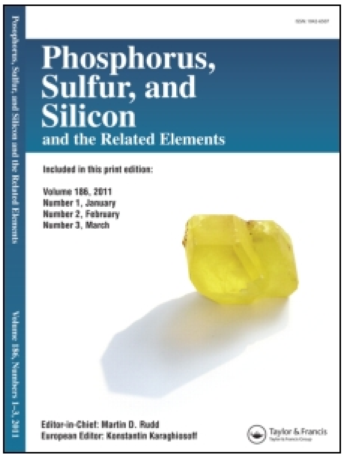

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Synthesis, Characterization, and Sol-Gel Behavior of Dichlorotitanium(IV) (O-Alkyl, O-Cycloalkyl, and O-Aryl Trithiophosphates)

U. N. Tripathi[a]; A. Siddiqui[a]; Mohd. Safi[b]; Nitya Sharma[c]; Neetu Srivastava[a]
[a] Department of Chemistry, D.D.U. Gorakhpur University, Gorakhpur, India [b] School of Studies in Chemistry, Vikram University, Ujjain, India [c] Department of Chemistry, A.K.G. Engineering College, Ghaziabad, India

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SYNTHESIS, CHARACTERIZATION, AND SOL-GEL BEHAVIOR OF DICHLOROTITANIUM(IV) (O-ALKYL, O-CYCLOALKYL, AND O-ARYL TRITHIOPHOSPHATES)

U. N. Tripathi,[1] A. Siddiqui,[1] Mohd. Safi,[2] Nitya Sharma,[3] and Neetu Srivastava[1]
[1]*Department of Chemistry, D.D.U. Gorakhpur University, Gorakhpur, India*
[2]*School of Studies in Chemistry, Vikram University, Ujjain, India*
[3]*Department of Chemistry, A.K.G. Engineering College, Ghaziabad, India*

Dichlorotitanium(IV) trithiophosphates of the type $TiCl_2[(RO)P(S)S_2]$ (where R = Me, Et, Pr^n, Pr^i, Bu^n, Bu^s, Bu^i, Am^i, Ph and cyclohexyl) have been synthesized for the first time by the reaction of titanium tetrachloride with potassium trithiophosphates in a 1:1 molar ratio in anhydrous benzene. Sol-gel chemistry of these titanium(IV) compounds has been studied in dry benzene by treatment with hydrogen sulfide gas. These newly synthesized derivatives have been characterized by elemental analysis (C, H, S, Cl, and Ti), molecular weight measurement, and spectral [IR and multinuclear NMR (^1H, ^{13}C, and ^{31}P)] studies. The bonding mode of trithiophosphate ligands and tentative structure around titanium(IV) are discussed.

Keywords ^{31}P NMR; sol-gel behavior; titanium(IV); trithiophosphate

INTRODUCTION

Titanium and other transition metal dichalcogenides are versatile materials that exhibit a wide range of electronic and optical properties.[1–5] TiS_2 has been used as the active cathode material in lithium-based rechargeable batteries.[6,7] This is mainly due to the facile reversibility of ion intercalation, high electronic property, and large current capacity.[8]

Several vapor phase and solution reactions have been investigated for the synthesis of TiS_2 powder and thin films.[9–13] More recently, titanium pyridine and pyridine thiolates have been used as precursors to synthesize titanium disulfide.[14] Mainwaring et al. have recently employed emulsion-based titanium tetrachloride precipitation techniques to prepare high purity titanium disulfide nano-sized clusters.[15]

The sol-gel method is a promising method for the preparation of transition metal dichalcogenides as TiS_2 using alkoxide or thiolate with H_2S in benzene or toluene. Sol-gel derived materials have diverse application in optics, electronics, and energy space sensors,

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Address correspondence to U. N. Tripathi, Department of Chemistry, D.D.U. Gorakhpur University, Gorakhpur, 273009, U.P., India. E-mail: un_tripathi@yahoo.com

and their most important application is in nanotechnology.[16] Synthesis of TiS_2 thin films via sol-gel route involving the reaction of $Ti(OPr^i)_2$ with H_2S in an amine solvent has been reported.[17]

Much study has been made on dithiocarbamates, thiolates,[18] and dithiolates of titanium, but titanium's dithio and trithiophosphate complexes only have been studied to a limited extent. In view of the above points, it was thought worthwhile to synthesize the trithiophosphato derivatives of titanium(IV) and study their sol-gel behavior with dry H_2S gas.

