

SYNTHESIS AND CHARACTERIZATION OF MIXED LIGAND  
COMPLEXES OF ZIRCONIUM(IV) WITH SULPHUR, NITROGEN  
AND OXYGEN DONOR LIGANDS*Abhishek Srivastava<sup>1,\*</sup>, Neetu Srivastava<sup>2</sup>, Umesh Nath Tripathi<sup>2</sup>, Afshan Siddiqui<sup>2</sup>*<https://doi.org/10.23939/chcht13.01.023>

**Abstract.** A new route to synthesize new nanosized mixed ligand complexes of Zr(IV) have been investigated by the reaction of zirconium(IV) chloride with 3-(2'-hydroxyphenyl)-5-(4-substituted phenyl)pyrazolines and ammonium salts of dithiophosphate, which after being treated with H<sub>2</sub>S gas acts as a precursor for ZrS<sub>2</sub>. These complexes have been examined for crystalline/amorphous nature through XRD. 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, <sup>1</sup>H NMR, <sup>31</sup>P NMR) studies reveal dimeric nature of the complexes, in which dithiophosphate and pyrazoline are bidentate. Scanning electron microscopic images indicate that the particles are in a nano range. Putting all the facts together, coordination number six is proposed for zirconium with octahedral geometry.

**Keywords:** zirconium(IV), dithiophosphate, pyrazoline, nanoparticle, sol-gel.

## 1. Introduction

Metal organic frameworks are made by linking metal and organic units by strong bonds [1-3]. Since most of the zirconium complexes are sensitive to hydrolysis, the metal organic frameworks of Zr(IV) complexes have been developed in anhydrous medium by the interaction of zirconium tetrachloride and various mixed ligands in different stoichiometric ratio [4-6]. The Zr(IV) complexes with nitrogen and sulphur donor ligands have received considerable attention due to their wide spread utilization as an effective precursor for making ZrO<sub>2</sub> and ZrS<sub>2</sub> by MOCVD technique [6-10].

It is well known that mixed ligand complexes can exhibit superior properties as compared to their pure counterpart. Biological activity of zirconium mixed ligand complexes were tested against various pathogenic microorganisms [11-14]. Mixed ligand complexes of Zr(IV) have been extensively used as a catalyst in various polymerization reactions [15-19]. The metal organic framework of Zr(IV) complexes acts as a precursor for the development of ZrO<sub>2</sub> and ZrS<sub>2</sub>. ZrO<sub>2</sub> exhibits wide range of applications in ceramics [20-21], chromatography [22-23] and pharmaceuticals [24-25]. By mixing ZrO<sub>2</sub> with other metallic oxides such as MgO, CaO and Y<sub>2</sub>O<sub>3</sub>, great molecular stability can be obtained [26]. Yttrium-stabilized zirconia also known as tetragonal zirconia polycrystals (TPZ) is presently the most studied combination for biomedical ceramics that can be used in manufacturing of ball heads for total hip replacements (THR) [27-28]. ZrS<sub>2</sub> nanoparticles have found application in the manufacturing of high-performance Schottky solar cells and nano discs [29-30].

A few complexes of Zr(IV) with pyrazolines ligands have been reported till now [31-32]. The wide range application of nanosized ZrO<sub>2</sub> and ZrS<sub>2</sub> has drawn our attention in developing a MOFs of Zr(IV) complexes with dithiophosphate and pyrazolines ligands, which can act as a precursor for the synthesis of nano range ZrS<sub>2</sub>.

The objective of the work is to synthesize and characterize some new mixed ligand complexes of Zr(IV).

## 2. Experimental

### 2.1. Material and Methods

All reactions were carried out under absolutely dry conditions. Solvents were distilled, dried and purified by standard techniques [33]. Pyrazolines and ammonium salt of dialkyl/alkylene dithiophosphates

<sup>1</sup>G.L.A. University, Chaumuhan, Mathura 281406, U.P., India

<sup>2</sup>Deen Dayal Upadhyaya Gorakhpur University, Gorakhpur 273001, U.P., India

\* aabhichem@gla.ac.in

© Srivastava A., Srivastava N., Tripathi U., Siddiqui A., 2019

were prepared by method described in [34, 35]. Chlorine was estimated by Volhard's method [34] and zirconium was estimated as zirconium phosphate [33]. The elemental analysis (C, H, N) were obtained by using a Coleman CHN analyzer (Table 1). IR spectra were recorded on Varian 3100 FT-IR spectrophotometer in the range of 4000–200  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR spectra and proton decoupled  $^{13}\text{C}$  NMR spectra were recorded at room temperature on JOEL AL 300 FT NMR spectrophotometer operated at 300.40 MHz. The X-ray diffraction studies were carried out on Bruker Nonious Kappa CCD diffractometer at room temperature. SEM studies have been carried out on JEOL 2010 high-resolution scanning electron microscope, operated at 200 keV. The FAB mass spectra were recorded on JOEL SX102 mass spectrometer using Argon or Xenon (6 kV, 10 mA) as the FAB gas.

## 2.2. Synthesis

### of $\text{ZrCl}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OH})(\text{OC}_3\text{H}_7)_2\text{PS}_2$

A benzene solution of pyrazoline (1.09 g, 4.60 mmol) was added drop-wise to the suspension of zirconium tetrachloride (1.07 g, 4.60 mmol) under constant stirring at room temperature. The reaction mixture was stirred for 2–3 h to ensure the completion of reaction. The solution of dithiophosphate in methanol (0.97 g, 4.60 mmol) was added drop-wise under constant stirring to the same reaction mixture and again stirred for

3–4 h. The by-product ( $\text{NH}_4\text{Cl}$ ) was filtered off through alkoxy funnel and the volatiles were removed from the filtrate under reduced pressure. A reddish brown colored solid was thus obtained. The remaining compounds were prepared by the same procedure.

## 2.3. Synthesis

### of $\text{Zr}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OH})_2(\text{OC}_3\text{H}_7)_4\text{P}_2\text{S}_6$

Dry  $\text{H}_2\text{S}$  gas was bubbled in the methanolic solution of zirconium complex. As the bubbling started, the formation of white colored precipitate was observed. The bubbling of the gas was continued for 2 h to ensure complete precipitation. This reaction mixture was filtered through alkoxy funnel and the precipitate was analyzed as the final product. The remaining compounds (1-24) were prepared by the same procedure.

## 3. Results and Discussion

All the compounds are white colored solids, hygroscopic and stable at room temperature. They are soluble in common organic solvents (methanol, benzene and chloroform) and coordinating solvents (THF, DMSO and DMF). The elemental analysis (C, H, S, Cl, Zr and N) data (Table 1) is in accordance with the stoichiometry proposed for respective compounds.

