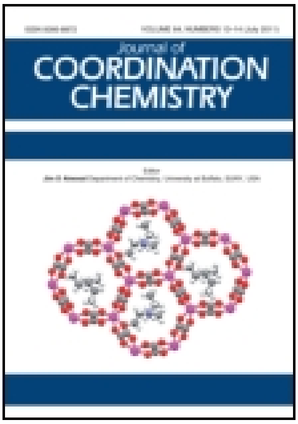

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Synthesis and spectral behavior of nanometric Ti(IV) complexes with nitrogen, sulfur, and oxygen donors

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Synthesis and spectral behavior of nanometric Ti(IV) complexes with nitrogen, sulfur, and oxygen donors

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To study the spectral behavior of Ti(IV) complexes with sulfur donors, several new nano-sized mixed ligand complexes of Ti(IV) have been synthesized by the reaction of titanium(IV) salts with 3(2′-hydroxyl phenyl)-5-(4-substituted phenyl)pyrazolines and ammonium salts of dithiophosphates. Spectroscopic and X-ray diffraction studies reveal amorphous and monomeric complexes. The Ti(IV) complexes show octahedral geometry in which dithiophosphate and pyrazoline are bidentate. Transmission electron microscopic image shows that the particle size ranges from 50 to 90 nm.

Keywords: Titanium(IV); Nano particle; Dithiophosphate; Pyrazolines

1. Introduction

Interest in the chemistry of metal complexes with sulfur containing ligands arises due to their biological activities [1–6]. Ligation of sulfur of O,O′-dialkyl and alkylene dithiophosphate derivatives to Cu(II), Ag(I), and Fe(II) has been reported by several authors [7–10]. Derivatives of arsenic, antimony, and bismuth with dithiophosphates are employed as lubricant additives [11, 12] and antitumor agents [13].

Synthesis of simple thiols of titanium is not possible due to the hard acid character of titanium [14]. To reduce the acidic strength of Ti(IV) several authors have attached electron-rich ligands such as cyclopentadienyl and dialkyl nitrogen, which then form stable complexes with sulfur donors [15–18]. To study the synthetic and spectral behavior of Ti(IV) complexes with nitrogen, sulfur and oxygen donors, a series of Ti(IV) complexes containing pyrazoline and dithiophosphate have been synthesized. The resulting complex may act as a precursor for formation of titanium disulfide thin film [19–21].

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2. Materials and methods

All reactions were carried out under absolutely dry conditions. Solvents were distilled, dried and purified by standard techniques [22]. Pyrazolines and the ammonium salts of dialkyl/alkylene dithiophosphates were prepared by literature methods [23, 24]. Chloride was estimated by Volhard's method [25] and titanium was determined gravimetrically by Cupferron's method [25]. Elemental analyses (C, H, N) were obtained by using a Coleman CHN analyzer (table 1). IR spectra were recorded on a Varian 3100 FT-IR spectrophotometer from 4000 to 200 cm^{-1}. ^{1}H NMR spectra and proton decoupled ^{13}C NMR spectra were recorded at room temperature on a JOEL AL 300 FT NMR spectrophotometer operated at 300.40 MHz. X-ray diffraction studies were carried out on a Bruker Nonius Kappa CCD diffractometer at room temperature. TEM studies have been carried out on a JEOL 2010 high-resolution transmission electron microscope, operated at 200 keV. FAB mass spectra were recorded on a JOEL SX102 mass spectrometer using Argon or Xenon (6 kV, 10 mA) as the FAB gas.

3. Experimental

3.1. *Synthesis of [$TiCl_2(C_{15}H_{12}N_2OH)(OC_3H_7)_2P(S)_2$] (1)*

Titanium tetrachloride suspension in benzene (0.97 g, 5.10 mmol) was added dropwise to a solution of pyrazoline (1.21 g, 5.10 mmol) in benzene at room temperature with constant stirring for 2–3 h. The ammonium salt of dithiophosphate solution (1.18 g, 5.08 mmol) in methanol was added dropwise to the reaction mixture and stirring continued for 4–5 h. The NH_4Cl was filtered off through an alkoxy funnel and the volatiles were removed from the filtrate under reduced pressure. Compounds **2–24** were synthesized by the same procedure.

