

SYNTHESIS, SPECTRAL AND SOL-GEL BEHAVIOR OF MIXED LIGAND COMPLEXES OF TITANIUM(IV) WITH OXYGEN, NITROGEN AND SULFUR DONOR LIGANDS

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ABSTRACT. A new route to synthesize nano-sized Ti(IV) mixed ligand complexes have been investigated by the reaction of titanium(IV) chloride with ammonium salts of dithiophosphate and 3(2-hydroxyphenyl)-5-(4-substituted phenyl) pyrazolines. The resultant complex is then treated with H₂S gas to get sulfur bridged dimer of Ti(IV) complex, a precursor of TiS₂. The morphology of the complexes was studied by employing XRD which shows that all the complexes are amorphous solid. Molecular weight measurements, elemental analysis in conjugation with spectroscopic (IR, ¹H NMR, ¹³C NMR and ³¹P NMR) studies revealed the dimeric nature of the complexes in which pyrazoline and dithiophosphate are bidentate. Scanning electron microscopic image and XRD indicate that the particles are in the nano range (50 nm). Putting all the facts together, coordination number six is proposed for titanium with octahedral geometry.

KEY WORDS: Titanium(IV), Dithiophosphate, Pyrazoline, Nano-sized, Sol-gel, Mixed ligand complexes

INTRODUCTION

Titanium proves to be an excellent corrosion-resistance material in many environments as it forms a protective oxide layer on its surface [1, 2]. The high tensile strength, light weight and excellent corrosion resistant make the titanium a useful alloying agent for many parts of high-speed aircraft, motorbikes, ships and missiles [3-5]. Titanium being a biocompatible material found application in prosthetic devices [6, 7].

The Ti(IV) complexes with nitrogen, oxygen and sulfur donor ligands have received considerable attention due to their widespread utilization as an active precursor for making TiO₂ and TiS₂ [8]. Owing to the hard acid character of titanium, the synthesis of its simple thiolates was not possible. Attempts have been made to reduce the acidic strength of titanium metal centre by attaching electron-rich ligands such as dialkyl nitrogen and cyclopentadienyl which then forms a stable complex with soft bases [9]. The highly sensitive nature of titanium complexes towards hydrolysis reduces its activity towards different applications [10]. Available reports showed that the addition of bulky electron-rich ligands to Ti metal centre increases the resistance of metal complexes towards hydrolysis [11, 12].

The excellent biological activity of sulfur containing transition metal complexes makes them interesting [13]. Several reports are available on alkylene and O,O'-dialkyl dithiophosphate derivatives of Ag(I), Zr(IV), Fe(II) and Cu(II) [14, 15]. Carmalt *et al.* [9] reported titanium pyridine and pyridine thiolates as a precursor for the production of titanium disulfide. Ti(IV) has been extensively used for the polymerization of ethylene and propylene [16, 17]. Salen-Ti(IV) complex has been effectively employed in the controlled polymerization of D,L-lactic acid [18]. Park *et al.* [19] designed and synthesized a new class of green colored titanium complexes with a dithiolate ligand for LCD and TFT panels. The first non-platinum anticancer drug exhibiting excellent efficacy was titanium based titanocene dichloride and budotitane [20]. Later on,

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numbers of complexes of titanium have been reported by several researchers which can act as a potent cytotoxic agent to kill cancer cells through apoptosis [21-24].

Several reports are available on titanium complexes of thiolates, dithiolates and dithiocarbamates [25-29]. The limited study on mixed ligand complexes of Ti(IV) in general and with pyrazoline [21-24, 30] and dithiophosphate in particular [31], furthermore the wide range application of nanosized TiS₂ [32-35] drawn our attention to develop new series of Ti(IV) complexes with dithiophosphate and pyrazoline ligands applying sol-gel method. The resulting complex may act as a precursor for nano TiS₂.

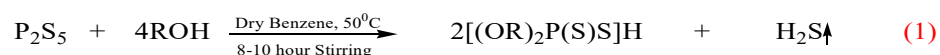
EXPERIMENTAL

Materials and methods

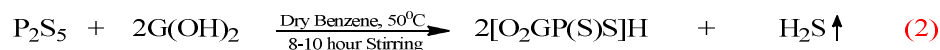
Absolutely dry conditions were maintained throughout the reaction process as titanium tetrachloride reacts violently with water to produce toxic and highly corrosive HCl gas. Standard procedures were used to distill, purify and dry the solvents [36]. Phosphorus pentasulfide (s.d. fine chemicals, Mumbai), titanium tetrachloride (E. Merck), O-hydroxy acetophenone (CDH), benzaldehydes (E. Merk), sodium hydroxide (Glaxo), hydrochloric acid (Ranbaxy), acetic acid (CDH), and hydrazine hydrate (Ranbaxy) were used as received without any further purification. Pyrazolines and ammonium salt of dialkyl/alkylene dithiophosphates were prepared by the literature method [37, 38]. Titanium was estimated gravimetrically by cupferron's method while chlorine by Volhard's method. Perkin Elmer (2400 Series II) CHNS/O analyzer was used for the elemental analysis (C, H, N and S). IR Spectra were recorded in the range of 4000-200 cm⁻¹ on the Varian 3100 FT-IR spectrophotometer. Proton decoupled NMR spectra (¹³C, ¹H NMR) were recorded (room temperature) on JOEL AL 300 FT NMR spectrophotometer at an operating frequency of 300.40 MHz. Bruker Nonious Kappa CCD diffractometer was used for X-ray diffraction studies. The FAB mass spectra were recorded on JOEL SX102 mass spectrometer using Argon or Xenon (6 kV, 10 mA) as the FAB gas.

Synthesis of substituted dithiophosphate ligands

O,O'-Dialkyl and alkylene dithiophosphoric acids were synthesized by reacting phosphorus pentasulfide with the corresponding phenols or alcohols (1:4 molar ratio) and with glycols (1:2 molar ratio) as shown in the following chemical reactions (Eq. 1-2).