Table 1

Analytical data for  $\text{Zr}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OX})_2[\text{S}_6\text{P}_2(\text{OR})_4]$

No.	Compound	Molecular weight Found (Calcd)	Analysis Found (Calcd.)				
			C	H	N	S	Metal
1	2	3	4	5	6	7	8
1	$\text{Zr}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OH})_2[\text{S}_6\text{P}_2(\text{OCH}_2\text{CH}_2\text{CH}_3)_4]$	1140 (1146.4)	43.92 (43.96)	3.80 (3.83)	2.45 (2.44)	16.70 (16.75)	15.87 (15.91)
2	$\text{Zr}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OH})_2[\text{S}_6\text{P}_2(\text{OC}_6\text{H}_5)_4]$	1280 (1282.4)	41.10 (41.17)	3.18 (3.21)	2.16 (2.18)	14.95 (14.97)	14.20 (14.22)
3	$\text{Zr}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OH})_2[\text{S}_6\text{P}_2\{\overline{\text{OC}(\text{CH}_3)_2\text{CH}_2\text{CH}(\text{CH}_3)\text{O}}\}_2]$	1150 (1142.4)	44.05 (44.12)	3.85 (3.86)	2.43 (2.45)	16.74 (16.81)	15.92 (15.97)
4	$\text{Zr}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OH})_2[\text{S}_6\text{P}_2\{\overline{\text{OCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{O}}\}_2]$	1108 (1114.4)	42.96 (43.07)	3.85 (3.87)	2.50 (2.51)	17.20 (17.23)	16.35 (16.37)
5	$\text{Zr}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OH})_2[\text{S}_6\text{P}_2\{\overline{\text{OC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{O}}\}_2]$	1140 (1142.4)	44.06 (44.12)	3.84 (3.86)	2.45 (2.45)	16.77 (16.81)	16.00 (15.97)
6	$\text{Zr}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OH})_2[\text{S}_6\text{P}_2\{\overline{\text{OCH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{O}}\}_2]$	1085 (1083.4)	4.00 (42.09)	3.85 (3.88)	2.56 (2.58)	17.70 (17.72)	16.80 (16.84)
7	$\text{Zr}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OCH}_3)_2[\text{S}_6\text{P}_2(\text{OCH}_2\text{CH}_2\text{CH}_3)_4]$	1170 (1174.4)	44.85 (44.96)	3.80 (3.83)	2.37 (2.38)	16.30 (16.35)	15.50 (15.53)
8	$\text{Zr}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OCH}_3)_2[\text{S}_6\text{P}_2(\text{OC}_6\text{H}_5)_4]$	1310 (1310.4)	42.04 (42.12)	3.15 (3.21)	2.12 (2.14)	14.61 (14.65)	13.93 (13.92)
9	$\text{Zr}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OCH}_3)_2[\text{S}_6\text{P}_2\{\overline{\text{OC}(\text{CH}_3)_2\text{CH}_2\text{CH}(\text{CH}_3)\text{O}}\}_2]$	1175 (1170.4)	45.05 (45.11)	3.80 (3.85)	2.36 (2.39)	16.36 (16.40)	15.55 (15.58)

Table 1 (continued)

1	2	3	4	5	6	7	8
10	$Zr_2(C_{15}H_{12}N_2OCH_3)_2[S_6P_2\{OCH_2C(CH_3)_2CH_2O\}_2]$	1140 (1142.4)	44.05 (44.12)	3.85 (3.86)	2.43 (2.45)	16.75 (16.81)	15.94 (15.97)
11	$Zr_2(C_{15}H_{12}N_2OCH_3)_2[S_6P_2\{OC(CH_3)_2C(CH_3)_2O\}_2]$	1175 (1170.4)	45.06 (45.11)	3.83 (3.85)	2.37 (2.39)	16.35 (16.40)	15.55 (15.58)
12	$Zr_2(C_{15}H_{12}N_2OCH_3)_2[S_6P_2\{OCH_2CH_2CH(CH_3)O\}_2]$	1110 (1111.4)	43.10 (43.19)	3.87 (3.89)	2.51 (2.52)	17.22 (17.28)	16.37 (16.41)
13	$Zr_2(C_{15}H_{12}N_2O_2CH_3)_2[S_6P_2(OCH_2CH_2CH_3)_4]$	1208 (1206.4)	43.68 (43.77)	3.60 (3.63)	2.30 (2.32)	15.90 (15.92)	15.09 (15.12)
14	$Zr_2(C_{15}H_{12}N_2O_2CH_3)_2[S_6P_2(OC_6H_5)_4]$	1345 (1342.4)	50.00 (50.06)	3.71 (3.73)	2.07 (2.09)	14.28 (14.30)	13.55 (13.59)
15	$Zr_2(C_{15}H_{12}N_2O_2CH_3)_2[S_6P_2\{OC(CH_3)_2CH_2CH(CH_3)O\}_2]$	1255 (1248.4)	42.25 (42.29)	3.36 (3.39)	2.23 (2.24)	15.36 (15.38)	14.59 (14.61)
16	$Zr_2(C_{15}H_{12}N_2O_2CH_3)_2[S_6P_2\{OCH_2C(CH_3)_2CH_2O\}_2]$	1120 (1129.4)	44.56 (44.63)	3.92 (3.95)	2.47 (2.48)	16.95 (17.00)	16.10 (16.15)
17	$Zr_2(C_{15}H_{12}N_2O_2CH_3)_2[S_6P_2\{OC(CH_3)_2C(CH_3)_2O\}_2]$	1245 (1248.4)	42.19 (42.29)	3.37 (3.39)	2.20 (2.24)	15.35 (15.38)	14.56 (14.61)
18	$Zr_2(C_{15}H_{12}N_2O_2CH_3)_2[S_6P_2\{OCH_2CH_2CH(CH_3)O\}_2]$	1095 (1098.4)	43.62 (43.70)	3.95 (3.98)	2.53 (2.55)	17.46 (17.48)	16.58 (16.61)
19	$Zr_2(C_{15}H_{12}N_2OCl)_2[S_6P_2(OCH_2CH_2CH_3)_4]$	1215 (1215.4)	26.63 (26.66)	2.18 (2.19)	2.29 (2.30)	15.77 (15.80)	14.96 (15.01)
20	$Zr_2(C_{15}H_{12}N_2OCl)_2[S_6P_2(OC_6H_5)_4]$	1352 (1351.4)	34.60 (34.63)	2.55 (2.56)	2.05 (2.07)	14.17 (14.21)	13.45 (13.50)
21	$Zr_2(C_{15}H_{12}N_2OCl)_2[S_6P_2\{OC(CH_3)_2CH_2CH(CH_3)O\}_2]$	1220 (1211.4)	26.72 (26.75)	2.20 (2.21)	2.28 (2.31)	15.80 (15.85)	15.03 (15.06)
22	$Zr_2(C_{15}H_{12}N_2OCl)_2[S_6P_2\{OCH_2C(CH_3)_2CH_2O\}_2]$	1185 (1183.4)	25.30 (25.35)	2.12 (2.14)	2.35 (2.37)	16.18 (16.22)	15.37 (15.41)
23	$Zr_2(C_{15}H_{12}N_2OCl)_2[S_6P_2\{OC(CH_3)_2C(CH_3)_2O\}_2]$	1215 (1211.4)	26.71 (26.75)	2.17 (2.21)	2.30 (2.31)	15.82 (15.85)	15.02 (15.06)
24	$Zr_2(C_{15}H_{12}N_2OCl)_2[S_6P_2\{OCH_2CH_2CH(CH_3)O\}_2]$	1150 (1152.4)	23.89 (23.95)	2.06 (2.08)	2.42 (2.43)	16.63 (16.66)	15.80 (15.83)