4. Results and discussion

All the compounds are red to reddish brown non-hygroscopic solids, stable at room temperature, and soluble in common organic solvents (methanol, chloroform, THF, DMSO, and DMF). Molecular weight measurement indicates monomers. Elemental analysis (C, H, S, Cl, Ti, and N) data are in accord with the stoichiometry proposed.

4.1. *IR spectral data*

IR spectra show bands of medium intensity at 3397–3348 cm^{-1} due to ν[N–H] [26] and bands at 1650–1603 cm^{-1} due to ν[C=N] [27]. In all compounds, ν[C=N] is shifted to lower wavenumber in comparison to spectra of free pyrazolines (at $\sim$1654 cm^{-1}), suggesting imino nitrogen coordination. The ν(O–H) originally at $\sim$3080 cm^{-1} is completely missing from spectra of complexes. Bands at 1090–1010 cm^{-1} and 890–850 cm^{-1} have been assigned to ν[(P)–O–C] [28, 29] and ν[P–O–(C)] [30, 31], respectively. The ν[P=S] may have bands at 710–660 cm^{-1}, indicating bidentate

Table 1. Physical and analytical data for $TiCl_2(C_{15}H_{12}N_2OX)[S_2P(OR)_2]$.

Compound No.	Chemical formula	Mol. wt. Found (Calcd)	Analysis [Found (Calcd)] Metal	S	C	H	N	Cl
1	$TiCl_2(C_{15}H_{12}N_2OH)[S_2P(OCH_2CH_2CH_3)_2]$	570.0 (568.9)	8.39 (8.42)	11.28 (11.24)	44.20 (44.29)	4.70 (4.74)	4.90 (4.92)	12.46 (12.50)
2	$TiCl_2(C_{15}H_{12}N_2OH)[S_2P(OC_6H_5)_2]$	612.0 (610.9)	7.82 (7.84)	10.44 (10.47)	52.96 (53.03)	3.75 (3.76)	4.54 (4.58)	11.57 (11.62)
3	$TiCl_2(C_{15}H_{12}N_2OH)[S_2POC(CH_3)_2CH_2CH(CH_3)O]$	580.0 (578.9)	8.25 (8.27)	11.09 (11.05)	43.45 (43.53)	4.29 (4.31)	4.82 (4.83)	12.20 (12.26)
4	$TiCl_2(C_{15}H_{12}N_2OH)[S_2POCH_2C(CH_3)_2CH_2O]$	550.0 (552.9)	8.70 (8.66)	11.60 (11.57)	43.33 (43.40)	4.12 (4.15)	5.10 (5.06)	12.80 (12.84)
5	$TiCl_2(C_{15}H_{12}N_2OH)[S_2POC(CH_3)_2C(CH_3)_2O]$	565.0 (567.9)	8.47 (8.44)	11.25 (11.28)	44.40 (44.45)	4.39 (4.40)	4.90 (4.93)	12.47 (12.53)
6	$TiCl_2(C_{15}H_{12}N_2OH)[S_2POCH_2CH_2CH(CH_3)O]$	535.0 (538.9)	8.85 (8.88)	11.84 (11.87)	42.15 (42.30)	5.36 (5.39)	5.15 (5.19)	13.15 (13.19)
7	$TiCl_2(C_{15}H_{12}N_2OCH_3)[S_2P(OCH_2CH_2CH_3)_2]$	580.0 (582.9)	8.24 (8.21)	10.95 (10.97)	45.17 (45.29)	4.95 (4.97)	4.78 (4.80)	12.15 (12.18)
8	$TiCl_2(C_{15}H_{12}N_2OCH_3)[S_2P(OC_6H_5)_2]$	650.0 (650.9)	7.33 (7.35)	9.81 (9.83)	51.50 (51.68)	3.80 (3.84)	4.27 (4.30)	10.87 (10.92)
9	$TiCl_2(C_{15}H_{12}N_2OCH_3)[S_2POC(CH_3)_2CH_2CH(CH_3)O]$	580.0 (580.9)	8.21 (8.25)	10.98 (11.01)	43.27 (43.39)	4.61 (4.64)	4.79 (4.82)	12.17 (12.22)
10	$TiCl_2(C_{15}H_{12}N_2OCH_3)[S_2POCH_2C(CH_3)_2CH_2O]$	570.0 (566.9)	8.46 (8.44)	11.25 (11.28)	44.32 (44.45)	4.39 (4.40)	4.91 (4.93)	12.55 (12.52)
11	$TiCl_2(C_{15}H_{12}N_2OCH_3)[S_2POC(CH_3)_2C(CH_3)_2O]$	580.0 (580.9)	8.22 (8.24)	10.99 (11.03)	45.40 (45.44)	4.63 (4.64)	4.80 (4.82)	12.24 (12.22)
12	$TiCl_2(C_{15}H_{12}N_2OCH_3)[S_2POCH_2CH_2CH(CH_3)O]$	550.0 (552.9)	8.65 (8.68)	11.52 (11.57)	43.32 (43.40)	4.12 (4.15)	5.03 (5.06)	12.81 (12.84)
13	$TiCl_2(C_{15}H_{12}N_2O_2CH_3)[S_2P(OCH_2CH_2CH_3)_2]$	595.0 (598.9)	8.10 (8.13)	10.65 (10.70)	44.02 (44.14)	4.81 (4.84)	4.65 (4.67)	11.81 (11.85)
14	$TiCl_2(C_{15}H_{12}N_2O_2CH_3)[S_2P(OC_6H_5)_2]$	660.0 (666.9)	7.15 (7.18)	9.52 (9.59)	50.20 (50.38)	3.69 (3.74)	4.15 (4.19)	12.59 (12.62)
15	$TiCl_2(C_{15}H_{12}N_2O_2CH_3)(S_2POC(CH_3)_2CH_2CH(CH_3)O]$	595.0 (596.9)	8.05 (8.02)	10.74 (10.71)	44.15 (44.22)	4.67 (4.63)	4.65 (4.68)	11.91 (11.89)