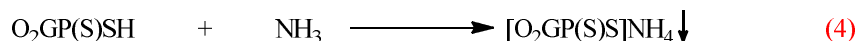
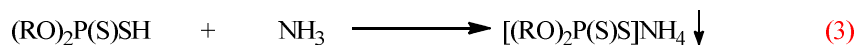


where R = -C₆H₅ or -CH₂CH₂CH₃



where G = -C(CH₃)₂C(CH₃)₂-, -CH₂C(C₂H₅)₂CH₂-, -CH₂CH₂CH(CH₃)-, -C(CH₃)₂CH₂CH(CH₃)-, -CH₂C(CH₃)₂CH₂- and -CH(CH₃)CH(CH₃)-

The corresponding ammonium salts of the synthesized dithiophosphoric acids have been prepared by passing dry ammonia gas through their benzene solutions (Eq. 3-4). The structure of ammonium salt of substituted dithiophosphate ligands are shown in Figure 1.



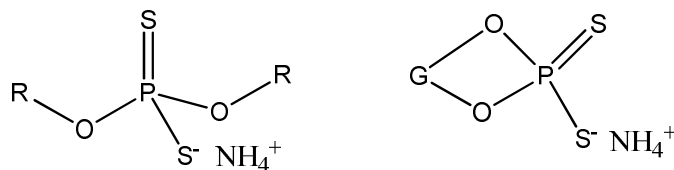


Figure 1. Structure of ammonium salt of substituted dithiophosphate ligands.

Synthesis of substituted pyrazoline ligands

Substituted pyrazoline ligands were synthesized by reported procedure [38].

(a) *Synthesis of substituted 2'-hydroxychalcone.* A hot solution of sodium hydroxide was added to a mixture of *o*-hydroxyacetophenone and substituted benzaldehyde in ethanol. The mixture was stirred at room temperature for 6-8 hours. The sodium salt of the chalcone was obtained as dark yellow thick mass. It was cooled in ice and neutralized with aqueous acetic acid (50%). The yellow solid separated was filtered and washed with water before drying. Crystallization from ethanol yielded yellow needles.

(b) *Synthesis of substituted pyrazoline.* A mixture of substituted 2'-hydroxychalcone and hydrazine hydrate in ethanol was refluxed for 3-4 hours. It was allowed to cool at room temperature. A white crystalline solid thus obtained was separated, washed with water and dried. Recrystallization with ethanol afforded white crystals of pyrazoline. The structure of substituted pyrazoline ligand is shown in Figure 2.

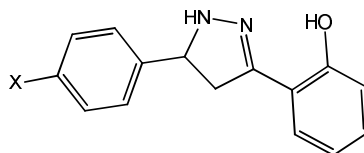


Figure 2. Structure of substituted pyrazoline.

Synthesis of $TiCl_2(C_{15}H_{12}N_2OX)(RO)_2PS_2$

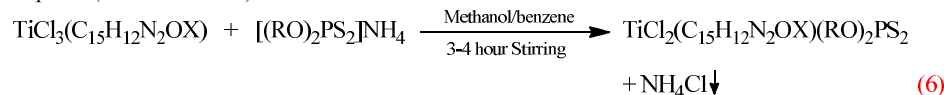
A benzene solution of pyrazoline (1.21 g, 5.10 mmol) was added dropwise with constant stirring to the titanium tetrachloride (0.96 g, 5.11 mmol) suspension at room temperature. To ensure the completion of reaction, the reaction mixture was stirred for 2-3 hours. To the above reaction mixture, the solution of ammonium salt of dithiophosphate in methanol was added dropwise under constant stirring for 3-4 hours. The by-product (NH_4Cl) was filtered off using alkoxy funnel. A reddish-brown solid compound was obtained (1.76 g, 88%) after removal of the volatiles from the filtrate under reduced pressure. The same procedure was adopted for the synthesis of all the compounds (2-24).

The two-step reaction scheme is proposed for the synthesis of mixed ligand titanium complexes of the general formula $TiCl_2(C_{15}H_{12}N_2OX)(RO)_2PS_2$] (Eq. 5-6).

Step 1: (1:1 molar ratio)

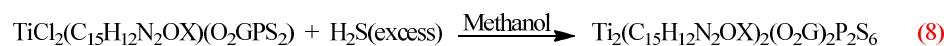


Step 2: (1:1 molar ratio)



Synthesis of $\text{Ti}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OX})_2[(\text{RO})_4\text{P}_2\text{S}_6]$

In the methanolic solution of $[\text{TiCl}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OX})(\text{RO})_2\text{PS}_2]$, dry H_2S gas was passed for 1-2 hours which result in the formation of orange-colored precipitate (Eq. 7-8).



where X = -H, -CH₃, -OCH₃, -Cl; R = -CH₂CH₂CH₃, -C₆H₅; G = -CH₂CMe₂CH₂, -CMe₂CMe₂-, CH₂CH₂CHMe-.

RESULTS AND DISCUSSION

All the synthesized compounds are non-hygroscopic orange-colored solid which are stable at room temperature. They are easily soluble in coordinating solvents (THF, DMSO and DMF) as well as in common organic solvents (benzene, chloroform and methanol). The proposed stoichiometries of the synthesized compounds are in good agreement with the elemental analysis (H, C, N, S, Cl, and Ti) data reported in Table 1.

Spectral analysis of $\text{Ti}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OX})_2[(\text{RO})_4\text{P}_2\text{S}_6]$

Infrared spectral data analysis

The medium intensity band observed at 3346-3325 cm⁻¹ could be assigned to vibrations corresponding to ν[N-H] stretching [39] while the spectral bands in the region 1624-1604 cm⁻¹ are due to the ν[C=N] stretching vibration [40]. As compared to free pyrazoline the ν[C=N] stretching in all the synthesized compounds is observed to be shifted to the lower wavenumber. This suggests that the imino nitrogen of pyrazoline is coordinated to a metal centre. The complete absence of a signal at ~3080 cm⁻¹ in synthesized metal complexes, which is due to ν(O-H) stretching originally present in pyrazoline ligands suggests that the oxygen is covalently bonded to Ti metal. This is further confirmed by the appearance of the band in the region 485-460 cm⁻¹ corresponding to ν[Ti-O] stretching vibration. The bands present in 824-899 cm⁻¹ and 1078-1050 cm⁻¹ region has been assigned respectively to ν[P-O-(C)] [41, 42] and ν[(P)-O-C] [43, 44]. The new bands of medium intensity observed in the region 549-529 cm⁻¹ may be assigned to ν[P-S] stretching modes [45].