### 3.1. IR Spectral Data

The IR spectra shows bands of medium intensity in the region of 3382–3328  $cm^{-1}$  due to  $\nu[N-H]$  stretching and vibrations and bands in the region of 1615–1580  $cm^{-1}$  due to the  $\nu[C=N]$  stretching vibration. In all the compounds the signal due to  $\nu[C=N]$  stretching is found to be shifted to the lower wave number in comparison to the spectra of free pyrazolines (at  $\sim 1654\text{ cm}^{-1}$ ), suggesting the involvement of imino nitrogen in coordination. The signal due to  $\nu(O-H)$  stretching originally present at  $\sim 3080\text{ cm}^{-1}$  in ligand is completely missing from the spectra of complexes. The bands observed in the region of 1042–1028 and 870–840  $cm^{-1}$  have been assigned to  $\nu[(P)-O-C]$  and  $\nu[P-O-(C)]$ , respectively. The  $\nu[P=S]$  mode may be characterized by the presence of bands in the region of 645–620  $cm^{-1}$  indicating the bidentate nature of dithiophosphate ligands. The bands present in the region of 533–510  $cm^{-1}$  may be ascribed to  $\nu[P-S]$  stretching modes. Appearance of two new bands (in comparison to

free ligand) in the region of 331–319 and 303–293  $cm^{-1}$  indicates the formation of  $\nu[Zr-S]$ . Splitting of bands into two regions indicates that two types of sulphur are present in the molecule, one is terminal sulphur and another is bridging sulphur. The appearance of bands in the region of 392–367 and 430–415  $cm^{-1}$  has been assigned to  $\nu[Zr-N]$  and  $\nu[Zr-O]$  stretching vibration. The data is summarized in Table 2.

### 3.2. $^1H$ NMR Spectra

The  $^1H$  NMR spectra of these new compounds have been recorded in  $CDCl_3$  exhibiting the characteristic signals. The aromatic protons of pyrazolines were observed as a complex pattern in the region  $\delta = 7.45\text{--}6.49$  ppm. The peak due to hydroxyl protons (originally present at  $\delta \sim 11.00$  ppm in free pyrazolines) is completely missing from the spectra of the complex suggesting the bonding through hydroxyl oxygen atom. The appearance of the peak at 5.32–4.75 ppm as a broad singlet could be assigned to N-H group (originally present at  $\delta = 5.4\text{--}5.0$  ppm) indicating

the non-involvement of –NH group. The skeletal protons of five membered rings are observed at  $\delta = 3.70$ – $3.12$  ppm as a triplet and  $\delta = 2.95$ – $1.02$  ppm could be assigned to –CH and –CH<sub>2</sub> group. Band at 5.54–

3.12 ppm could be for –OCH<sub>2</sub> and –OCH group and at 3.82– $3.00$  ppm may be due to –CH group. The skeletal protons of phenyl ring are observed at 7.28– $7.10$  ppm.

Table 2

IR spectral data (cm<sup>-1</sup>) for Zr<sub>2</sub>(C<sub>15</sub>H<sub>12</sub>N<sub>2</sub>OX)<sub>2</sub>[S<sub>6</sub>P<sub>2</sub>(OR)<sub>4</sub>]

No	$\nu$ [N–H]	$\nu$ [C=N]	$\nu$ [C–O]	$\nu$ [(P)–O–C]	$\nu$ [P–O–(C)]	$\nu$ [P=S]	$\nu$ [P–S]	Ring vib	$\nu$ [Zr–O]	$\nu$ [Zr–S]	$\nu$ [Zr–N]
1	3371	1585	–	1031	867	623	511	–	423	320 295S <sub>b</sub>	367
2	3375	1591	–	1033	856	633	523	–	416	324 298S <sub>b</sub>	372
3	3381	1609	–	1040	850	639	520	945	419	321 296S <sub>b</sub>	382
4	3369	1614	–	1029	860	625	517	956	420	329 302S <sub>b</sub>	390
5	3370	1608	–	1033	850	636	519	963	431	331 295S <sub>b</sub>	369
6	3379	1595	–	1041	853	641	521	954	428	321 298S <sub>b</sub>	374
7	3380	1588	–	1029	845	638	523	–	419	323 301S <sub>b</sub>	386
8	3371	1592	–	1034	849	642	530	–	416	325 294S <sub>b</sub>	379
9	3380	1603	–	1028	868	625	518	971	422	328 297S <sub>b</sub>	381
10	3379	1608	–	1030	854	631	529	963	426	324 298S <sub>b</sub>	372
11	3372	1583	–	1037	859	626	531	968	420	327 295S <sub>b</sub>	385
12	3376	1599	–	1041	870	642	516	945	429	319 298S <sub>b</sub>	377
13	3381	1600	1023	1038	842	645	518	–	421	329 303S <sub>b</sub>	389
14	3368	1611	1017	1031	857	633	525	–	417	320 301S <sub>b</sub>	390
15	3379	1610	1020	1035	863	635	533	956	419	330 295S <sub>b</sub>	381
16	3373	1590	1015	1042	870	638	511	963	431	327 297S <sub>b</sub>	392
17	3382	1598	1017	1029	860	631	516	961	427	324 294S <sub>b</sub>	387
18	3370	1610	1022	1030	851	638	519	953	423	329 297S <sub>b</sub>	376
19	3375	1615	–	1036	850	632	523	–	429	321 294S <sub>b</sub>	370
20	3380	1589	–	1039	869	637	525	–	425	320 297S <sub>b</sub>	379
21	3373	1593	–	1029	860	640	528	971	420	327 298S <sub>b</sub>	383
22	3378	1603	–	1040	852	632	521	964	416	328 303S <sub>b</sub>	389
23	3371	1598	–	1033	857	629	519	944	431	322 298S <sub>b</sub>	381
24	3377	1611	–	1039	870	639	525	959	422	325 297S <sub>b</sub>	290

### 3.3. $^{13}\text{C}$ NMR Spectra

The proton decoupled  $^{13}\text{C}$  NMR spectra show the presence of all important signals with reference to dithiophosphates and pyrazolines. The signals observed in the region  $\delta = 135.20\text{--}123.30$  ppm as a complex pattern could be assigned to aromatic carbon atoms<sup>233</sup>. The signal observed at  $\delta = 167.75\text{--}162.35$  ppm due to imino carbon of C=N has shifted downfield in comparison to spectra of free pyrazolines ( $\delta = 143.50\text{--}142.80$  ppm), suggesting the involvement of imino nitrogen in coordination. The peaks due to  $-\text{CH}$  and  $-\text{CH}_2$  are observed at 46.15–41.08 ppm. The peaks due to  $-\text{OC}$  and  $-\text{OCH}$  group of dithiophosphates are observed at 90.15–91.26 and 77.35–75.29 ppm, respectively.