RESULTS AND DISCUSSION

All the complexes of the type $TiCl_2[(RO)P(S)S_2]$ and $\{Ti[(RO)P(S)S_2]\}_2S_2$ are red to reddish-brown solids, and are soluble in common organic (benzene, dichloromethane, acetone, and chloroform) and coordinating (dimethylsulphoxide, dimethylformamide, pyridine, and tetrahydrofuran) solvents. These compounds are hygroscopic in nature and undergo slow decomposition at room temperature. They can be stored under inert and dry atmosphere at lower temperature. The molecular weight measurements in dilute chloroform solution at 45°C show the monomeric nature of all these compounds. The elemental analysis (C, H, S, Cl, and Ti) data are in accordance with stoichiometry proposed for respective compounds and is summarized in Table I.

IR Spectra

All the complexes of the type $TiCl_2[(RO)P(S)S_2]$ and $\{Ti[(RO)P(S)S_2]\}_2S_2$ exhibit bands in the region 1022–1010 and 820–809 cm^{-1}, which may be assigned to $\nu[(P){-}O{-}C]$ and $\nu[P{-}O{-}(C)]$, respectively.[19,20] A strong band present in the region 644–635 cm^{-1} may be assigned to $\nu(P{=}S)$.[19,20] The bands of medium intensity present in the region 429–420 cm^{-1} may be ascribed to $\nu(P–S)$.[19,20] The signal due to $\nu(Ti–Cl)$ in $TiCl_2[(RO)P(S)S_{2]}$ is found in the region 358–348 cm^{-1}.[21]

The new band in the IR spectra of $TiCl_2[(RO)P(S)S_2]$ (as compared to potassium trithiophosphates) in the region 332–320 cm^{-1} is assigned to $\nu(Ti{-}S)$.[21,22]

The new bands in the IR spectra of $\{Ti[(RO)P(S)S_2]\}_2S_2$ (in comparison to potassium trithiophosphates) in the region 326–320 and 302–294 cm^{-1} are assigned to $\nu(Ti{-}S)$.[21,22] IR spectral data clearly indicate that $\{Ti[(RO)P(S)S_2]\}_2S_2$ has two different types of Ti–S linkages in its structure.

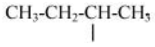
NMR Spectra

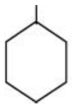
The ^1H NMR and ^{13}C NMR spectral data of these compounds are summarized in Table II. All the complexes of the type $TiCl_2[(RO)P(S)S_2]$ and $\{Ti[(RO)P(S)S_2]\}_2S_2$ show characteristic ^1H NMR and ^{13}C NMR signals due to the alkoxy, cyclohexyloxy, and phenoxy groups. The ^{13}C resonance for the carbon atom of the $P{-}O{-}C$ group appears as a doublet due to coupling with the ^{31}P nucleus. The ^1H NMR and ^{13}C NMR spectral data do not give sufficient information about the geometry around the central titanium(IV) in $TiCl_2[(RO)P(S)S_2]$ and $\{Ti[(RO)P(S)S_2]\}_2S_2$, although these do indicate that in these compounds the alkyl, cyclohexyl, and phenyl groups of the trithiophosphate moiety are intact.

Table I Physical and analytical data for $TiCl_2[(RO)P(S)S_2]$ and $\{Ti[(RO)P(S)S_2]\}_2S_2$