In comparison to free ligands, the appearance of two new bands in 335-321 cm⁻¹ and 302-290 cm⁻¹ region corresponds to ν[Ti-S] stretching vibrations. Splitting of bands into two regions indicates that two types of sulfur are present in the molecule, one is terminal sulfur and another is bridging sulfur. The appearance of bands in the region 396-380 cm⁻¹ has been ascribed to vibrations corresponding to ν[Ti-N] stretching [46]. The IR data of synthesized complexes are compiled in Table 2.

Table 1. Analytical data for $Ti_2(C_{15}H_{12}N_2OH)_2[S_6P_2(OCH_2CH_2CH_3)_4]$.

S. No.	Compound	Mol. Wt. found (calculated)	Analysis found (calculated)					
			Metal	S	C	N	H	Cl
1	$Ti_2(C_{15}H_{12}N_2OH)_2[S_6P_2(OCH_2CH_2CH_3)_4]$	1055 (1059.8)	9.09 (9.04)	18.06 (18.12)	47.49 (47.56)	5.36 (5.28)	5.02 (5.09)	-
2	$Ti_2(C_{15}H_{12}N_2OH)_2[S_6P_2(OC_6H_5)_4]$	1195 (1195.8)	8.08 (8.01)	16.02 (16.06)	54.24 (54.19)	4.65 (4.68)	3.82 (3.85)	-
3	$Ti_2(C_{15}H_{12}N_2OH)_2[S_6P_2\{OC(CH_3)_2CH_2CH(CH_3)O\}_2]$	1059 (1055.8)	9.03 (9.07)	18.16 (18.19)	47.69 (47.74)	5.27 (5.30)	4.72 (4.74)	-
4	$Ti_2(C_{15}H_{12}N_2OH)_2[S_6P_2\{OCH_2C(CH_3)_2CH_2O\}_2]$	1030 (1027.8)	9.28 (9.32)	18.62 (18.68)	46.63 (46.70)	5.39 (5.45)	4.52 (4.48)	-
5	$Ti_2(C_{15}H_{12}N_2OH)_2[S_6P_2\{OC(CH_3)_2C(CH_3)_2O\}_2]$	1055 (1055.8)	9.01 (9.07)	18.23 (18.19)	47.70 (47.74)	5.28 (5.30)	4.80 (4.74)	-
6	$Ti_2(C_{15}H_{12}N_2OH)_2[S_6P_2\{OCH_2CH_2CH(CH_3)O\}_2]$	995 (996.8)	9.54 (9.61)	19.20 (19.26)	45.81 (45.75)	5.66 (5.61)	3.45 (3.41)	-
7	$Ti_2(C_{15}H_{12}N_2OCH_3)_2[S_6P_2(OCH_2CH_2CH_3)_4]$	1085 (1087.8)	8.78 (8.81)	17.60 (17.65)	48.61 (48.54)	5.23 (5.15)	3.82 (3.86)	-
8	$Ti_2(C_{15}H_{12}N_2OCH_3)_2[S_6P_2(OC_6H_5)_4]$	1125 (1223.8)	7.80 (7.83)	18.74 (18.69)	54.85 (54.91)	4.52 (4.58)	4.02 (4.09)	-
9	$Ti_2(C_{15}H_{12}N_2OCH_3)_2[S_6P_2\{OC(CH_3)_2CH_2CH(CH_3)O\}_2]$	1080 (1083.8)	8.80 (8.84)	17.85 (17.72)	48.79 (48.72)	5.13 (5.17)	4.92 (4.98)	-
10	$Ti_2(C_{15}H_{12}N_2OCH_3)_2[S_6P_2\{OCH_2C(CH_3)_2CH_2O\}_2]$	1055 (1055.8)	9.15 (9.07)	18.16 (18.19)	47.80 (47.74)	5.25 (5.30)	4.70 (4.74)	-
11	$Ti_2(C_{15}H_{12}N_2OCH_3)_2[S_6P_2\{OC(CH_3)_2C(CH_3)_2O\}_2]$	1082 (1083.8)	8.80 (8.84)	17.68 (17.72)	48.78 (48.72)	5.23 (5.17)	5.02 (4.98)	-
12	$Ti_2(C_{15}H_{12}N_2OCH_3)_2[S_6P_2\{OCH_2CH_2CH(CH_3)O\}_2]$	1025 (1024.8)	9.28 (9.34)	18.65 (18.74)	46.78 (46.84)	5.42 (5.46)	4.42 (4.49)	-
13	$Ti_2(C_{15}H_{12}N_2O_2CH_3)_2[S_6P_2(OCH_2CH_2CH_3)_4]$	1120 (1119.8)	8.48 (8.56)	17.10 (17.15)	47.21 (47.15)	5.07 (5.00)	5.12 (5.18)	-
14	$Ti_2(C_{15}H_{12}N_2O_2CH_3)_2[S_6P_2(OC_6H_5)_4]$	1260 (1255.8)	7.60 (7.63)	15.22 (15.29)	53.42 (53.51)	4.51 (4.46)	3.96 (3.98)	-
15	$Ti_2(C_{15}H_{12}N_2O_2CH_3)_2[S_6P_2\{OC(CH_3)_2CH_2CH(CH_3)O\}_2]$	1160 (1161.8)	8.31 (8.25)	16.50 (16.53)	45.52 (45.45)	4.87 (4.82)	4.68 (4.64)	-
16	$Ti_2(C_{15}H_{12}N_2O_2CH_3)_2[S_6P_2\{OCH_2C(CH_3)_2CH_2O\}_2]$	1045 (1042.8)	9.17 (9.19)	18.35 (18.41)	48.28 (48.33)	5.42 (5.37)	4.75 (4.79)	-
17	$Ti_2(C_{15}H_{12}N_2O_2CH_3)_2[S_6P_2\{OC(CH_3)_2C(CH_3)_2O\}_2]$	1160 (1161.8)	8.19 (8.25)	16.50 (16.53)	43.29 (43.38)	4.78 (4.82)	4.60 (4.64)	-
18	$Ti_2(C_{15}H_{12}N_2O_2CH_3)_2[S_6P_2\{OCH_2CH_2CH(CH_3)O\}_2]$	1015 (1011.8)	9.36 (9.47)	18.91 (18.98)	47.40 (47.44)	5.50 (5.53)	4.50 (4.55)	-