### 3.4. $^{31}\text{P}$ NMR Data

In  $^{31}\text{P}$  NMR spectra of these compounds only one signal has been observed for the phosphorus atom. The  $^{31}\text{P}$  NMR signals of Zr dichlorodithio-compounds are observed at  $\delta = 90$  ppm, while the  $^{31}\text{P}$  NMR signals of synthesized Zr compounds are obtained at  $\delta = 107.7\text{--}93$  ppm. The downfield shifting of the signal at  $\sim 15.0$  ppm due to dithiophosphate phosphorus atom confirms the bidentate nature of the ligands. Despite the presence of two phosphorus atoms, only one signal is obtained, indicating similar environment for both phosphorus atoms. The NMR ( $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$ ) data are summarized in Table 3.

Table 3

NMR data for  $\text{Zr}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OX})_2[\text{S}_6\text{P}_2(\text{OR})_4]$ 

No.	Compound	Chemical shift ( $\delta$ ), ppm		
		$^1\text{H}$ NMR	$^{13}\text{C}$ NMR	$^{31}\text{P}$ NMR
1	2	3	4	5
1	$\text{Zr}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OH})_2[\text{S}_6\text{P}_2(\text{OCH}_2\text{CH}_2\text{CH}_3)_4]$	7.45–6.80(m, 18H, Ar-H) 0.96(t, 12H, $-\text{CH}_3$ ) 5.17(m, 8H, $-\text{OCH}_2-$ ) 1.70(m, 8H, $-\text{CH}_2$ ) 5.21(s, 2H, $-\text{NH}$ ) 3.19(t, 2H, $-\text{CH}$ ) 2.19(d, 4H, $-\text{CH}_2$ )	–	103.00
2	$\text{Zr}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OH})_2[\text{S}_6\text{P}_2(\text{OC}_6\text{H}_5)_4]$	7.74–6.95(m, 18H, Ar-H) 7.25(s, 20H, $-\text{C}_6\text{H}_5$ ) 4.82(s, 2H, $-\text{NH}$ ) 3.21(t, 2H, $-\text{CH}$ ) 2.54(d, 4H, $-\text{CH}_2$ )	–	93.00
3	$\text{Zr}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OH})_2[\text{S}_6\text{P}_2\{\text{OC}(\text{CH}_3)_2\text{CH}_2\text{CH}(\text{CH}_3)\text{O}\}_2]$	7.64–6.90(m, 18H, Ar-H) 2.97–2.60(m, 22H, $-\text{CH}_3$ , $\text{CH}_2$ ) 5.54(m, 2H, $-\text{OCH}$ ) 4.64(s, 2H, $-\text{NH}$ ) 3.52(t, 2H, $-\text{CH}$ ) 2.18(d, 4H, $-\text{CH}_2$ )	91.45( $-\text{OC}$ , dtp) 24.45( $-\text{CH}_3$ , dtp) 77.01( $-\text{OCH}$ , dtp) 26.32( $-\text{CH}_2$ , dtp) 136.72(Ar-C) 167.75(C=N) 43.02( $-\text{CH}$ ) 25.83( $-\text{CH}_2$ )	102.20
4	$\text{Zr}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OH})_2[\text{S}_6\text{P}_2\{\text{OCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{O}\}_2]$	7.64–6.83(m, 18H, Ar-H) 0.97(s, 12H, $-\text{CH}_3$ ) 5.17(d, 8H, $-\text{OCH}_2-$ ) 4.76(s, 2H, $\text{NH}$ ) 3.43(t, 2H, $-\text{CH}$ ) 2.19(d, 4H, $-\text{CH}_2$ )	21.87( $\text{CH}_3$ , dtp) 31.82(qC, dtp) 76.32( $-\text{OCH}_2$ , dtp) 136.83(Ar-C) 165.51(C=N) 42.92(CH) 27.63( $\text{CH}_2$ )	97.80
5	$\text{Zr}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OH})_2[\text{S}_6\text{P}_2\{\text{OC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{O}\}_2]$	1.12(s, 24H, $-\text{CH}_3$ ) 7.69–6.78(m, 18H, ArH) 4.75(s, 2H, $-\text{NH}$ ) 3.02(t, 2H, $-\text{CH}$ ) 2.05(d, 4H, $-\text{CH}_2$ )	23.95( $\text{CH}_3$ , dtp) 90.52(OC, dtp) 136.61–122.14(Ar-C) 165.24(C=N) 42.18(CH) 27.78( $\text{CH}_2$ )	104.50

Table 3 (continued)