16	$TiCl_2(C_{15}H_{12}N_2O_2CH_3)[S_2POCH_2C(CH_3)_2CH_2O]$	580.0 (582.9)	8.20 (8.23)	10.99 (10.97)	43.20 (43.23)	4.26 (4.28)	4.78 (4.80)	12.08 (12.11)
17	$TiCl_2(C_{15}H_{12}N_2O_2CH_3)[S_2POC(CH_3)_2C(CH_3)_2O]$	596.0 (596.9)	8.05 (8.02)	10.66 (10.71)	44.17 (44.22)	4.69 (4.64)	4.65 (4.69)	11.85 (11.89)
18	$TiCl_2(C_{15}H_{12}N_2O_2CH_3)[S_2POCH_2CH_2CH(CH_3)O]$	565.0 (568.9)	8.38 (8.41)	11.24 (11.28)	41.17 (41.21)	4.02 (4.04)	4.89 (4.92)	12.45 (12.48)
19	$TiCl_2(C_{15}H_{12}N_2OCl)[S_2P(OCH_2CH_2CH_3)_2]$	600.0 (603.4)	7.89 (7.93)	10.55 (10.60)	41.70 (41.76)	3.13 (3.14)	4.60 (4.63)	17.09 (17.05)
20	$TiCl_2(C_{15}H_{12}N_2OCl)[S_2P(OC_6H_5)_2]$	665.0 (671.4)	7.10 (7.13)	9.51 (9.53)	48.15 (48.25)	3.25 (3.27)	4.16 (4.17)	15.83 (15.86)
21	$TiCl_2(C_{15}H_{12}N_2OCl)[S_2POC(CH_3)_2CH_2CH(CH_3)O)]$	600.0 (601.4)	7.91 (7.95)	10.61 (10.64)	41.80 (41.86)	3.98 (3.99)	4.61 (4.65)	17.68 (17.70)
22	$TiCl_2(C_{15}H_{12}N_2OCl)[S_2POCH_2C(CH_3)_2CH_2O]$	590.0 (587.4)	8.17 (8.14)	10.85 (10.89)	40.76 (40.85)	3.71 (3.74)	4.73 (4.76)	18.10 (18.13)
23	$TiCl_2(C_{15}H_{12}N_2OCl)[S_2POC(CH_3)_2C(CH_3)_2O]$	605.0 (601.4)	7.89 (7.96)	10.59 (10.64)	41.75 (41.86)	3.93 (3.98)	4.63 (4.65)	17.64 (17.70)
24	$TiCl_2(C_{15}H_{12}N_2OCl)[S_2POCH_2CH_2CH(CH_3)O]$	575.0 (573.4)	8.31 (8.35)	11.20 (11.16)	39.75 (39.76)	3.47 (3.48)	4.85 (4.88)	18.47 (18.50)