19	$\text{Ti}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OCl})_2[\text{S}_6\text{P}_2(\text{OCH}_2\text{CH}_2\text{CH}_3)_4]$	1130 (1128.8)	8.441 (8.49)	16.99 (17.00)	46.65 (46.78)	4.93 (4.96)	4.63 (4.61)	6.25 (6.28)
20	$\text{Ti}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OCl})_2[\text{S}_6\text{P}_2(\text{OC}_6\text{H}_5)_4]$	1265 (1264.8)	7.69 (7.57)	15.13 (15.18)	51.17 (51.29)	4.52 (4.49)	3.46 (3.48)	5.64 (5.61)
21	$\text{Ti}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OCl})_2[\text{S}_6\text{P}_2\{\text{OC}(\text{CH}_3)_2\text{CH}_2\text{CH}(\text{CH}_3)\text{O}\}_2]$	1120 (1124.8)	8.47 (8.52)	17.17 (17.07)	44.90 (44.81)	4.91 (4.98)	4.23 (4.27)	6.29 (6.31)
22	$\text{Ti}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OCl})_2[\text{S}_6\text{P}_2\{\text{OCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{O}\}_2]$	1095 (1096.8)	8.68 (8.73)	17.45 (17.51)	43.85 (43.76)	5.04 (5.11)	4.05 (4.01)	6.50 (6.47)
23	$\text{Ti}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OCl})_2[\text{S}_6\text{P}_2\{\text{OC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{O}\}_2]$	1125 (1124.8)	8.49 (8.52)	17.15 (17.07)	44.69 (44.81)	4.93 (4.98)	4.24 (4.27)	6.29 (6.31)
24	$\text{Ti}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OCl})_2[\text{S}_6\text{P}_2\{\text{OCH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{O}\}_2]$	1065 (1065.8)	8.91 (8.99)	18.07 (18.01)	42.88 (42.78)	5.19 (5.25)	3.76 (3.75)	6.62 (6.66)

¹H NMR spectra analysis

The ¹H NMR spectra of synthesized mixed ligand complexes, recorded in CDCl₃ exhibit characteristic signals (Table 3). In the region δ 7.42-6.39 ppm, a very complex pattern may be assigned to the aromatic protons of ligand pyrazoline [47]. The pyrazoline ligand exhibits a characteristic peak at δ~11.00 ppm due to hydroxyl protons, the absence of that particular peak in the ¹H NMR spectra of the metal complex suggests that the hydroxyl oxygen atom is bonded to Ti metal. A broad singlet peak observed at δ 5.37-4.86 ppm may be attributed to the N-H group (primarily at δ 5.40-4.90 ppm in free pyrazoline) indicating that the -NH group is not involved in metal complex formation [47]. The bands at 3.82-3.07 and 2.25-2.02 ppm could be ascribed, respectively to -CH and -CH₂ groups. The band at δ 5.54-4.19 ppm for -OCH₂ and at δ 4.94-4.21 ppm for -OCH group and bands for methyl group are observed at δ 1.10-0.90 ppm. The complex pattern observed at δ 7.21-7.04 ppm may be due to the skeletal protons of the phenyl ring. The hydrogen atom calculated through the integrations ratio suggests that two of the dithiophosphate ligands and two pyrazoline ligands are present in synthesized mixed ligand complexes.

³¹P NMR spectra analysis

The synthesized compounds exhibit only one signal for the phosphorus atoms in proton-decoupled ³¹P NMR spectra. The ³¹P NMR signals of Ti dichlorodithio-compounds are obtained at δ = 90.0 ppm while that of synthesized Ti mixed ligand complexes are observed at δ = 110.0-91.3 ppm. The downfield shifting of the signal due to dithiophosphato phosphorus atom at about δ15.0 ppm confirms the bidentate nature of the ligand [48]. Although two phosphorus atoms are there only one signal is obtained, indicates a similar environment for both the phosphorus atom (Table 3).

Table 2. IR spectral data (cm^{-1}) for $\text{Ti}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OH})_2[\text{S}_6\text{P}_2(\text{OR})_4]$.

S. No.	$\nu[\text{N-H}]$	$\nu[\text{C=N}]$	$\nu[\text{C-O}]$	$\nu[(\text{P})\text{-O-C}]$	$\nu[\text{P-O-(C)}]$	$\nu[\text{P=S}]$	$\nu[\text{P-S}]$	Ring vib	$\nu[\text{Ti-O}]$	$\nu[\text{Ti-S}]$	$\nu[\text{Ti-N}]$
1	3329	1620	-	1058	842	654	546	--	463	335 295S _b	387
2	3339	1616	-	1075	846	650	537	-	471	327 290S _b	391
3	3341	1604	-	1036	878	692	529	961	485	330 294S _b	396
4	3328	1619	-	1067	842	647	549	957	467	325 302S _b	389
5	3329	1623	-	1068	832	662	538	948	468	327 300S _b	387
6	3339	1621	-	1069	832	656	548	978	460	321 298S _b	381
7	3336	1614	-	1073	832	646	529	-	463	326 295S _b	384
8	3328	1618	-	1052	898	658	546	-	471	321 297S _b	393
9	3328	1619	-	1073	833	649	537	968	470	325 298S _b	394
10	3340	1620	-	1067	824	664	546	947	472	329 302S _b	387
11	3328	1612	-	1078	835	648	529	958	463	328 297S _b	390
12	3342	1617	-	1058	836	648	547	973	467	331 298S _b	395
13	3329	1621	1025	1059	892	657	533	-	466	335 301S _b	383
14	3327	1623	1022	1065	872	669	539	-	469	322 294S _b	382
15	3338	1618	1015	1076	835	650	546	940	470	321 301S _b	389
16	3325	1619	1030	1062	894	649	529	965	474	324 300S _b	393
17	3331	1623	1023	1064	898	673	537	948	468	331 298S _b	391
18	3327	1614	1017	1076	826	659	546	965	463	329 295S _b	381
19	3345	1618	-	1050	835	663	528	-	469	321 299S _b	388
20	3343	1619	-	1074	843	653	537	-	466	326 301S _b	380
21	3329	1620	-	1058	834	659	530	955	465	322 294S _b	394
22	3330	1612	-	1072	826	660	531	953	461	324 298S _b	387
23	3340	1623	-	1057	899	670	537	961	474	329 293S _b	386
24	3346	1622	-	1078	887	658	542	970	475	320 302S _b	383

