

Synthesis and Physiochemical studies of some metal complexes of Ti(III) with Phthalimide or Succinimide

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Abstract— Mixed ligand complexes of Ti(III) with phthalimide or succinimide as primary ligands and amino acids as secondary ligands have been synthesized. The general formula of these complexes are follows: $K[Ti(L)_2(L')_2]$ where L= phthalimide; $C_8H_4O_2N(1-3)$, succinimide; $C_4H_4O_2N(4-6)$; and L' =amino acids. The complexes were prepared in the solid form and characterization by elemental analysis, conductivity, magnetic moment measurement, IR, 1H -NMR, ^{13}C -NMR, FAB⁺ mass and electronic spectroscopic studies. The value of $10 Dq$ was found to be $12250-13965\text{ cm}^{-1}$ for all complexes. The value of B , β and ligand field stabilization energy have also been calculated from the bands obtained in the electronic spectra of the complexes . Electronic and other measurements confirmed their octahedral structure.

Index Terms— Ti(III), phthalimide , succinimide , amino acids, 1H -NMR, ^{13}C -NMR and FAB⁺ mass.

I. INTRODUCTION

Scanty details on the studies of simple metal imide complexes are available in the literature but a very little work has been done on their mixed lignd complexes. The salts of imides with varies metal ions were prepared under anhydrous conditions¹⁻³ because of their hydrolysable nature. Mercuric acetate with succinimide in the presence of potassium hydroxide gave a golden yellow compound $(C_4N_4O_2N)_3HgK$ and reacts with gold salts or fulminating gold to give its complexes⁴. The copper complexes having the formula $(C_4H_4O_2N)_4Cu.M.nH_2O$ were prepared by the interaction of succinimide solution and copper acetate or chloride containing minimum amounts of caustic alkalies⁵ where $M = Li, Na, K, Rb$ or Cs ions and $n = 1, 2, 4$ or 6 . Rising prepared the brownish red Ba, Cu succinimide complexes $[BaCu(C_4H_4O_2N)_4]$. In the same mannar the metal complexes of phthalimide have been studied in relation to their preparation, chemical analysis, magnetic properties and infrared studies^{4,6-12,19,20}. Scanty information is found in recent literature about the mixed ligand complexes of amino acids^{13,14}.

We report here the preparation and characterization of some mixed ligand complexes of Ti(iii) with phthalimide, succinimide as primary and amino acids, viz. L-Serine,

L-phenylalanine, DL-leucine, L-cystine and L-cysteine as secondary ligands.

II. EXPERIMENTAL

Reagents

All the chemicals were of reagent grade and were used as received. The solvents were purified using conventional methods.

Physical Measurement

Infrared spectra were recorded on Shimadzu IR-470, Perkin Elmer IR-883 and Genesis Series FTIR TM 9423-240-08061 spectrophotometer as KBr pellets in the region $4500-400\text{ cm}^{-1}$ in the Department of Chemistry, Rajshahi University, Rajshahi. Carbon, hydrogen and analyses were caried out at the Department of Chemistry, University Putra Malaysia. The electronic spectra were run on a Ultrospee K4033 spectrophotometer. The spectra of the complexes in solid state were recorded as nujol mull spread on a piece of filter paper. Metal was determined by weighing as the oxide produced by direct ignition¹⁵. The molar conductance of 10^{-3} M solution of the metal complex in amyl alcohol was measured at $30^\circ C$ using a Jenway 4310 conductivity meter and a dip-cell with platinized electrode (cell constant=1.12). Melting points were determined using an Electrothermal digital melting point apparatus. Magnetic susceptibility was measured with a Jonshon Matthey magnetic susceptibility balance at 298K. All susceptibilities were corrected for diamagnetic contribution using Pascal's constant¹⁶. 1H NMR spectra were recorded on a Varian Gemini 200/MHz pulsed FT NMR spectrometer. TMS was used as the internal standard. The ^{13}C -NMR spectra were recorded in $CDCl_3$ and $DMSO-d_6$ using TMS as internal standard with Bruker 500 MHz high resolution NMR spectrometer. FAB⁺ mass spectra of the complexes were recorded using a JEOL SX-120 instrument.

A. Preparation of the imide salts

A saturated solution of phthalimide or succinimide and potassium hydroxide in ethyal alcohol separately were mixed in a volume ratio 1:1, white precipitates were formed immediately which were filtered off, washed several times with alcohol and dried in a vacuum desicator over anhydrous $CaCl_2$.

B. Preparation of the complexess

The aquous solution of Titanium(III) chloride and of amino acids containing minimum amount of KOH were mixed in a molar ratio of 1:2 and then allowed to stand for about ten minutes. Two moles of potassium phthalimide or potassium

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succinimide were than added. To get the precipitates of complexes, the mixer was then heated at 60°C for about twenty minutes and then allowed to stand for ten minutes. The precipitates formed were removed by filtration, washed several times with distilled water and finally with alcohol and dried in a vacuum desiccator over anhydrous CaCl₂.