dithiophosphate [28, 29]. The bands at 610–554 cm^{-1} may be ascribed to ν[P–S] [32]. New bands (in comparison to free ligand) at 334–320 cm^{-1} have been assigned to ν[Ti–S] [33]; bands at 360–348 cm^{-1}, 449–429 cm^{-1}, and 383–371 cm^{-1} are assigned to ν[Ti–Cl], ν[Ti–O], and ν[Ti–N] [33]. The IR spectral data are given in table 2.

4.2. ^{1}H *NMR spectra*

^{1}H NMR spectra have been recorded in $CDCl_3$. The aromatic protons of pyrazolines were observed as a complex pattern at δ 7.85–6.89 [34]. The peak due to hydroxyl protons (originally present at $\delta \sim 11.00$ in free pyrazolines) is absent from spectra of the complex, suggesting bonding through hydroxyl oxygen. The appearance of a peak at δ 5.35–4.95 as a broad singlet is assigned to –NH (originally at δ 5.4–5.0), indicating non-involvement of –NH [34]. Peaks at δ 3.54–3.05 and δ 2.56–2.01 are assigned to –CH and $–CH_2$. Bands at δ 5.32–4.18 are assigned to $–OCH_2$ and –OCH. Skeletal protons of phenyl are at δ 7.25–7.0.

4.3. ^{31}P *NMR data*

In ^{31}P NMR spectra of these compounds only one signal is observed. Downfield (δ 15–19) shifting of the signal due to dithiophosphate confirms bidentate dithiophosphate [35, 36].

4.4. ^{13}C *NMR data*

The proton decoupled ^{13}C NMR spectra show all signals of dithiophosphates and pyrazolines. Signals at 137.90–121.32 ppm as a complex pattern are assigned to aromatic carbons. The signal at 167.81–162.95 ppm due to imino carbon of C=N group shifts downfield in comparison to free pyrazolines (143.50–142.80 ppm), suggesting imino nitrogen coordination. Resonances of –OC and –OCH of dithiophosphates are observed at 91.45–93.00 ppm and 75.93–77.52 ppm. Peaks of –CH and CH_2 are at 45.73–43.09 and 27.85–24.23, respectively. The NMR (^{1}H, ^{13}C, and ^{31}P) data are summarized in table 3.

4.5. *XRD and TEM studies*

These complexes have been examined for crystalline/amorphous nature through XRD; all complexes are amorphous solids. Broadening of diffraction peaks was used to estimate the average domain size in terms of the "Debye–Scherrer" expression.

$$\text{Particle size} = D = 0.9\lambda/\beta\ \cos\theta_B.$$

The average diameter was in the range 20–50 nm. TEM studies showed that the particle size ranged from 50 to 90 nm. The mean diameters of the different particles synthesized are summarized in table 4. XRD micrograph and TEM images of **3** are shown in figures 1 and 2, respectively.

Table 2. IR spectral data (cm^{-1}) for $TiCl_2(C_{15}H_{12}N_2OX)(RO)_2PS(S)$.