Table 3. NMR data (δ ppm) for $\text{Ti}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OH})_2[\text{S}_6\text{P}_2(\text{OR})_4]$.

S. No.	Compound	Chemical shift (δ ppm)		
		^1H NMR	^{13}C NMR	^{31}P NMR
1	$\text{Ti}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OH})_2[\text{S}_6\text{P}_2(\text{OCH}_2\text{CH}_2\text{CH}_3)_4]$	7.65-6.80 (m, 18H, Ar-H) 5.12 (m, 8H, -OCH ₂ -) 0.92 (t, 12H, -CH ₃) 1.68 (m, 8H, -CH ₂) 5.18 (s, 2H, NH) 3.32 (t, 2H, -CH) 2.15 (d, 4H, -CH ₂)	-	106.10
2	$\text{Ti}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OH})_2[\text{S}_6\text{P}_2(\text{OC}_6\text{H}_5)_4]$	7.47-6.89 (m, 18H, Ar-H) 7.14 (s, 20H, -C ₆ H ₅) 4.87 (s, 2H, -NH) 3.18 (t, 4H, -CH) 2.49 (d, 8H, -CH ₂)	-	92.40
3	$\text{Ti}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OH})_2[\text{S}_6\text{P}_2\{\text{OC}(\text{CH}_3)_2\text{CH}_2\text{CH}(\text{CH}_3)\text{O}\}_2]$	7.59-6.85 (m, 18H, Ar-H) 2.97-2.60 (m, 22H, -CH ₃ , -CH ₂) 4.19 (m, 2H, -OCH) 5.14 (s, 24H, -NH) 3.52 (t, 2H, -CH) 2.18 (d, 8H, -CH ₂)	91.52 (-OC, dtp) 24.64 (-CH ₃ , dtp) 76.93 (-OCH, dtp) 26.46 (-CH ₂ , dtp) 136.82 (Ar-C) 167.43 (C=N) 43.05 (-CH) 25.97 (-CH ₂)	93.60
4	$\text{Ti}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OH})_2[\text{S}_6\text{P}_2\{\text{OCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{O}\}_2]$	7.64-6.83 (m, 18H, Ar-H) 0.98 (s, 12H, -CH ₃) 4.24 (d, 8H, -OCH ₂ -) 4.84 (s, 4H, NH) 3.03 (t, 2H, -CH) 2.25 (d, 8H, -CH ₂)	21.95 (CH ₃ , dtp) 32.72 (q C, dtp) 76.02 (d, -OCH ₂ , dtp) 136.74 (Ar-C) 27.63 (-CH ₂) 42.31 (-CH) 165.56 (C=N)	91.50
5	$\text{Ti}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OH})_2[\text{S}_6\text{P}_2\{\text{OC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{O}\}_2]$	1.02 (s, 24H, -CH ₃) 7.69-6.82 (m, 18H, ArH) 4.89 (s, 4H, -NH) 3.15 (t, 2H, -CH) 2.25 (d, 4H, -CH ₂)	24.45 (-CH ₃ , dtp) 91.92 (-OC, dtp) 27.42 (-CH ₂) 136.81-123.12 (Ar-C) 43.08 (-CH) 163.65 (C=N)	104.82
6	$\text{Ti}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OH})_2[\text{S}_6\text{P}_2\{\text{OCH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{O}\}_2]$	4.12-3.35 (m, 6H, -OCH ₂ , OCH) 2.65-1.09 (m, 10H, -CH ₃ , -CH ₂) 7.68-6.42 (m, ArH) 5.16 (s, 4H, -NH) 3.07 (t, 2H, -CH) 2.17 (d, 8H, -CH ₂)	23.95 (-CH ₃ , dtp) 76.34 (-OCH, -OCH ₂ , dtp) 27.72 (-CH ₂) 135.57-123.19 (Ar-C) 43.19 (-CH) 162.94 (C=N)	107.00
7	$\text{Ti}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OCH}_3)_2[\text{S}_6\text{P}_2(\text{OCH}_2\text{CH}_2\text{CH}_3)_4]$	7.63-6.65 (m, 16H, Ar-H) 1.34 (m, 8H, -CH ₂) 4.25 (m, 8H, -OCH ₂ -) 0.96 (t, 12H, -CH ₃) 5.10 (s, 2H, NH) 3.42 (t, 2H, -CH) 2.10 (d, 4H, -CH ₂) 0.97 (s, 6H, -CH ₃)	-	105.82
8		7.61-6.87 (m, 16H,	-	92.72