III. RESULTS AND DISCUSSION

A. Conductivity measurement and elemental analysis

The complexes of Ti(III) were soluble in benzene, amyl alcohol and DMF but insoluble in water. The molar conductance of the complexes were measured in benzene and amyl alcohol and high conductance values were found which indicated that these complexes were highly electrolytic in nature. Some physical properties, viz; colour, melting points, molar conductance and magnetic moments are given in table 1. Analytical results for metal, carbon, hydrogen and nitrogen are given in table 2.

Table 1. Physical properties of the complexes

Complex	Name of the complexes	Colour	Melting points (±5°C)	Molar conductance (ohm ⁻¹ cm ² mole ⁻¹)
01	K[Ti(Pim) ₂ (leu) ₂]	white powder	145-150(d)	80
02	K[Ti(Pim) ₂ (cystine) ₂]	lemon	190-195(d)	83
03	K[Ti(Pim) ₂ (cystein) ₂]	cream	185-190(d)	84
04	K[Ti(Sim) ₂ (ser) ₂]	white powder	230-235(d)	79
05	K[Ti(Sim) ₂ (cystine) ₂]	white powder	240-245(d)	83
06	K[Ti(Sim) ₂ (cystein) ₂]	white powder	250-255(d)	81

Pim = phthalimide, Sim = succinimide, ser = serine, leu = leucine, cystine = cystine, cystein = cystein, d = decomposition

Table 2. Analytical data of the complexes

Complex	Metal (%)	Carbon (%)	Hydrogen (%)	Nitrogen (%)
01	7.50 (7.40)	52.69 (52.58)	4.70 (4.60)	8.78 (8.67)
02	5.59 (5.45)	39.26 (39.17)	2.80 (2.69)	9.81 (9.70)
03	9.77 (9.00)	42.88 (45.57)	2.92 (2.55)	9.09 (10.54)
04	9.78 (9.67)	34.33 (34.24)	3.67 (3.58)	11.44 (11.33)
05	6.30 (6.16)	31.58 (31.50)	3.15 (3.06)	7.37 (7.26)
06	9.18 (9.10)	32.22 (32.10)	3.45 (3.36)	10.74 (10.75)

(Calculated values are given in the parenthesis)

IV. IR STUDIES:

The distinction between O and N⁻ coordination of imides are not readily made by IR spectroscopy but it is expected that co-ordination will occur

preferentially through nitrogen and coordination through oxygen will be inhibited by steric hindrance. Although the C=O group in imides does not take part in coordination, the shift of $\nu(\text{C}=\text{O})$ to lower frequency as compared to the non coordinated state may be due to the mass effect of heavy metal ion¹⁷. In all the complexes $\nu(\text{C}=\text{O})$ fall within the range 1550-1660 cm⁻¹ compared to 1720 cm⁻¹ in free imides. The stretching frequency obtained at 1360 cm⁻¹ due to $\nu\text{C-N}$ for the succinimide or phthalimide is shifted to about 1400 cm⁻¹ in the complexes indicating thereby N⁻ formation and co-ordination^{10,14}. In the spectrum of free imide, the frequency of the stretching N-H vibration observed at around 3400 cm⁻¹ should disappear in the spectra of the complexes for the coordination of the imino group after deprotonation. But a broad band at around the same wave number is observed in the spectra of the complexes showed a strong band at about 1600 cm⁻¹ and a shift of νNH_2 band from 3400 cm⁻¹ to ~ 2860 cm⁻¹ indicating coordination of the amino acids through its carboxyl oxygen and amino nitrogen¹⁸ or S⁻ ion. The stretching frequency of $\nu\text{M-S}$ or $\nu\text{M-N}$ with $\nu\text{M-O}$ were observed at around 406-454 cm⁻¹ due to coordination of M-S or M-N and M-O of amino acids to metal ion respectively.

Table 3. Infrared spectral data of the complexes (Band maxima in cm⁻¹)

Complex	$\nu(\text{NH})$	$\nu(\text{C}=\text{O})$	$\nu(\text{C-N})$	$\nu(\text{M-N})$	$\nu(\text{M-O})$	$\nu(\text{M-s})$
01	2962	1585.4	1408.4	535	408	.
02	2968.2	1584.4	1407.9	.	540	452.3
03	2880	1622	1407.1	.	540	452
04	2940.3	1652.9	1391.5	422	406	.
05	2868	1628	1398	.	540	408
06	2583.5	1585.4	1407.9	.	539.1	452.3

V. ELECTRONIC SPECTRA AND MAGNETIC STUDIES:

The magnetic moment of Ti(III) complexes were found to be 1.65-1.95 B.M. at room temperature which indicates that these are paramagnetic with one unpaired electron. These complexes consistent with essentially octahedral stereo chemistry.