1	2	3	4	5
6	$Zr_2(C_{15}H_{12}N_2OH)_2[S_6P_2\{OCH_2CH_2CH(CH_3)O\}_2]$	2.46–1.05(m, 10H, $-CH_3$ , $CH_2$ ) 4.42–3.15(m, 6H, $-OCH_2$ , OCH) 7.80–6.92(m, 18H, ArH) 4.96(s, 2H, $-NH$ ) 3.27(t, 2H, $-CH$ ) 2.21(d, 4H, $-CH_2$ )	23.81( $CH_3$ , dtp) 76.12( $-OCH$ , $OCH_2$ , dtp) 135.25–123.24(Ar–C) 163.21(C=N) 43.05(CH) 27.51( $CH_2$ )	103.90
7	$Zr_2(C_{15}H_{12}N_2OCH_3)_2[S_6P_2(OCH_2CH_2CH_3)_4]$	7.73–6.72(m, 16H, Ar–H) 0.97(t, 12H, $-CH_3$ ) 5.07(m, 8H, $-OCH_2-$ ) 1.24(m, 8H, $-CH_2$ ) 4.97(s, 2H, NH) 3.22(t, 2H, $-CH$ ) 2.15(d, 4H, $-CH_2$ ) 1.02(s, 6H, $CH_3$ )	–	93.60
8	$Zr_2(C_{15}H_{12}N_2OCH_3)_2[S_6P_2(OC_6H_5)_4]$	7.67–6.57(m, 16H, Ar–H) 7.26(s, 20H, $-C_6H_5$ ) 5.02(s, 2H, $-NH$ ) 3.20(t, 2H, $-CH$ ) 2.27(d, 4H, $-CH_2$ ) 0.98(s, 6H, $-CH_3$ )	–	99.00
9	$Zr_2(C_{15}H_{12}N_2OCH_3)_2[S_6P_2\{OC(CH_3)_2CH_2CH(CH_3)O\}_2]$	7.56–6.71(m, 16H, Ar–H) 2.47–2.17(m, 22H, $-CH_3$ , $CH_2$ ) 4.96–4.58(m, 2H, $-OCH$ ) 5.10(s, 2H, $-NH$ ) 3.21(t, 2H, $-CH$ ) 2.03(d, 4H, $CH_2$ ) 1.05(s, 6H, $-CH_3$ )	91.26( $-OC$ , dtp) 25.81( $-CH_3$ , dtp) 76.75( $-OCH$ , dtp) 23.34( $-CH_2$ , dtp) 135.75(Ar–C) 163.72(C=N) 42.31( $-CH$ ) 23.91( $-CH_2$ ) 13.51( $-CH_3$ )	105.00
10	$Zr_2(C_{15}H_{12}N_2OCH_3)_2[S_6P_2\{OCH_2C(CH_3)_2CH_2O\}_2]$	7.71–6.49(m, 16H, Ar–H) 0.97(s, 12H, $-CH_3$ ) 4.23(d, 8H, $-OCH_2-$ ) 5.17(s, 4H, NH) 3.71(t, 2H, $-CH$ ) 2.03(d, 8H, $-CH_2$ ) 0.95(s, 6H, $-CH_3$ )	22.30( $CH_3$ , dtp) 31.31(q C, dtp) 75.29( $-OCH_2$ , dtp) 136.39(Ar–C) 165.75(C=N) 43.17(CH) 26.37( $CH_2$ ) 13.47( $-CH_3$ )	104.60
11	$Zr_2(C_{15}H_{12}N_2OCH_3)_2[S_6P_2\{OC(CH_3)_2C(CH_3)_2O\}_2]$	1.32(s, 24H, $-CH_3$ ) 7.57–6.68(m, 16H, ArH) 4.83(s, 2H, $-NH$ ) 3.35(t, 2H, $-CH$ ) 2.15(d, 4H, $-CH_2$ ) 0.97(s, 6H, $-CH_3$ )	26.12( $CH_3$ , dtp) 91.95( $OC$ , dtp) 136.36–123.42(Ar–C) 166.85(C=N) 46.15(CH) 25.15( $CH_2$ ) 13.36( $-CH_3$ )	105.95
12	$Zr_2(C_{15}H_{12}N_2OCH_3)_2[S_6P_2\{OCH_2CH_2CH(CH_3)O\}_2]$	2.05–1.10(m, 10H, $-CH_3$ , $CH_2$ ) 4.56–3.15(m, 6H, $-OCH_2$ , OCH) 7.60–6.75(m, 16H, ArH) 5.15(s, 2H, $-NH$ ) 2.76(t, 2H, $-CH$ ) 1.97(d, 4H, $-CH_2$ ) 1.02(s, 6H, $-CH_3$ )	24.29( $CH_3$ , dtp) 76.54( $-OCH$ , $OCH_2$ , dtp) 136.29–123.65(Ar–C) 165.25(C=N) 42.92(CH) 27.29( $CH_2$ ) 13.54( $-CH_3$ )	101.76

Table 3 (continued)

1	2	3	4	5
13	$\text{Zr}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}_2\text{CH}_3)_2[\text{S}_6\text{P}_2(\text{OCH}_2\text{CH}_2\text{CH}_3)_4]$	7.82–6.95(m, 16H, Ar–H) 1.05(t, 12H, –CH <sub>3</sub> ) 5.10(m, 8H, –OCH <sub>2</sub> –) 1.45(m, 8H, –CH <sub>2</sub> ) 5.07(s, 2H, NH) 3.76(t, 2H, –CH) 2.19(d, 4H, –CH <sub>2</sub> ) 3.46(s, 6H, OCH <sub>3</sub> )	–	93.50
14	$\text{Zr}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}_2\text{CH}_3)_2 [\text{S}_6\text{P}_2(\text{OC}_6\text{H}_5)_4]$	7.85–6.90(m, 16H, Ar–H) 7.28(s, 20H, –C <sub>6</sub> H <sub>5</sub> ) 4.95(s, 2H, –NH) 3.09(t, 2H, –CH) 2.02(d, 4H, –CH <sub>2</sub> ) 3.39(s, 6H, OCH <sub>3</sub> )	–	98.90
15	$\text{Zr}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}_2\text{CH}_3)_2[\text{S}_6\text{P}_2\{\overline{\text{OC}(\text{CH}_3)_2\text{CH}_2\text{CH}(\text{CH}_3)\text{O}}\}_2]$	7.75–6.81(m, 16H, Ar–H) 2.30–1.95(m, 22H, –CH <sub>3</sub> , CH <sub>2</sub> ) 4.56–4.20(m, 2H, –OCH) 5.02(s, 2H, –NH) 3.10(t, 2H, –CH) 2.17(d, 4H, CH <sub>2</sub> ) 3.32(s, 6H, OCH <sub>3</sub> )	91.95(–OC, dtp) 24.75(–CH <sub>3</sub> , dtp) 76.43(–OCH, dtp) 23.15(–CH <sub>2</sub> , dtp) 136.34(Ar–C) 167.10(C=N) 43.12(–CH) 24.19(–CH <sub>2</sub> ) 57.49(–OCH <sub>3</sub> )	100.60
16	$\text{Zr}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}_2\text{CH}_3)_2 [\text{S}_6\text{P}_2\{\overline{\text{OCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{O}}\}_2]$	7.50–6.85(m, 16H, Ar–H) 1.21(s, 12H, –CH <sub>3</sub> ) 4.12(d, 8H, –OCH <sub>2</sub> –) 5.32(s, 2H, NH) 3.12(t, 2H, –CH) 2.32(d, 4H, –CH <sub>2</sub> ) 3.45(s, 6H, OCH <sub>3</sub> )	22.75(CH <sub>3</sub> , dtp) 32.32(q C, dtp) 75.85(d, –OCH <sub>2</sub> , dtp) 137.30(Ar–C) 167.26(C=N) 42.84(CH) 27.16(CH <sub>2</sub> ) 57.24(–OCH <sub>3</sub> )	97.95
17	$\text{Zr}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}_2\text{CH}_3)_2[\text{S}_6\text{P}_2\{\overline{\text{OC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{O}}\}_2]$	1.27(s, 24H, –CH <sub>3</sub> ) 7.76–6.93(m, 16H, ArH) 5.17(s, 2H, –NH) 3.21(t, 2H, –CH) 2.03(d, 4H, –CH <sub>2</sub> ) 3.64(s, 6H, OCH <sub>3</sub> )	23.12(CH <sub>3</sub> , dtp) 90.15(OC, dtp) 136.12–123.45(Ar–C) 165.56(C=N) 41.08(CH) 27.09(CH <sub>2</sub> ) 57.20(–OCH <sub>3</sub> )	107.70
18	$\text{Zr}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}_2\text{CH}_3)_2[\text{S}_6\text{P}_2\{\overline{\text{OCH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{O}}\}_2]$	2.75–1.32(m, 10H, –CH <sub>3</sub> , CH <sub>2</sub> ) 4.09–3.76(m, 6H, –OCH <sub>2</sub> , OCH) 7.79–6.65(m, 16H, ArH) 5.21(s, 2H, –NH) 3.34(t, 2H, –CH) 2.19(d, 4H, –CH <sub>2</sub> ) 3.60(s, 6H, OCH <sub>3</sub> )	22.28(CH <sub>3</sub> , dtp) 76.10(–OCH, OCH <sub>2</sub> , dtp) 136.36–123.35(Ar–C) 162.35(C=N) 42.34(CH) 27.87(CH <sub>2</sub> ) 56.89(–OCH <sub>3</sub> )	103.70
19	$\text{Zr}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OCl})_2[\text{S}_6\text{P}_2(\text{OCH}_2\text{CH}_2\text{CH}_3)_4]$	7.75–6.56(m, 16H, Ar–H) 1.03(t, 12H, –CH <sub>3</sub> ) 5.34(m, 8H, –OCH <sub>2</sub> –) 1.60(m, 8H, –CH <sub>2</sub> ) 5.21(s, 2H, NH) 3.45(t, 2H, –CH) 2.15(d, 4H, –CH <sub>2</sub> )	–	93.30