					Analysis (%): Found (Calcd.)					
S. No.	Compound	Color	Yield (%)	Dp* (°C)	C	H	S	Cl	Ti	Mol. Wt. Found (Calcd.)
1	$TiCl_2[(MeO)P(S)S_2]$	Reddish brown	97	152	4.36 (4.35)	— (1.10)	— (34.88)	24.68 (25.21)	17.28 (17.37)	273 (275.79)
2	$TiCl_2[(EtO)P(S)S_2]$	Reddish brown	98	154	8.24 (8.29)	— (1.74)	— (33.19)	24.36 (24.47)	15.47 (16.53)	291 (289.81)
3	$TiCl_2[(Pr^nO)P(S)S_2]$	Reddish brown	94	156	11.80 (11.86)	2.34 (2.32)	31.52 (31.66)	23.38 (23.34)	15.79 (15.76)	300 (303.82)
4	$TiCl_2[(Pr^iO)P(S)S_2]$	Reddish brown	96	153	11.82 (11.86)	2.29 (2.32)	— (31.66)	23.25 (23.31)	15.68 (15.76)	299 (303.82)
5	$TiCl_2[(Bu^nO)P(S)S_2]$	Reddish brown	95	154	15.07 (15.11)	2.83 (2.85)	29.95 (30.26)	22.16 (22.31)	15.15 (15.07)	318 (317.84)
6	$TiCl_2[(Bu^sO)P(S)S_2]$	Reddish brown	94	155	15.05 (15.11)	2.84 (2.85)	29.98 (30.26)	22.24 (22.31)	15.02 (15.07)	315 (317.84)
7	$TiCl_2[(Bu^iO)P(S)S_2]$	Reddish brown	97	151	15.14 (15.11)	2.88 (2.85)	30.35 (30.26)	22.35 (22.31)	14.95 (15.07)	316 (317.84)
8	$TiCl_2[(Am^iO)P(S)S_2]$	Reddish brown	96	154	18.02 (18.10)	3.31 (3.34)	28.74 (28.99)	21.41 (21.37)	14.38 (14.43)	329 (331.86)
9	$TiCl_2[(PhO)P(S)S_2]$	Red	98	152	20.89 (20.96)	3.25 (3.22)	27.86 (27.97)	20.51 (20.62)	13.86 (13.93)	340 (343.86)
10	$TiCl_2[(PhO)P(S)S_2]$	Red	95	156	20.22 (21.33)	— (1.49)	27.96 (28.18)	20.87 (20.99)	14.07 (14.18)	339 (337.81)
11	$\{Ti[(MeO)P(S)S_2]\}_2S_2$	Orange	75	140	5.01 (5.04)	— (1.27)	53.73 (53.86)	—	19.92 (20.11)	474 (476.28)
12	$\{Ti[(EtO)P(S)S_2]\}_2S_2$	Orange	78	142	9.49 (9.53)	— (2.00)	50.79 (50.86)	—	18.87 (18.98)	502 (504.32)
13	$\{Ti[(Pr^nO)P(S)S_2]\}_2S_2$	Orange	76	143	13.52 (13.54)	2.66 (2.65)	48.39 (48.18)	—	17.95 (17.98)	529 (532.37)
14	$\{Ti[(Pr^iO)P(S)S_2]\}_2S_2$	Orange	79	144	13.57 (13.54)	2.63 (2.65)	47.89 (48.18)	—	17.83 (17.98)	531 (532.37)
15	$\{Ti[(Bu^nO)P(S)S_2]\}_2S_2$	Orange	74	142	17.09 (17.14)	3.21 (3.24)	45.65 (45.77)	—	16.96 (17.08)	558 (560.43)
16	$\{Ti[(Bu^sO)P(S)S_2]\}_2S_2$	Orange	76	141	17.18 (17.14)	3.27 (3.24)	45.79 (45.77)	—	17.01 (17.08)	562 (560.43)
17	$\{Ti[(Bu^iO)P(S)S_2]\}_2S_2$	Orange	77	143	17.06 (17.14)	3.19 (3.24)	45.58 (45.77)	—	16.97 (17.08)	556 (560.43)
18	$\{Ti[(Am^iO)P(S)S_2]\}_2S_2$	Orange	74	144	20.31 (20.40)	3.75 (3.77)	43.62 (43.59)	—	16.14 (16.27)	583 (588.48)
19	$\{Ti[(CyO)P(S)S_2]\}_2S_2$	Brown	78	140	23.45 (23.53)	3.61 (3.62)	41.62 (41.88)	—	15.66 (15.63)	610 (612.50)
20	$\{Ti[(PhO)P(S)S_2]\}_2S_2$	Brown	80	144	23.88 (24.01)	— (1.68)	42.65 (42.72)	—	15.85 (15.94)	597 (600.41)

*Decomposition point. Me = CH_3-; Et = $CH_3{-}CH_2{-}$; Pr^n = $CH_3{-}CH_2{-}CH_2$-; Pr^i = $(CH_3)_2{-}CH{-}$; Bu^n = $CH_3{-}CH_2{-}CH_2{-}CH_2{-}$; Bu^i = $(CH_3)_2{-}CH{-}CH_2{-}$; Am^i = $(CH_3)_2{-}CH{-}CH_2{-}CH_2{-}$;