The electronic spectra of Titanium(III) complexes in DMF gave one band at 19500-20920 cm⁻¹ with a shoulder at 18519-19000 cm⁻¹. The band is obviously derived from the transition ${}^2\text{T}_{2g} \rightarrow {}^2\text{E}_g$ for O_h symmetry.

Table 4. Electronic spectral data of Ti(III) complexes

No. of complexes*	Spectral band (cm ⁻¹) with assignment
	¹ T _{1g} → ¹ E _g
01	19500
02	20242
03	19785
04	19656
05	20450
06	19875

Table-5: ¹H-NMR & ¹³C-NMR spectral data of Ti(III) complexes.

Comp	¹ H-NMR spectral data	¹³ C-NMR spectral data
01	δ: 2.21 (s, 2H), 7.3 (t, 4H, Ar-H), 7.5 (m, 4H, Ar-H), 7.6 (m, 4H, Ar-H), 8.2 (m, 4H, Ar-H) 8.5 (d, 1H, Ar-H), 9.2 (d, 1H, NH) ppm	δ: 76 (-CH-), 110, 112, 115, 118(Aromatic carbons), 120, 126, 127, 128, 129, 145, 165 (C=O) ppm
02	δ: 7.3 (s, 7H, Ar-H), 7.75 (m, 6H, Ar-H), 7.90 (m, 6H, Ar-H), 8.5 (m, 1H, Ar-H) 9.20 (m, 1H, Ar-H) ppm	δ: 77 (-CH-), 110, 113, 115, 117(Aromatic carbons), 130, 133, 162(C=N), 173(C=O) ppm
03	δ: 1.82 (s, 6H,-CH ₃), 1.83 (s, 3H,-CH ₂), 4.4 (s, 3H), 7.20 (s, 7H, Ar-H) ppm	δ: 20, 21, 24(CH ₃ ,CH ₂), 39, 52, 75, 111(Aromatic carbons), 161, 162(C=N)ppm
04	δ: 3.36 (q, 4H,-CH ₂), 3.55 (d, 4H,-CH) 4.72 (s, 2H,-NH) 7.27 (m, Ar-H) ppm	δ: 76.74(-CH-), 111, 113, 115, 117 (Aromatic carbons), 161(C=N), 162 (C=O) ppm
05	δ: 2.17 (s, 12H,-CH ₂) 2.35 (s, 4H,-OH ₂) 4.72 (s, 2H,-NH), 7.3 (m, Ar-H) ppm	δ: 76.74(-CH-), 111, 113, 115, 118 (Aromatic carbons), 161.55(C=N), 162.58 (C=O) ppm
06	δ: 2.18 (s, 12H,-CH ₂) 2.37 (s, 4H,-OH ₂) 4.72 (s, 4H,-NH), 7.6 (m, Ar-H) ppm	δ: 76.75 (-CH-), 111, 114, 117 (Aromatic carbons), 161(C=N), 163 (C=O) ppm

Table-6: FAB⁺ mass fragment spectral data for Ti(III) complexes

Comp.	FAB+ mass spectral data
01	460.2, 307.2, 289.1, 154.1, 136.1, 107.0, 89.0
02	360.0, 348.8, 307.2, 289.2, 217, 192.1.
03	459.0, 307.2, 289.2, 154.10, 136.10, 107.0, 89.0, 57.0
04	459.0, 307.2, 289.2, 154.1, 136.1, 107.0, 89.0, 77.0
05	459.0, 307.2, 289.2, 154.1, 136.1, 107.0, 89.0, 65.0
06	425, 307.2, 289.2, 154.1, 136.1, 107.0, 89.0, 65.0

VI. CONCLUSION

On the basis of the above assesment an octahedral structure is proposed for the Ti(III) complexes. Fig.1.shows the structure of K[Ti(pim)₂(gly)₂] may be given below:

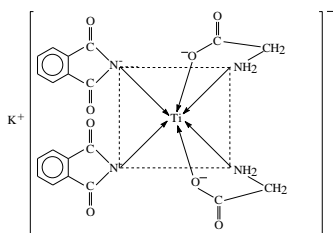


Fig1. Proposed structure of the complex K[Ti(Pim)₂(gly)₂]