Table 3 (continued)

1	2	3	4	5
20	$\text{Zr}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OCl})_2[\text{S}_6\text{P}_2(\text{OC}_6\text{H}_5)_4]$	7.85–6.70(m, 16H Ar–H) 7.10(s, 20H, –C <sub>6</sub> H <sub>5</sub> ) 4.97(s, 2H, –NH) 3.10(t, 2H, –CH) 2.15(d, 4H –CH <sub>2</sub> )	–	105.50
21	$\text{Zr}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OCl})_2[\text{S}_6\text{P}_2\{\overline{\text{OC}(\text{CH}_3)_2\text{CH}_2\text{CH}(\text{CH}_3)\text{O}}\}_2]$	7.65–6.80(m, 16H, Ar–H) 2.40–1.59(m, 22H, –CH <sub>3</sub> , CH <sub>2</sub> ) 4.70–4.15(m, 2H, –OCH) 5.07(s, 2H, –NH) 3.12(t, 2H, –CH) 2.21(d, 4H, CH <sub>2</sub> )	91.83(–OC, dtp) 23.72(–CH <sub>3</sub> , dtp) 77.35(–OCH, dtp) 24.62(–CH <sub>2</sub> , dtp) 136.73(Ar–C) 167.48(C=N) 42.73(–CH) 27.32(–CH <sub>2</sub> )	101.50
22	$\text{Zr}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OCl})_2[\text{S}_6\text{P}_2\{\overline{\text{OCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{O}}\}_2]$	7.75–6.65(m, 16H, Ar–H) 1.07(s, 12H, –CH <sub>3</sub> ) 4.13(d, 8H, –OCH <sub>2</sub> –) 4.75(s, 2H, NH) 3.23(t, 2H, –CH) 2.10(d, 4H, –CH <sub>2</sub> )	22.59(CH <sub>3</sub> , dtp) 36.16(q C, dtp) 76.28(–OCH <sub>2</sub> , dtp) 135.34(Ar–C) 167.56(C=N) 42.65(CH) 27.30(CH <sub>2</sub> )	95.00
23	$\text{Zr}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OCl})_2[\text{S}_6\text{P}_2\{\overline{\text{OC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{O}}\}_2]$	1.35(s, 24H, –CH <sub>3</sub> ) 7.76–6.96(m, 16H, ArH) 4.76(s, 2H, –NH) 3.15(t, 2H, –CH) 2.10(d, 4H, –CH <sub>2</sub> )	23.59(CH <sub>3</sub> , dtp) 91.85(OC, dtp) 137.75–123.30(Ar–C) 167.13(C=N) 43.23(CH) 27.55(CH <sub>2</sub> )	105.00
24	$\text{Zr}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OCl})_2[\text{S}_6\text{P}_2\{\overline{\text{OCH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{O}}\}_2]$	2.15–1.23(m, 10H, –CH <sub>3</sub> , CH <sub>2</sub> ) 4.10–3.90(m, 6H, –OCH <sub>2</sub> , OCH) 7.45–6.96(m, 16H, ArH) 5.07(s, 2H, –NH) 3.00(t, 2H, –CH) 2.02(d, 4H, –CH <sub>2</sub> )	23.45(CH <sub>3</sub> , dtp) 76.29(–OCH, OCH <sub>2</sub> , dtp) 136.65–123.45(Ar–C) 165.15(C=N) 43.10(CH) 27.29(CH <sub>2</sub> )	93.50

Table 4

FAB Mass spectral data for  $\text{Zr}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OX})_2[\text{S}_6\text{P}_2(\text{OR})_4]$ 

No.	Compound	m/z	-py	-2py	-dtp	-2dtp
3	$\text{Zr}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OH})_2[\text{S}_6\text{P}_2\{\overline{\text{C}(\text{CH}_3)_2\text{CH}_2\text{CH}(\text{CH}_3)\text{O}}\}]$	1150	913	676	939	728
9	$\text{Zr}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OCH}_3)_2[\text{S}_6\text{P}_2\{\overline{\text{OC}(\text{CH}_3)_2\text{CH}_2\text{CH}(\text{CH}_3)\text{O}}\}]$	1175	924	673	964	753
15	$\text{Zr}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}_2\text{CH}_3)_2[\text{S}_6\text{P}_2\{\overline{\text{OC}(\text{CH}_3)_2\text{CH}_2\text{CH}(\text{CH}_3)\text{O}}\}]$	1255	988	721	1044	833
21	$\text{Zr}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OCl})_2[\text{S}_6\text{P}_2\{\overline{\text{OC}(\text{CH}_3)_2\text{CH}_2\text{CH}(\text{CH}_3)\text{O}}\}]$	1220	949	678	1009	798

## 3.5. FAB Mass Spectra

The molecular weights of the synthesized complexes have been determined by FAB mass spectra. The molecular ion peak clearly indicates the dimeric nature of the complexes. FAB mass spectra of all the possible compounds have been carried out but for convenience of presentation and discussion, major

fragments of compound number 3, 9, 15, and 21 (compounds with different substituted pyrazoline ligands in each series has been selected) have been given (Table 4).