Bu^s =

CH_3-CH_2-CH-CH_3

Cy =


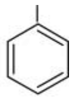
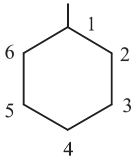
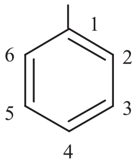
Ph =


Table II ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR data (in δ ppm) for $TiCl_2[(RO)P(S)S_2]$ and $\{Ti[(RO)P(S)S_2]\}_2S_2$

		Chemical shift (in δ ppm)					
		^{1}H NMR		^{13}C NMR		^{31}P NMR	
S. No.	R	$TiCl_2[(RO)O(S)S_2]$	$\{Ti[(RO)P(S)S_2]\}_2S_2$	$TiCl_2[(RO)O(S)S_2]$	$\{Ti[(RO)P(S)S_2]\}_2S_2$	$TiCl_2[(RO)O(S)S_2]$	$\{Ti[(RO)P(S)S_2]\}_2S_2$
1	Me = CH_3-	4.42 (s, 1H, $-OCH_3$)	4.36 (s, 1H, $-OCH_3$)	57.26, d, C, $^2J_{p\text{-}c} = 19$ Hz	59.28, d, C, $^2J_{p\text{-}c} = 20$ Hz	98.90	106.81
2	Et = $\overset{2}{CH_3}$-$\overset{1}{CH_2}$-	4.43 (q, 2H, $-OCH_2$) 2.31 (t, 3H, $-CH_3$, $^2J = 7.6$ Hz)	4.41 (q, 2H, $-OCH_2$) 2.43 (t, 3H, $-CH_3$, $^2J = 7.5$ Hz)	65.14, d, C^1, $^2J_{p\text{-}c} = 22$ Hz 21.21, C^2	66.19, d, C^1, $^2J_{p\text{-}c} =$ 23 Hz 21.82, C^2	94.29	107.19
3	Pr^n = $\overset{3}{CH_3}$-$\overset{2}{CH_2}$-$\overset{1}{CH_2}$-	4.41 (t, 2H, $-OCH_2$ $^2J = 7.8$ Hz) 2.21 (m, 2H, $-CH_2$) 1.10 (t, 3H, $-CH_3$, $^2J = 7.5$ Hz)	4.39 (t, 2H, $-OCH_2$ $^2J = 7.6$ Hz) 2.92 (m, 2H, $-CH_2$) 1.21 (t, 3H, $-CH_3$, $^2J = 7.5$ Hz)	72.23, d, C^1, $^2J_{p\text{-}c} = 21$ Hz 28.67, C^2 14.98, C^3	74.17, d, C^1, $^2J_{p\text{-}c} =$ 22 Hz 29.81, C^2 16.58, C^3	95.32	102.68
4	Pr^i = $\overset{3}{CH_3}$-$\overset{2}{CH}$-$\overset{1}{CH_3}$	5.23 (m, 1H, $-OCH$) 2.33 (d, 6H, $(-CH_3)_2$, $^2J =$ 7.6 Hz)	5.42 (m, 1H, $-OCH$) 2.65 (d, 6H, $(-CH_3)_2$, $^2J =$ 7.6 Hz)	68.82, d, C^2, $^2J_{p\text{-}c} = 21$ Hz 27.83, d, C^1	69.93, d, C^2, $^2J_{p\text{-}c} =$ 22 Hz 28.16, d, C^1	99.82	101.92
5	Bu^n = $\overset{4}{CH_3}$-$\overset{3}{CH_2}$-$\overset{2}{CH_2}$-$\overset{1}{CH_2}$-	4.82 (t, 2H, $-OCH_2$, $^2J =$ 7.8 Hz) 2.20 (m, 2H, 2H, $-CH_2$, $-CH_2$) 1.21 (t, 3H, $-CH_3$, $^2J = 7.6$ Hz)	5.13 (t, 2H, $-OCH_2$, $^2J =$ 7.7 Hz) 2.30 (m, 2H, 2H, $-CH_2$, $-CH_2$) 1.42 (t, 3H, $-CH_3$, $^2J = 7.5$ Hz)	70.82, d, C^1, $^2J_{p\text{-}c} = 18$ Hz 24.36, C^2 25.26, C^3 14.18, C^4	71.21, d, C^1, $^2J_{p\text{-}c} =$ 19 Hz 25.10, C^2 25.18, C^3 14.19, C^4	100.72	103.88
6	Bu^s = $\overset{4}{CH_3}$-$\overset{3}{CH_2}$-$\overset{2}{CH}$-$\overset{1}{CH_3}$	4.81 (d, 2H, $-OCH_2$, $^2J =$ 7.6 Hz) 2.15 (m, 1H, $-CH$) 1.61(m, 2H, $-CH_2$) 1.13 (m, 6H, $(-CH_3)_2$)	4.93 (d, 2H, $-OCH_2$, $^2J =$ 7.7 Hz) 2.41 (m, 1H, $-CH$) 1.71(m, 2H, $-CH_2$) 1.44 (m, 6H, $(-CH_3)_2$)	73.28, d, C^2, $^2J_{p\text{-}c} = 18$ Hz 43.68, C^3 29.28, C^1 26.31, C^4	73.69, d, C^2, $^2J_{p\text{-}c} =$ 19 Hz 44.52, C^3 29.39, C^1 26.82, C^4	100.21	102.78
7	Bu^i = $\overset{3}{(CH_3)_2}$-$\overset{2}{CH}$-$\overset{1}{CH_2}$-	4.87 (t, 2H, $-OCH_2$, $^2J =$ 7.8 Hz) 2.13 (q, 2H, $-CH_2$) 1.13 (d, 6H, $(-CH_3)_2$, $^2J =$ 7.6 Hz)	4.90 (t, 2H, $-OCH_2$, $^2J =$ 7.9 Hz) 2.32 (q, 2H, $-CH_2$) 1.31 (d, 6H, $(-CH_3)_2$, $^2J =$ 7.6 Hz)	73.16, d, C^1, $^2J_{p\text{-}c} = 19$ Hz 33.82, C^2 23.19, C^3	74.19, d^1, C, $^2J_{p\text{-}c} =$ 20 Hz 34.21, C^2 23.86, C^3	99.92	102.86