	$\text{Ti}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OCH}_3)_2[\text{S}_6\text{P}_2(\text{OC}_6\text{H}_5)_4]$	Ar-H) 7.21 (s, 2H, -C ₆ H ₅) 5.12 (s, 2H, -NH) 3.26 (t, 4H, -CH) 2.17 (d, 8H -CH ₂)		
9	$\text{Ti}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OCH}_3)_2[\text{S}_6\text{P}_2\{\text{OC}(\text{CH}_3)_2\text{CH}_2\text{CH}(\text{CH}_3)\text{O}\}_2]$	7.52-6.72 (m, 16H, Ar-H) 2.56-2.09 (m, 22H, -CH ₃ , CH ₂) 4.94-4.58 (m, 2H, -OCH) 5.15 (s, 4H, -NH) 3.27 (t, 2H, -CH) 2.12 (d, 8H, CH ₂) 0.96 (s, 6H, -CH ₃)	91.23 (-OC, dtp) 25.91 (-CH ₃ , dtp) 76.85 (-OCH, dtp) 24.04 (-CH ₂ , dtp) 136.85-129.15 (Ar-C) 163.83 (C=N) 42.19 (-CH) 24.62 (-CH ₂) 13.51 (-CH ₃)	110.00
10	$\text{Ti}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OCH}_3)_2[\text{S}_6\text{P}_2\{\text{OCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{O}\}_2]$	7.87-6.59 (m, 16H, Ar-H) 0.97 (s, 12H, -CH ₃) 4.12 (d, 8H, -OCH ₂ -) 5.27 (s, 4H, NH) 3.82 (t, 2H, -CH) 2.15 (d, 8H, -CH ₂) 0.94 (s, 6H, -CH ₃)	22.79 (-CH ₃ , dtp) 31.52 (q C, dtp) 75.91 (d, -OCH ₂ , dtp) 43.26 (-CH) 165.81 (C=N) 26.56 (-CH ₂) 136.72 (Ar-C) 13.56 (-CH ₃)	91.82
11	$\text{Ti}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OCH}_3)_2[\text{S}_6\text{P}_2\{\text{OC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{O}\}_2]$	1.42 (s, 24H, -CH ₃) 7.52-6.78 (m, 16H, ArH) 4.62 (s, 4H, -NH) 3.42 (t, 2H, -CH) 2.19 (d, 4H, -CH ₂) 0.96 (s, 6H, -CH ₃)	26.19 (-CH ₃ , dtp) 92.05 (OC, dtp) 136.76-123.16 (Ar-C) 165.63 (C=N) 45.62 (-CH) 25.71 (-CH ₂) 13.51 (-CH ₃)	107.62
12	$\text{Ti}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OCH}_3)_2[\text{S}_6\text{P}_2\{\text{OCH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{O}\}_2]$	4.23-3.27 (m, 6H, -OCH ₂ , OCH) 2.10-1.09 (m, 14H, -CH ₃ , CH ₂) 7.82-6.79 (m, 16H, ArH) 5.04 (s, 4H, -NH) 2.82 (t, 2H, -CH) 2.02 (d, 8H, -CH ₂)	136.19-123.72 (Ar-C) 76.85 (-OCH, OCH ₂ , dtp) 165.76 (C=N) 13.60 (-CH ₃) 43.19 (-CH) 24.35 (CH ₃ , dtp) 27.04 (-CH ₂)	96.50
13	$\text{Ti}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}_2\text{CH}_3)_2[\text{S}_6\text{P}_2(\text{OCH}_2\text{CH}_2\text{CH}_3)_4]$	7.42-6.78 (m, 16H, Ar-H) 1.02 (t, 12H, -CH ₃) 1.51 (m, 8H, -CH ₂) 5.07 (m, 8H, -OCH ₂ -) 5.17 (s, 2H, NH) 3.81 (t, 2H, -CH) 2.27 (d, 4H, -CH ₂) 4.29 (s, 6H, -OCH ₃)	-	105.95
14	$\text{Ti}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}_2\text{CH}_3)_2[\text{S}_6\text{P}_2(\text{OC}_6\text{H}_5)_4]$	7.56-6.83 (m, 16H, Ar-H) 7.19 (s, 12H, -C ₆ H ₅) 4.78 (s, 2H, -NH) 3.12 (t, 4H, -CH) 2.05 (d, 8H -CH ₂) 4.00 (s, 6H, -CH ₃)	-	108.20
15		7.68-6.72 (m, 16H, Ar-H) 2.32-1.97 (m, 22H, -CH ₃ , CH ₂)	91.89 (-OC, dtp) 24.82 (-CH ₃ , dtp) 76.52 (-OCH, dtp)	95.00