## 3.6. XRD and SEM Studies

These complexes have been examined for crystalline/amorphous nature through XRD. The



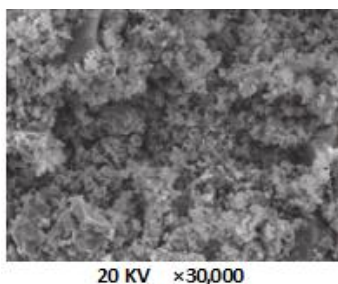
morphology of the complexes was studied by employing XRD, which shows that all the complexes are amorphous solid. Broadening of diffraction peaks was used to estimate the average domain size in terms of “Debye Scherrer” expression.

$$\text{Particle size} = D = \frac{0.9\lambda}{b \cos \theta}$$

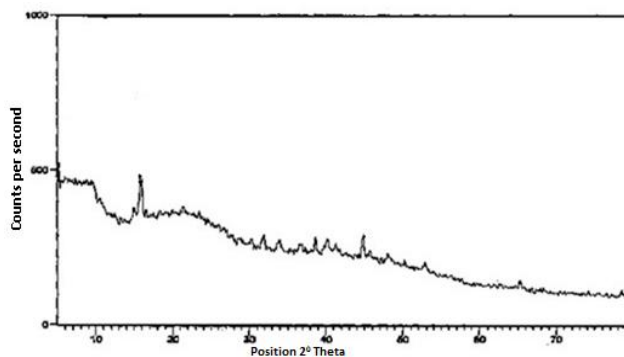
where  $D$  is the average nanocrystal domain diameter, Å;  $\beta$  is corrected band broadening (full width at half maxima);  $\lambda$  is the X-ray wave length (1.5418 Å);  $\theta$  is the diffraction angle.

The value of full width at half maximum intensity ( $\beta$ ) and corresponding diffraction angle ( $\theta$ ) is calculated using Fig. 2. The average diameter thus obtained was found to be in the range of 20–30 nm. SEM studies showed that the particle size ranged to about 20 nm. The mean diameter of the different particles synthesized is summarized in Table 5. SEM image and X-ray diffractogram of  $\text{Zr}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OR})_2[\text{S}_6\text{P}_2\{\text{OC}(\text{CH}_3)_2\text{CH}_2\text{CH}(\text{CH}_3)\text{O}\}]$  are shown in Figs. 1 and 2, respectively.

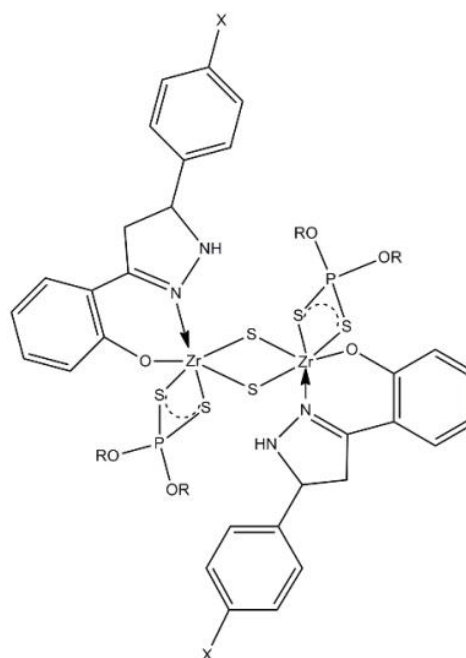
On the basis of these studies and available literature octahedral geometry may be proposed for Zr(IV) complexes (Fig. 3).



**Fig. 1.** SEM image  
 $\text{Zr}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OH})_2[\text{S}_6\text{P}_2\{\text{OC}(\text{CH}_3)_2\text{CH}_2\text{CH}(\text{CH}_3)\text{O}\}]$



**Fig. 2.** X-ray diffractogram  
 of  $\text{Zr}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OH})_2[\text{S}_6\text{P}_2\{\text{OC}(\text{CH}_3)_2\text{CH}_2\text{CH}(\text{CH}_3)\text{O}\}]$



**Fig. 3.** Proposed structure  
 for  $\text{Zr}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OX})_2[\text{S}_6\text{P}_2(\text{OR})_4]$

Table 5

Average diameter of particles determined by XRD and SEM

No.	Compound	$2\theta$	Average diameter determined by XRD, nm	Average diameter determined by SEM, nm
3	$\text{Zr}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OH})_2[\text{S}_6\text{P}_2\{\text{C}(\text{CH}_3)_2\text{CH}_2\text{CH}(\text{CH}_3)\text{O}\}]$	40	27	17
9	$\text{Zr}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OCH}_3)_2[\text{S}_6\text{P}_2\{\text{OC}(\text{CH}_3)_2\text{CH}_2\text{CH}(\text{CH}_3)\text{O}\}]$	52	33	12
15	$\text{Zr}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}_2\text{CH}_3)_2[\text{S}_6\text{P}_2\{\text{OC}(\text{CH}_3)_2\text{CH}_2\text{CH}(\text{CH}_3)\text{O}\}]$	42	23	25
21	$\text{Zr}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OCl})_2[\text{S}_6\text{P}_2\{\text{OC}(\text{CH}_3)_2\text{CH}_2\text{CH}(\text{CH}_3)\text{O}\}]$	44	19	15

## 4. Conclusions

The present study describes the synthesis of a series of complexes of dithiophosphate and pyrazolines with zirconium(IV). The dithiophosphate ligand and pyrazolines behave as bidentate ligand. Elemental analysis data indicate the dimeric nature of the complexes. Octahedral geometry is proposed for the synthesized Zr(IV) complexes. This class of compound may prove useful precursor for the formation of ZrS<sub>2</sub> by sulphide sol gel due to reduced acidity of metal centre. Further studies regarding sulphide sol gel of these derivatives are under investigation.