8	Am^i = $\overset{4}{(CH_3)_2}$-$\overset{3}{CH}$-$\overset{2}{CH_2}$-$\overset{1}{CH_2}$-	4.62 (t, 2H, $-OCH_2$, ^2J = 7.7 Hz) 2.13 (q, 1H, $-CH_2$) 1.62(m, 2H, $-CH$) 1.13 (d, 6H, $(-CH_3)_2$, ^2J = 7.6 Hz)	4.83 (t, 2H, $-OCH_2$, ^2J = 7.8 Hz) 2.21 (q, 1H, $-CH_2$) 1.81(m, 2H, $-CH$) 1.01 (d, 6H, $(-CH_3)_2$, ^2J = 7.6 Hz)	64.32, d, C^1, $^2J_{p-c}$ = 29 Hz 43.39, C^2 28.43, C^3 28.82, C^4	65.48, d, C^1, $^2J_{p-c}$ = 30 Hz 43.92, C^2 31.68, C^3 28.41, C^4	97.26	100.29
9	Cy = 	4.95 (m, 1H, $-OCH$) 1.68−2.32 (m, 10H, $(-CH_2)_5$)	5.07 (m, 1H, $-OCH$) 1.71−2.39 (m, 10H, $(-CH_2)_5$)	75.68, d, C^1, $^2J_{p-c}$ = 35 Hz 36.28, $C^{2,6}$ 29.82, $C^{3,5}$ 31.24, C^4	76.91, d, C^1, $^2J_{p-c}$ = 35 Hz 36.72, C^2 29.86, C^3 30.14, C^4	98.28	102.38
10	Ph = 	10.60−11.32(m, 5H, Arom)	10.78−11.69 (m, 5H, Arom)	163.82, d, C^1, $^2J_{p-c}$ = 44 Hz 121.83, $C^{2,6}$ 138.32, $C^{3,5}$ 128.69, C^4	164.03, d, C^1, $^2J_{p-c}$ = 44 Hz 122.34, $C^{2,6}$ 139.32, $C^{3,5}$ 128.71, C^4	98.92	103.73

m = multiplet, s = singlet, d = doublet, t = triplet, and q = quartet.