Compound No.	ν[N–H]	ν[C=N]	ν[C–O]	ν[(P)–O–C]	ν[P–O–(C)]	ν[P=S]	ν[P–S]	Ring vib	ν[Ti–O]	ν[Ti–S]	ν[Ti–N]	ν[Ti-Cl]
1	3365	1636	–	1090	860	660	560	–	435	328	376	360
2	3375	1650	–	1075	890	685	590	–	431	320	381	350
3	3348	1604	–	1010	850	710	580	910	433	324	384	352
4	3348	1620	–	1050	880	680	540	960	429	326	371	357
5	3350	1603	–	1030	870	695	610	910	436	322	381	348
6	3368	1616	–	1035	890	670	605	920	430	324	385	351
7	3357	1647	–	1042	860	690	595	–	441	321	375	350
8	3356	1645	–	1052	850	675	580	–	430	331	379	348
9	3362	1610	–	1010	890	664	583	941	429	327	380	356
10	3350	1635	–	1085	875	690	572	970	431	331	372	360
11	3352	1624	–	1025	875	715	554	915	449	320	374	349
12	3385	1610	–	1015	883	674	583	950	443	330	381	357
13	3363	1635	1017	1042	887	678	593	–	447	325	370	360
14	3364	1622	1021	1017	870	680	570	–	433	327	380	352
15	3390	1612	1017	1176	885	660	597	940	448	331	382	358
16	3375	1632	1020	1047	872	685	594	930	429	324	377	351
17	3372	1636	1015	1090	890	670	554	912	432	324	379	359
18	3358	1642	1018	1045	855	650	610	965	441	320	370	357
19	3379	1608	–	1082	880	710	550	–	447	320	378	360
20	3378	1615	–	1011	870	665	607	–	442	329	383	352
21	3372	1605	–	1037	875	712	593	955	436	331	381	360
22	3397	1647	–	1093	890	685	590	915	429	327	374	357
23	3362	1650	–	1015	830	670	542	925	450	327	379	360
24	3349	1612	–	1023	885	695	580	970	445	334	375	351

Table 3. NMR data (δ ppm) for $TiCl_2(C_{15}H_{12}N_2OX)(RO)_2PS(S)$.

Compound No.	Chemical shift (δ ppm)		
	^{1}H NMR	^{13}C NMR	^{31}P NMR
1	7.45–6.85(m, Ar–H) 0.96(t, 12H, $-CH_3$) 5.18(m, 8H, $-OCH_2-$) 1.65(m, 8H, $-CH_2$) 5.25–5.04(s, 2H, NH) 3.45–3.12(t, 2H, –CH) 2.18–2.01(d, 4H, $-CH_2$)	–	106.10
2	7.67–6.89(m, Ar–H) 7.23(s, 2H, $-C_6H_5$) 4.67(s, 2H, –NH) 3.21(t, 4H, –CH) 2.56(d, 8H, $-CH_2$)	–	92.40
3	7.56–6.82(m, Ar–H) 2.92–2.65(m, 22H, $-CH_3$, CH_2) 5.32(m, 2H, –OCH) 4.73(s, 4H, –NH) 3.54(t, 2H, –CH) 2.21(d, 8H, CH_2)	91.67(–OC, dtp) 24.71($-CH_3$, dtp) 77.05(–OCH, dtp) 26.52($-CH_2$, dtp) 136.94(Ar–C) 167.55(C=N) 43.09(–CH) 26.53($-CH_2$)	93.60
4	7.56–6.93(m, Ar–H) 0.97(s, 12H, $-CH_3$) 4.16(d, 8H, $-OCH_2-$), J = 16 Hz 4.75(s, 4H, NH) 3.05(t, 2H, –CH) 2.19(d, 8H, $-CH_2$)	21.84(CH_3, dtp) 32.75(q, C, dtp) 75.71(d, $-OCH_2$, dtp) 136.32(Ar–C) 165.71(C=N) 42.29(CH) 27.59(CH_2)	91.50
5	1.24(s, 24H, $-CH_3$) 7.65–6.88(m, Ar–H) 4.93(s, 4H, –NH) 3.19(t, 2H, –CH) 2.28(d, 4H, $-CH_2$)	24.59(CH_3, dtp) 92.09(OC, dtp) 136.75–123.09(Ar–C) 163.82(C=N) 43.25(CH) 27.53(CH_2)	104.82
6	2.52–1.10(m, 10H, $-CH_3$, CH_2) 4.18–3.37(m, 6H, $-OCH_2$, OCH) 7.34–6.53(m, Ar–H) 4.80(s, 4H, –NH) 3.15(t, 2H, –CH) 2.25(d, 8H, $-CH_2$)	23.72(CH_3, dtp) 76.05(–OCH, OCH_2, dtp) 136.52–122.45(Ar–C) 162.83(C=N) 43.25(CH) 27.63(CH_2)	107.00
7	7.59–6.72(m, Ar–H) 0.99(t, 12H, $-CH_3$) 5.15(m, 8H, $-OCH_2-$) 1.23(m, 8H, $-CH_2$) 5.07(s, 2H, NH) 3.45(t, 2H, –CH) 2.13(d, 4H, $-CH_2$)	–	105.82
8	7.42–6.89(m, Ar–H) 7.15(s, 2H, $-C_6H_5$) 5.02(s, 2H, –NH) 3.72(t, 4H, –CH) 2.35(d, 8H, $-CH_2$)	–	92.72
9	7.45–6.79(m, Ar–H) 2.42–2.15(m, 22H, $-CH_3$, CH_2) 4.85–4.45(m, 2H, –OCH) 5.19(s, 4H, –NH)	91.45(–OC, dtp) 26.03($-CH_3$, dtp) 76.95(–OCH, dtp) 24.15($-CH_2$, dtp)	110.00

