol	230(4.50)	257sh	390(4.10)		
XVI	methanol	230(4.49)	257sh	390(4.12)		

TABLE IV. DTA/TG Data for some Titanium(IV) Complexes

Compound	DTA results		Stage	TG results			
	Peak temperature (°C) endothermic (-) exothermic (+)			Temperature range (°C)	Mass loss (%)	Evolved moiety formula	Mass calculated (%)
TiCl ₂ (TBH-H) ₂			a	70–200	12.0	Cl ₂	12.28
	360(+)		b	275–370	26.0	2C ₆ H ₅	26.71
	395(+)		c	370–420	30.0	2C ₄ H ₄ S	29.14
	435(+)		d	420–480	16.5	2C ₂ N ₄	18.02
	470(+)		residue	>480	15.5	TiO ₂	13.84
TiCl ₃ (DoClBH-H)	105(-)		a	100–150	7.2	Cl	7.23
			b	150–185	6.7	Cl	7.23
	245(+)		c	185–260	7.2	Cl	7.23
			d	260–350	31.0	2C ₅ H ₄ N	31.87
	475(+)		e	400–500	22.3	C ₆ H ₄ Cl	22.76
			residue	>500	25.6	TiO ₂ C ₂ N ₂	23.67

Fig. 1. Thermoanalytical curves of TiCl₂(TBH-H)₂ in nitrogen atmosphere.Fig. 2. Thermoanalytical curves of TiCl₃(DoClBH-H) in nitrogen atmosphere.

where X = O, S, NH

Scheme 1.

The electronic spectral data of the complexes under investigations are shown in Table III. The two intense absorption bands in the region 230–273 and 304–331 nm in the spectra of the free ligands are attributed to intraligand transitions of $\pi^* \leftarrow \pi$ and

$\pi^* \leftarrow n$ type located mainly on the C=N and C=O groups respectively [35]. These bands also occur in the spectra of the complexes but are shifted towards higher frequencies (first band) and lower frequencies (second band), a fact which further supports the idea of the coordination of the hydrazones via the azomethine nitrogen and carbonyl oxygen atoms. Finally, the band envelope in the region of 350–405 nm of the spectra of each of the complexes can be attributed to ligand-to-metal charge-transfer transition and is responsible for the colour of the complexes.

The thermal behaviour of two representative complexes was also investigated. The thermoanalytical curves (DTA and TG) are shown in Figs. 1 and 2.

Both theoretical and experimental percentage mass losses, along with the possible formulae of the corresponding fragments, the temperature ranges and the DTA data are given in Table IV. The TG curve of the yellow compound, $\text{TiCl}_2(\text{TBH}\cdot\text{H})_2$, shows that the first decomposition step, in the temperature range 70–200 °C, includes the evolution of two chlorine atoms. The second and third steps (275–370 and 370–420) are accompanied by mass losses corresponding to two phenyl and two thienyl groups respectively. The final stage of decomposition (420–480 °C) accounts for the removal of two $\{\text{C}_2\text{N}_4\}$ moieties. The weight of the residue left corresponds to $\{\text{TiO}_2\}$. The TG curve of the orange complex $\text{TiCl}_3(\text{DoClBH}\cdot\text{H})$ shows three stages (100–150, 150–185 and 185–260 °C), corresponding to a stepwise evolution of chlorine atoms. The fourth (260–350 °C) and fifth (400–500 °C) steps correspond to the removal of two pyridyl and one chlorophenyl groups respectively.

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