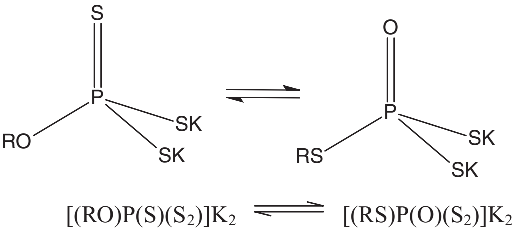


Figure 1 Molecular structure of potassium trithiophosphate (where R = Me, Et, Pr^n, Pr^i, Bu^n, Bu^s, Bu^i, Am^i, Ph, and Cy = cyclohexyl).

In the proton-decoupled ^{31}P NMR spectra of $TiCl_2[(RO)P(S)S_2]$ and $\{Ti[(RO)P(S)S_2]\}_2S_2$, only one peak for each compound in the range 107.19–94.29 ppm is observed. The proton decoupled ^{31}P NMR spectral data of these compounds are summarized in Table II.

Although potassium trithiophosphates exist in two isomeric forms (Figure 1), $TiCl_2[(RO)P(S)S_2]$ and $\{Ti[(RO)P(S)S_2]\}_2S_2$ do not show isomerism as indicated by ^{31}P NMR spectral data. Most probably, one of the isomers has more stability when coordinated with the metal ion and therefore predominates in the compounds. IR spectral data clearly indicate ν[P—O—(C)] and ν(P=S) stretching vibrations in these titanium(IV) compounds and thus $[(RO)P(S)S_2]^{-}$ suggest the tentative geometry around the central titanium(IV) ion in these compounds.

In the compounds of the type $TiCl_2[(RO)P(S)S_2]$ and $\{Ti[(RO)P(S)S_2]\}_2S_2$, the central titanium(IV) ion appears to acquire the coordination number four, and the most plausible geometry around the titanium(IV) is tetrahedral (Figures 2 and 3).[22] The trithiophosphate moieties behave as a bidentate ligand in these titanium(IV) compounds.

Sol-Gel Study of $TiCl_2[(RO)P(S)S_2]$

The sol-gel chemistry of dichlorotitanuim(IV) trithiophosphates using dry hydrogen sulfide gas in dry benzene was studied and can be described by the following chemical

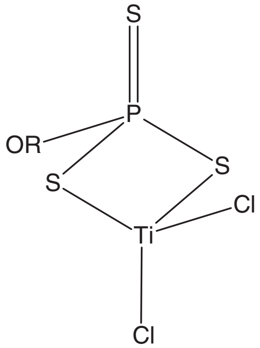


Figure 2 Molecular structure of $TiCl_2[(RO)P(S)S_2]$ (where R = Me, Et, Pr^n, Pr^i, Bu^n, Bu^s, Bu^i, Am^i, Ph, and Cy = cyclohexyl).

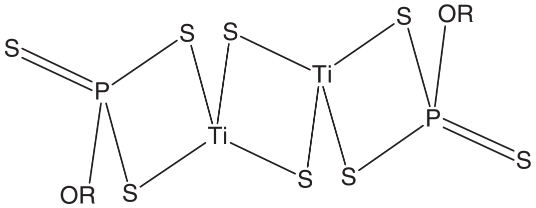


Figure 3 Molecular structure of $\{Ti[(RO)P(S)S_2]\}_2S_2$ (where R = Me, Et, Pr^n, Pr^i, Bu^n, Bu^s, Bu^i, Am^i, Ph, and Cy = cyclohexyl).

equation:

$$2TiCl_2[(RO)P(S)S_2] + 2H_2S \xrightarrow{\text{Benzene}} \{Ti[(RO)P(S)S_2]\}_2S_2 + 4HCl$$

[where R = Me, Et, Pr^n, Pr^i, Bu^n, Bu^s, Bu^i, Am^i, Ph and Cy = cyclohexyl]

Reaction of dichlorotitanuim(IV) trithiophosphates with hydrogen sulfide resulted in the formation of trithiophosphato titanium(IV)-di-μ-sulfido-trithiophosphato titanium(IV) of the type $\{Ti[(RO)P(S)S_2]\}_2S_2$, which was characterized by various physicochemical techniques.