	$\text{Ti}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}_2\text{CH}_3)_2[\text{S}_6\text{P}_2\{\text{OC}(\text{CH}_3)_2\text{CH}_2\text{CH}(\text{CH}_3)\text{O}\}_2]$	4.63-4.21 (m, 2H, -OCH) 5.07 (s, 3H, -NH) 3.18 (t, 2H, -CH) 2.23 (d, 8H, -CH ₂) 4.13 (s, 6H, -OCH ₃)	23.29 (-CH ₂ , dtp) 136.76 (Ar-C) 167.18 (C=N) 43.17 (-CH) 24.18 (-CH ₂) 57.51 (-OCH ₃)	
16	$\text{Ti}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}_2\text{CH}_3)_2[\text{S}_6\text{P}_2\{\text{OCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{O}\}_2]$	7.54-6.75 (m, 16H, Ar-H) 1.13 (s, 12H, -CH ₃) 4.08 (d, 8H, -OCH ₂ -) 5.37 (s, 4H, NH) 3.16 (t, 2H, -CH) 2.53 (d, 8H, -CH ₂) 4.05 (s, 6H, -OCH ₃)	22.83 (CH ₃ , dtp) 32.02 (q C, dtp) 75.86 (d, -OCH ₂ , dtp) 137.43 (Ar-C) 167.54 (C=N) 42.92 (CH) 27.32 (CH ₂) 57.29 (-OCH ₃)	94.72
17	$\text{Ti}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}_2\text{CH}_3)_2[\text{S}_6\text{P}_2\{\text{OC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{O}\}_2]$	1.37 (s, 24H, -CH ₃) 7.63-6.81 (m, 16H, ArH) 2.08 (d, 4H, -CH ₂) 3.41 (t, 2H, -CH) 4.19 (s, 6H, -OCH ₃) 5.21 (s, 4H, -NH)	23.17 (CH ₃ , dtp) 90.76 (dtp) 42.17 (CH) 57.45 (-OCH ₃) 26.73 (CH ₂) 164.68 (C=N) 136.31-122.43 (m, Ar-C)	94.06
18	$\text{Ti}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}_2\text{CH}_3)_2[\text{S}_6\text{P}_2\{\text{OCH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{O}\}_2]$	2.69-1.29 (m, 10H, -CH ₃ , CH ₂) 4.10-3.82 (m, 6H, -OCH ₂ , OCH) 7.65-6.70 (m, 16H, ArH) 5.12 (s, 4H, -NH) 3.14 (t, 2H, -CH) 2.23 (d, 8H, -CH ₂) 4.12 (s, 6H, -OCH ₃)	22.71 (CH ₃ , dtp) 76.14 (-OCH, OCH ₂ , dtp) 42.76 (CH) 162.76 (C=N) 27.92 (CH ₂) 136.75-123.18 (Ar-C) 57.21 (-OCH ₃)	91.29
19	$\text{Ti}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OCl})_2[\text{S}_6\text{P}_2(\text{OCH}_2\text{CH}_2\text{CH}_3)_4]$	0.94 (t, 12H, -CH ₃) 7.51-6.76 (m, 16H, Ar-H) 2.19 (d, 4H, -CH ₂) 1.61 (m, 8H, -CH ₂) 5.13 (s, 2H, NH) 5.51 (m, 8H, -OCH ₂ -) 3.75 (t, 2H, -CH)	-	106.20
20	$\text{Ti}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OCl})_2[\text{S}_6\text{P}_2(\text{OC}_6\text{H}_5)_4]$	7.57-6.79 (m, 16H, Ar-H) 7.04 (s, 20H, -C ₆ H ₅) 4.73 (s, 2H, -NH) 3.09 (t, 4H, -CH) 2.18 (d, 8H, -CH ₂)	-	101.2
21	$\text{Ti}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OCl})_2[\text{S}_6\text{P}_2\{\text{OC}(\text{CH}_3)_2\text{CH}_2\text{CH}(\text{CH}_3)\text{O}\}_2]$	7.82-6.85 (m, 16H, Ar-H) 4.74-4.19 (m, 2H, -OCH) 2.42-1.62 (m, 22H, -CH ₃ , CH ₂) 5.11 (s, 2H, -NH) 3.16 (t, 2H, -CH) 2.27 (d, 8H, CH ₂)	91.83 (-OC, dtp) 23.72 (-CH ₃ , dtp) 77.35 (-OCH, dtp) 24.62 (-CH ₂ , dtp) 136.73 (Ar-C) 167.48 (C=N) 42.73 (-CH) 27.32 (-CH ₂)	93.25

22	$\text{Ti}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OCl})_2[\text{S}_6\text{P}_2\{\text{OCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{O}\}_2]$	7.52-6.69 (m, Ar-H) 1.10 (s, 12H, -CH ₃) 4.12 (d, 8H, -OCH ₂ -) 4.79 (s, 2H, NH) 3.29 (t, 2H, -CH) 2.07 (d, 8H, -CH ₂)	22.63 (CH ₃ , dtp) 36.27 (q C, dtp) 76.32 (d, -OCH ₂ , dtp) 135.29 (Ar-C) 167.76 (C=N) 42.23 (CH) 26.22 (CH ₂)	96.49
23	$\text{Ti}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OCl})_2[\text{S}_6\text{P}_2\{\text{OC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{O}\}_2]$	1.42 (s, 24H, -CH ₃) 7.85-6.63 (m, 16H, ArH) 4.92 (s, 2H, -NH) 3.20 (t, 2H, -CH) 2.13 (d, 4H, -CH ₂)	23.67 (CH ₃ , dtp) 91.92 (OC, dtp) 137.81-123.47 (Ar-C) 167.23 (C=N) 43.21 (CH) 27.73 (CH ₂)	107.70
24	$\text{Ti}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OCl})_2[\text{S}_6\text{P}_2\{\text{OCH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{O}\}_2]$	2.27-1.19 (m, 10H, -CH ₃ , CH ₂) 4.09-3.82 (m, 6H, -OCH ₂ , OCH) 7.54-6.72 (m, 16H, ArH) 5.12 (s, 2H, -NH) 3.08 (t, 2H, -CH) 2.07 (d, 8H, -CH ₂)	23.76 (CH ₃ , dtp) 76.38 (-OCH, CH ₂) OCH ₂ , dtp) 43.12 (CH) 165.27 (C=N) 27.35 (CH ₂) 136.72-123.51 (Ar-C)	91.52

¹³C NMR spectra analysis

The signals observed in the proton decoupled ¹³C NMR spectra are in good agreement with reference to dithiophosphates and pyrazolines ligands. A complex pattern of signals detected in the region δ 136.19-123.18 ppm could be ascribed to aromatic carbon atoms. The downfield shifting of the imino carbon of C=N from δ 167.45-163.78 ppm to δ 143.50-142.80 ppm (free pyrazoline) suggests that the imino nitrogen of pyrazoline is coordinated to the metal centre. The peaks due to -CH₂ and -CH are observed at 27.72-24.62 ppm and 45.75-43.09 ppm, respectively. The peaks due to -OC and -OCH group of dithiophosphates are observed at 91.23-93.09 ppm and 75.86-77.35 ppm. The NMR (¹H, ¹³C and ³¹P) data are summarized in Table 3.

Table 4. FAB mass spectral data for $\text{Ti}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OH})_2[\text{S}_6\text{P}_2\{\text{OCH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{O}\}_2]$.

S.No.	Compound	m/z	py	2py	dtp	2dtp
6	$\text{Ti}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OH})_2[\text{S}_6\text{P}_2\{\text{OCH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{O}\}_2]$	1059	882	585	375	163
12	$\text{Ti}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OCH}_3)_2[\text{S}_6\text{P}_2\{\text{OCH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{O}\}_2]$	1085	834	582	372	161
18	$\text{Ti}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}_2\text{CH}_3)_2[\text{S}_6\text{P}_2\{\text{OCH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{O}\}_2]$	1165	897	629	418	207
24	$\text{Ti}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OCl})_2[\text{S}_6\text{P}_2\{\text{OCH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{O}\}_2]$	1124	893	582	371	160

dtp = O,O'-alkylene and dialkyl dithiophosphates. Py = 3(2'-hydroxyl phenyl)-5-(4-substituted phenyl) pyrazolines.