## References

- [1] Peng Y., Krungleviciute V., Eryazici I. *et al.*: J. Am. Chem. Soc., 2013, **135**, 11887. <https://doi.org/10.1021/ja4045289>
- [2] Lee Y., Kim J., Ahm W.: Korean J. Chem. Eng., 2013, **30**, 1667. <https://doi.org/10.1007/s11814-013-0140-6>
- [3] Long J., Yaghi O.: Chem. Soc. Rev., 2009, **38**, 1213. <https://doi.org/10.1039/b903811f>
- [4] Sharma S., Jain A., Saxena S.: J. Korean Chem. Soc., 2012, **56**, 440. <https://doi.org/10.5012/jkcs.2012.56.4.440>
- [5] Bhatt S., Kumari R., Sharma N., Chaudhary S.: Ind. J. Chem. A, 2004, **43**, 778.
- [6] Grafov A., Mazurenko E., Battiston G. *et al.*: J. Phys. IV France, 1995, **5**, C5-497. <https://doi.org/10.1051/jphyscol:1995557>
- [7] Thomas R., Milanov A., Bhakta R. *et al.*: Chem. Vap. Deposition, 2006, **12**, 295. <https://doi.org/10.1002/cvde.200506481>
- [8] Pasko S., Abrutis A., Hubert-Pfalzgraf L.: Mater. Lett., 2005, **59**, 261. <https://doi.org/10.1016/j.matlet.2004.07.061>
- [9] Banerjee M., Seidel R., Winter M. *et al.*: Dalton Trans., 2014, **43**, 2384. <https://doi.org/10.1039/C3DT52335G>
- [10] Fleeting K., O'Brien P., Jones A. *et al.*: J. Chem. Soc., Dalton Trans., 1999, 2853. <https://doi.org/10.1039/A901666J>
- [11] Malghe Y., Prabhu R., Raut R.: Acta. Pol. Pharm., 2009, **66**, 45.
- [12] Tret'yakova I., Chemii V., Tomachinskaya L. *et al.*: Theor. Exp. Chem., 2006, **42**, 175. <https://doi.org/10.1007/s11237-006-0034-3>
- [13] Bajju G., Devi G., Kotcha S. *et al.*: Bioinorg. Chem. Appl., 2013, **2013**. <https://doi.org/10.1155/2013/903616>
- [14] Kostova I., Momekov G.: Eur. J. Med. Chem., 2006, **41**, 717. <https://doi.org/10.1016/j.ejmech.2006.03.020>
- [15] Liu K., Wu Q., Mu X. *et al.*: Polyhedron, 2013, **52**, 222. <https://doi.org/10.1016/j.poly.2012.09.044>
- [16] El-Zoghbi I., Whyehorne T., Schaper F.: Dalton Trans., 2013, **42**, 9376. <https://doi.org/10.1039/C2DT31761C>
- [17] Lenton T., Bercaw J., Panchenko V. *et al.*: J. Am. Chem. Soc., 2013, **135**, 10710. <https://doi.org/10.1021/ja403170u>
- [18] Saha T., Chakraborty D.: Polym. Int., 2013, **62**, 1507. <https://doi.org/10.1002/pi.4450>
- [19] Whitelaw E., Jones M., Mahon M., Kociok-Kohn G.: Dalton Trans., 2009, **41**, 9020. <https://doi.org/10.1039/b911545e>
- [20] Manicone P., Iommetti P., Raffaelli L.: J. Dentistry, 2007, **35**, 819. <https://doi.org/10.1016/j.jdent.2007.07.008>
- [21] Denry I., Kelly R.: Dent. Mater., 2008, **24**, 299. <https://doi.org/10.1016/j.dental.2007.05.007>
- [22] Yarita T., Aoyagi Y., Sasai H. *et al.*: Anal. Sci., 2013, **29**, 213.
- [23] Saxena S., Chakravarty R., Kumar Y. *et al.*: Separ. Sci. Technol., 2013, **48**, 2108. <https://doi.org/10.1080/01496395.2013.765472>
- [24] Li W., Deng Q., Fang G. *et al.*: J. Mater. Chem. B, 2013, **1**, 1947. <https://doi.org/10.1039/c3tb20127a>
- [25] Kara A., Tobyn M., Stevens R.: J. Eur. Ceramic Soc., 2004, **24**, 3091. <https://doi.org/10.1016/j.jeurceramsoc.2003.11.004>
- [26] Piconi C., Maccauro G.: Biomaterials, 1999, **20**, 25. [https://doi.org/10.1016/S0142-9612\(98\)00010-6](https://doi.org/10.1016/S0142-9612(98)00010-6)
- [27] ISO TC 150/SC 1. Implants for surgery ceramic materials based on yttria-stabilized tetragonal zirconia (Y-TZP). ISO/DIS13356, 1995.
- [28] von Schewelov T., Sanzen L., Onsten I. *et al.*: J. Bone Joint Surg. Br., 2005, **87**, 1631. <https://doi.org/10.1302/0301-620X.87B12.16873>
- [29] Li L., Wang H., Fang X. *et al.*: Energ. Environ. Sci., 2011, **7**, 2586. <https://doi.org/10.1039/c1ee01286j>
- [30] Jang J., Jeong S., Seo J. *et al.*: J. Am. Chem. Soc., 2011, **133**, 7636. <https://doi.org/10.1021/ja200400n>
- [31] Srivastava T.: J. Ind. Chem. Soc., 1981, **58**, 710.
- [32] Raman N., Raja S., Sakthivel A.: J. Coord. Chem., 2009, **62**, 691. <https://doi.org/10.1080/00958970802326179>
- [33] Vogel A.: A Text Book of Qualitative Inorganic Analysis. ELBS Longman Group Ltd, London 1998.
- [34] Sharma T., Saxena V., Reddy N.: Acta Chim., 1977, **93**, 4.
- [35] Chauhan H., Chauhan B., Srivastava G., Mehrotra R.: Phosphorus Sulphur, 1983, **15**, 99. <https://doi.org/10.1080/03086648308073283>

Received: November 17, 2017 / Revised: December 12, 2017 / Accepted: May 22, 2018

## СИНТЕЗ І ХАРАКТЕРИСТИКА ЗМІШАНИХ ЛІГАНДНИХ КОМПЛЕКСІВ ЦИРКОНІЮ(IV) З СУЛЬФУР-, НІТРОГЕН- ТА ОКСИГЕН-ДОНОР ЛІГАНДАМИ

**Анотація.** Досліджено новий спосіб синтезу наномірних змішаних лігандних комплексів Zr(IV) за реакцією хлориду цирконію(IV) з 3(2'-гідроксифеніл)-5-(4-заміщеним феніл) піразолінами та солями дитіофосфату амонію, який після оброблення H<sub>2</sub>S діє як прекурсор для ZrS<sub>2</sub>. За допомогою рентгено-дифракційного аналізу досліджено кристалічну/аморфну природу синтезованих комплексів. Визначено, що всі комплекси є аморфними твердими речовинами. При визначенні молекулярної маси та проведенні елементарного аналізу і спектроскопічних досліджень (ІЧ, <sup>1</sup>H ЯМР, <sup>31</sup>P ЯМР) доведена димерна природа комплексів, в яких дитіофосфат та піразолін є бідентатним лігандом. З використанням скануючої електронної мікроскопії показано, що частинки знаходяться в нанодіапазоні. Запропоновано координаційне число 6 для цирконію з восьмигранною геометрією.

**Ключові слова:** цирконій(IV), дитіофосфат, піразолін, наночастинка, соль-гель.