(*Continued*)

Table 3. Continued.

Compound No.	Chemical shift (δ ppm)		
	^{1}H NMR	^{13}C NMR	^{31}P NMR
	3.36(t, 2H, –CH)	136.75(Ar–C)	
	2.25(d, 8H, CH_2)	163.94(C=N)	
		42.27(–CH)	
		24.75(–CH_2)	
10	7.85–6.50(m, Ar–H)	22.93(CH_3, dtp)	91.82
	0.97(s, 12H, –CH_3)	31.76(q, C, dtp)	
	4.17(d, 8H, –OCH_2–)	75.93(d, –OCH_2, dtp)	
	J = 17 Hz	136.93(Ar–C)	
	5.32(s, 4H, NH)	165.54(C=N)	
	3.73(t, 2H, –CH)	43.45(CH)	
	2.20(d, 8H, –CH_2)	26.75(CH_2)	
11	1.45(s, 24H, –CH_3)	26.32(CH_3, dtp)	107.62
	7.46–6.80(m, Ar–H)	92.10(OC, dtp)	
	4.76(s, 4H, –NH)	136.56–123.32(Ar–C)	
	3.36(t, 2H, –CH)	166.32(C=N)	
	2.25(d, 4H, –CH_2)	45.73CH)	
		25.93(CH_2)	
12	2.12–1.15(m, 10H, –CH_3, CH_2)	24.64(CH_3, dtp)	96.50
	4.12–3.32(m, 6H, –OCH_2, OCH)	76.94(–OCH, OCH_2, dtp)	
	7.45–6.82(m, Ar–H)	135.23–123.57(Ar–C)	
	5.10(s, 4H, –NH)	165.94(C=N)	
	2.95(t, 2H, –CH)	43.25(CH)	
	2.07(d, 8H, –CH_2)	27.15(CH_2)	
13	7.50-6.82(m, Ar–H)	–	105.95
	0.93(t, 12H, –CH_3)		
	5.10(m, 8H, –OCH_2–)		
	1.45(m, 8H, –CH_2)		
	5.13(s, 2H, NH)		
	3.75(t, 2H,–CH)		
	2.15(d, 4H, –CH_2)		
14	7.42–6.85(m, Ar–H)	–	108.20
	7.25(s, 2H, –C_6H_5)		
	4.81(s, 2H, –NH)		
	3.15(t, 4H, –CH)		
	2.09(d, 8H, –CH_2)		
15	7.75–6.85(m, Ar–H)	92.15(–OC, dtp)	95.00
	2.35–1.93(m, 22H, –CH_3, CH_2)	24.95(–CH_3, dtp)	
	4.75–4.23(m, 2H, –OCH)	76.75(–OCH, dtp)	
	5.10(s, 4H, –NH)	23.32(–CH_2, dtp)	
	3.23(t, 2H, –CH)	136.55(Ar–C)	
	2.20(d, 8H, CH_2)	167.21(C=N)	
		43.21(–CH)	
		24.23(–CH_2)	
16	7.54–6.80(m, Ar–H)	22.75(CH_3, dtp)	94.72
	1.09(s, 12H, –CH_3)	32.05(q, C, dtp)	
	4.15(d, 8H, –OCH_2–)	75.95(d, –OCH_2, dtp)	
	5.32(s, 4H, NH)	137.52(Ar–C)	
	3.09(t, 2H, –CH)	167.32(C=N)	
	2.32(d, 8H, –CH_2)	42.92(CH)	
		27.23(CH_2)	
17	1.45(s, 24H, –CH_3)	23.26(CH_3, dtp)	94.06
	7.59–6.75(m, Ar–H)	90.82(dtp)	
	5.12 (4H, –NH)	136.27–122.32(m, Ar–C)	
	3.54 (2H, –CH)	164.75(C=N)	
	2.07 (4H, –CH_2)	42.15(CH)	
		26.98(CH_2)	