EXPERIMENTAL

Moisture was carefully excluded throughout experimental manipulations. Synthesis of potassium trithiophosphates and dichloro titanium(IV) trithiophosphates were carried out under dry conditions. Solvents (methanol, benzene, and acetone), alcohols (methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 2-methyl-1-propanol, and 3-methyl-1-butanol), cyclohexanol, phenol, and triethyl amine were dried by standard methods.[23] Potassium salt of O-alkyl, O-cycloalkyl, and O-aryltrithiophosphoric acids were prepared by previously reported methods.[19,20]

Synthesis of $TiCl_2[(RO)P(S)S_2]$

The new dichlorotitanium(IV) trithiophosphates of the general formula $TiCl_2[(RO)P(S)S_2]$ were prepared by the following route:

$$TiCl_4 + [(RO)P(S)S_2]K_2 \xrightarrow{\text{Benzene}} TiCl_2[(RO)P(S)S_2] + 2KCl$$

[where R = Me, Et, Pr^n, Pr^i, Bu^n, Bu^s, Bu^i, Am^i, Ph and Cy = cyclohexyl]

$TiCl_2[(C_2H_5O)P(S)S_2]$. A benzene solution of titanium tetrachloride (1.129 g, 5.97 mmol) was added dropwise with constant stirring to the suspension of potassium trithiophosphates (1.490 g, 5.95 mmol) in dry benzene (40 mL) at 0–3°C. The reaction mixture was further stirred for 4 h at 0–3°C to ensure the completion of the reaction. The insolubles, including byproduct (potassium chloride), were filtered off through an alcoxy funnel, and the volatiles were removed from the filtrate under reduced pressure. The reddish-brown colored solid thus obtained was removed and stored under nitrogen atmosphere at 10–15°C

(1.47 g, 98.0%). Compounds **1–10** were prepared by this method. The analytical results are presented in Table I.

Sol-Gel Study of $TiCl_2[(RO)P(S)S_2]$

The sol-gel chemistry of dichlorotitanuim(IV) trithiophosphates using dry hydrogen sulfide gas in dry benzene were studied and can be described by the following chemical equation:

$$2TiCl_2[(RO)P(S)S_2] + 2H_2S \xrightarrow{\text{Benzene}} \{Ti[(RO)P(S)S_2]\}_2S_2 + 4HCl$$

$$[\text{where } R = Me, Et, Pr^n, Pr^i, Bu^n, Bu^s, Bu^i, Am^i, Ph \text{ and } Cy = \text{cyclohexyl}]$$

Reaction of dichlorotitanuim(IV) trithiophosphates with hydrogen sulfide resulted in the formation of trithiophosphato titanium(IV)-di-μ-sulphido-trithiophosphato titanium(IV) of the type $\{Ti[(RO)P(S)S_2]\}_2S_2$.

$\{Ti[(C_2H_5O)P(S)S_2]\}_2S_2$. A solution of dichlorotitanium(IV) (O-ethyl trithiophosphate) (1.86 g, 6.42 mmol) in dry benzene was prepared. Dry nitrogen gas was purged to create the inert atmosphere. Hydrogen sulfide gas was produced by the reaction of dilute sulfuric acid with ferrous sulfide and dried over fused calcium chloride. Hydrogen sulfide gas was bubbled through the benzene solution of $TiCl_2[(C_2H_5O)P(S)S_2]$ at 25–30°C for 2–3 h. The reaction mixture was further stirred for 4 h at 25–30°C to ensure the completion of the reaction. The orange solid thus obtained was filtered off through an alcoxy funnel, washed with dry benzene, and solvent traces were removed from the solid compound under reduced pressure. $\{Ti[(C_2H_5O)P(S)S_2]\}_2S_2$ thus formed was stored under nitrogen atmosphere at 10–15°C (1.26 g, 78.0%). Compounds **11–20** were prepared by this method. The analytical results are presented in Table I.

Physical Measurements

Chlorine, sulfur, and titanium were estimated by standard methods.[24] Infrared spectra were recorded as nujol mulls using CsI cells on a Perkin-Elmer Model 557 FT-IR spectrophotometer in the range 4000–200 cm^{-1}. The ^1H NMR spectra and proton-decoupled ^{13}C NMR spectra were recorded at room temperature in DMSO-d_6 on a Bruker DRX-300 spectrometer, operating at 300.1 and 75.45 MHz for ^1H and ^{13}C, respectively, using tetramethylsilane as internal standard. ^{31}P NMR spectra were recorded at room temperature in DMSO-d_6 on a Bruker DRX-300 spectrometer operating at 121.5 MHz using H_3PO_4 as internal standard. Molecular weights were determined on a Knoauer Vapor Pressure osmometer in $CHCl_3$ at 45°C. The elemental analysis (C, H, and N) was obtained by using a Coleman CHN analyzer.

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