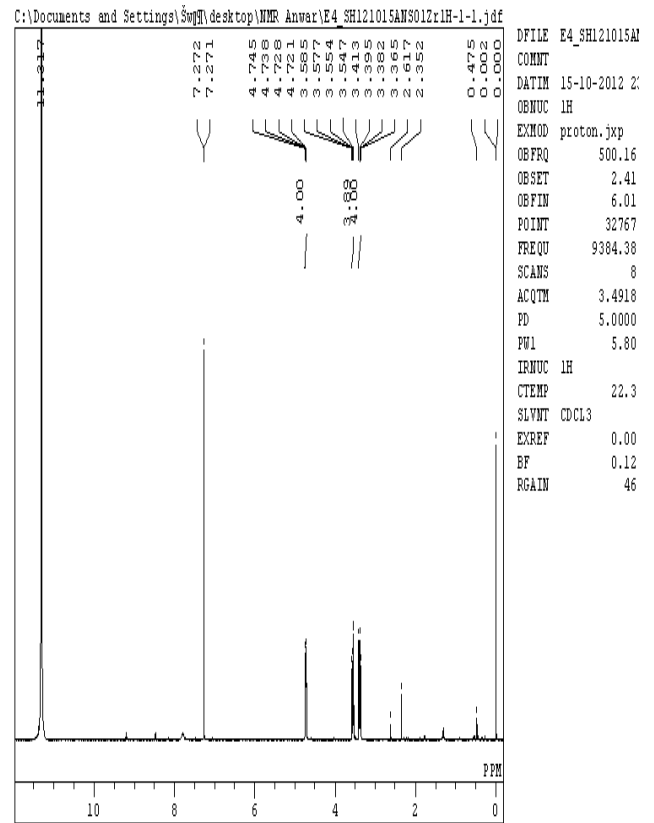


FIG1.1: ¹H-NMR FOR COMP-1

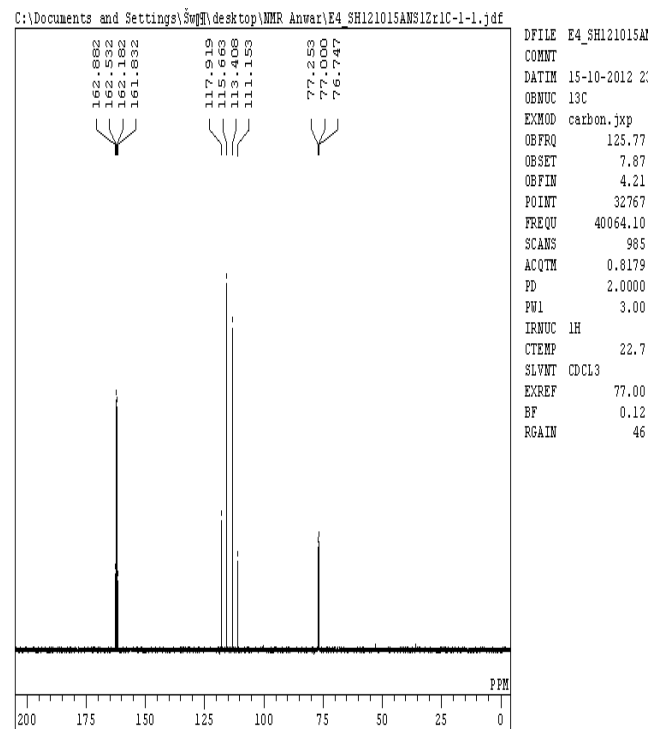


Fig.1.2: ¹³C-NMR for comp-1

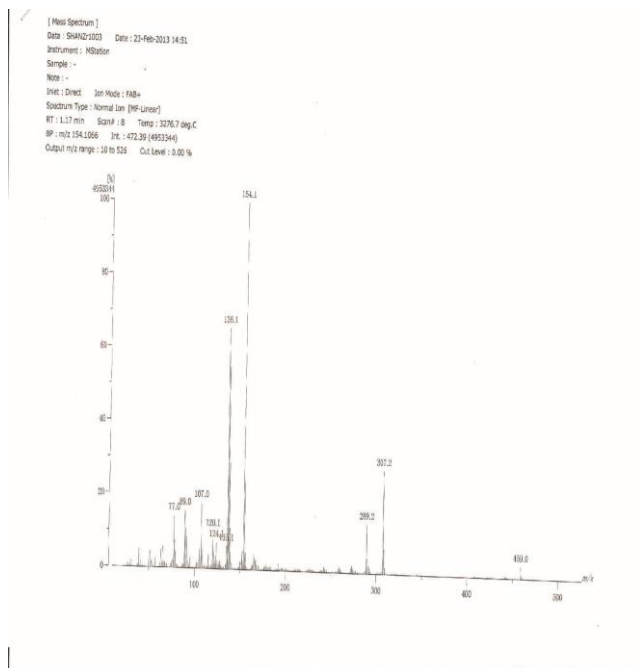


FIG.1.3: FAB⁺ MASS SPECTRUM FOR COMP-4

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