(*Continued*)

Table 3. Continued.

Compound No.	Chemical shift (δ ppm)		
	^{1}H NMR	^{13}C NMR	^{31}P NMR
18	2.67–1.32(m, 10H, $–CH_3$, CH_2) 4.06–3.71(m, 6H, $–OCH_2$, OCH) 7.51–6.75(m, Ar–H) 5.09(s, 4H, –NH) 3.25(t, 2H, –CH) 2.12(d, 8H, $–CH_2$)	22.72(CH_3, dtp) 76.32(–OCH, OCH_2, dtp) 136.81–123.25(Ar–C) 162.95(C=N) 42.97(CH) 27.85(CH_2)	91.29
19	7.43–6.70(m, Ar–H) 0.97(t, 12H, $–CH_3$) 5.63(m,8H, $–OCH_2–$) 1.65(m, 8H, $–CH_2$) 5.17(s, 2H, NH) 3.81(t, 2H, –CH) 2.21(d, 4H, $–CH_2$)	–	106.20
20	7.54–6.75(m, Ar–H) 7.09(s, 2H, $–C_6H_5$) 4.85(s, 2H, –NH) 3.12(t, 4H, –CH) 2.32(d, 8H, $–CH_2$)	–	101.22
21	7.60–6.87(m, Ar–H) 2.34–1.75(m, 22H, $–CH_3$, CH_2) 4.81–4.25(m, 2H, –OCH) 5.15(s, 4H, –NH) 3.19(t, 2H, –CH) 2.23(d, 8H, CH_2)	91.60(–OC, dtp) 23.65($–CH_3$, dtp) 77.52(–OCH, dtp) 24.81($–CH_2$, dtp) 136.45(Ar–C) 167.56(C=N) 42.92(–CH) 27.45($–CH_2$)	93.25
22	7.45–6.70(m, Ar–H) 1.13(s, 12H, $–CH_3$) 4.09(d, 8H, $–OCH_2–$) J = 16 Hz 4.85(s, 4H, NH) 3.43(t, 2H, –CH) 2.13(d, 8H, $–CH_2$)	22.75(CH_3, dtp) 36.35(q, C, dtp) 76.45(d, $–OCH_2$, dtp) 135.20(Ar–C) 167.81(C=N) 42.93(CH) 27.46(CH_2)	96.49
23	1.39(s, 24H, $–CH_3$) 7.52–6.75(m, Ar–H) 4.95(s, 4H, –NH) 3.15(t, 2H, –CH) 2.10(d, 4H, $–CH_2$)	23.55(CH_3, dtp) 92.07(OC, dtp) 137.52–123.26(Ar–C) 167.45(C=N) 43.15(CH) 27.82(CH_2)	107.70
24	2.35–1.25(m,10H, $–CH_3$, CH_2) 4.01–3.90(m, 6H, $–OCH_2$, OCH) 7.42–6.65(m, Ar–H) 5.10(s, 4H, –NH) 3.12(t, 2H, –CH) 2.13(d, 8H, $–CH_2$)	23.92(CH_3, dtp) 76.45(–OCH, OCH_2, dtp) 136.75–123.41(Ar–C) 165.32(C=N) 43.23(CH) 27.35(CH_2)	91.52