FAB Mass spectra analysis

The FAB mass spectra of the synthesized metal complexes have been recorded to determine the molecular weight. The molecular ion peak confirms that the metal complexes exist in dimeric

form. FAB mass spectra of compound numbers 6, 12, 18 and 24 with different substituted pyrazoline ligands in each series have been reported in Table 4.

XRD and SEM studies

These crystalline/amorphous natures of the complexes have been examined through XRD. The morphology of the complexes was studied by employing XRD which shows that all the complexes are amorphous solid. The average diameter of the complexes has been calculated using "Debye Scherrer" expression (Eq. 9).

$$\text{Particle size} = D = 0.9 \lambda / \beta \cos \theta_B \quad (9)$$

where, λ is the X-ray wavelength (1.5418Å), β is corrected band broadening (full width at half maxima), θ_B is the diffraction angle, D is the average nanocrystal domain diameter.

The value of full width at half maximum intensity (β) and corresponding diffraction angle (θ_B) is calculated using an X-ray diffractogram. The average particle size thus obtained was found to be in the range of 41-62 nm, which is further confirmed by the SEM studies (Table 5). The SEM image and X-Ray diffractogram of $\text{Ti}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OH})_2[\text{S}_6\text{P}_2\{\text{OC}(\text{CH}_3)_2\text{CH}_2\text{CH}(\text{CH}_3)\text{O}\}_2]$ are shown in Figure 3 and Figure 4, respectively.

Table 5. Average diameter of particles determined by XRD and SEM.

S.No.	Compound	2 θ	Average particle size (nm)*	Average particle size (nm)†
3	$\text{Ti}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OH})_2[\text{S}_6\text{P}_2\{\text{OC}(\text{CH}_3)_2\text{CH}_2\text{CH}(\text{CH}_3)\text{O}\}_2]$	38.50	55	48

*Determined by XRD technique. †Determined by SEM technique.

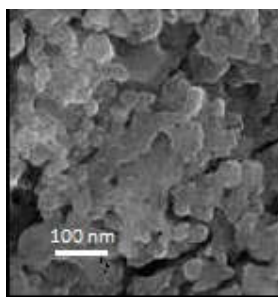


Figure 3. SEM image of $\text{Ti}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OH})_2[\text{S}_6\text{P}_2\{\text{OC}(\text{CH}_3)_2\text{CH}_2\text{CH}(\text{CH}_3)\text{O}\}_2]$.

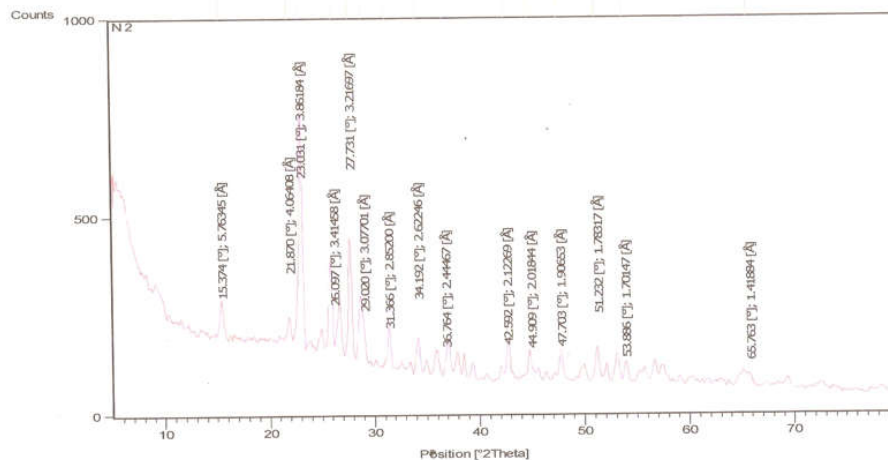


Figure 4. X-Ray diffractogram of $Ti_2(C_{15}H_{12}N_2OH)_2[S_6P_2\{OC(CH_3)_2CH_2CH(CH_3)O\}_2]$.

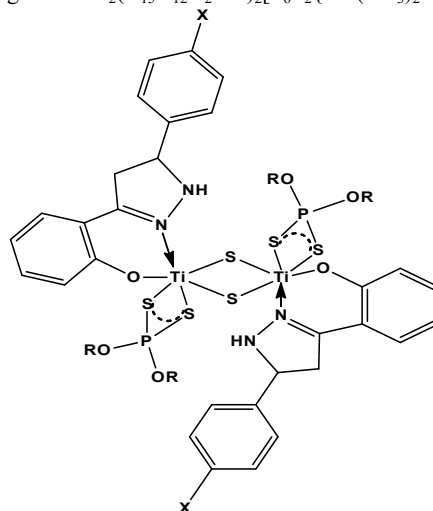


Figure 5. Proposed structure of $[Ti_2(C_{15}H_{12}N_2OX)_2(RO)_4P_2S_6]$.

Molecular weight measurement, elemental and spectral analysis confirms the dimeric nature of the synthesized metal complexes and proposes octahedral geometry (Figure 5).

CONCLUSION

The present study describes the new route for the synthesis of Ti(IV) mixed ligand complexes with dithiophosphate and substituted pyrazoline ligands. Molecular weight measurements, elemental analysis in conjunction with spectroscopic (IR, 1H NMR, ^{13}C NMR and ^{31}P NMR) studies reveal the dimeric nature of the complexes in which pyrazoline and dithiophosphate are bidentate. Scanning electron microscopic image and XRD indicate that the particles are in the nano range (50 nm). Coordination number six is proposed for titanium with octahedral

geometry. This class of compound may prove to be a useful precursor for the formation of TiS_2 by sulphide sol-gel due to reduced acidity of the metal centre. Further studies regarding sulphide sol-gel of these derivatives are under investigation.

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