5. Conclusion

This study describes the synthesis of a series of complexes of bidentate dithiophosphate and pyrazolines with titanium(IV). Elemental analyses indicate monomeric complexes. On the basis of these studies and available literature, octahedral geometry may be proposed for Ti(IV) [37] (figure 3). These compounds may prove useful for formation of

Table 4. Average diameters of particles determined by XRD and TEM.

Compound No.	2θ	Average diameter (nm)[a]	Average diameter (nm)[b]
3	44.8	24	67
9	47.7	32	59
15	45.4	26	82
21	51.2	44	75

Particle size $= D = 0.9\ \lambda/\beta \cos \theta_B$.
[a]Determined by XRD technique using the following the Scherer formula.
[b]Determined by TEM technique.

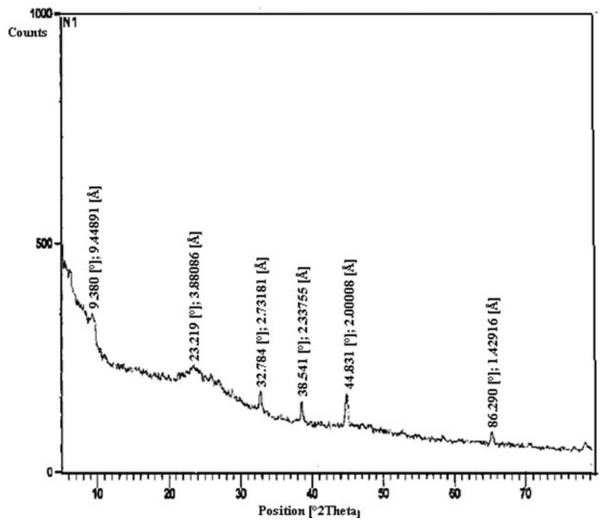

Figure 1. The XRD image of **3** as an example, suggesting the complexes are amorphous solids.

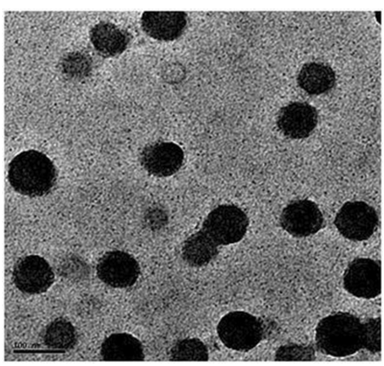

Figure 2. The TEM image of **3** showing particle sizes from 50 to 90 nm.

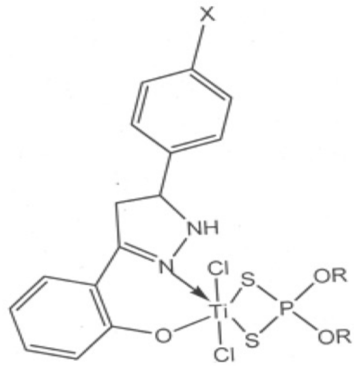

Figure 3. The octahedral geometry for $TiCl_2(C_{15}H_{12}N_2OX)(RO)_2PS(S)$ in which dithiophosphate ligand and pyrazolines are bidentate.

TiS_2 by sulfide sol-gel due to reduced acidity of the metal centre. Further studies of sulfide sol gels of these derivatives are under investigation.

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