



Research Article

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O,O'-Ditolyl/dibenzyl dithiophosphates of copper(II) and copper(I)

K. R. Sharma^a and S. K. Pandey^b

^aDepartment of Chemistry, IEC University, Baddi, Himachal Pradesh, India

^bDepartment of Chemistry, Baba Saheb Ambedkar Road, University of Jammu, Jammu(J&K), India

ABSTRACT

Copper(II) bisditolyl/dibenzyl dithiophosphates $[(RO)_2PS_2]_2Cu$ ($R = o-, m-$ or $p-CH_3C_6H_4-$ or $C_6H_5CH_2-$) were precipitated from aqueous solution of $CuSO_4 \cdot 5H_2O$ with sodium ditolyl/dibenzyl phosphorodithioates, $(RO)_2PS_2Na$. These copper(II) complexes were reduced to copper(I) dithiophosphates by methanol corresponding to $[(RO)_2PS_2]Cu$ in dichloromethane. The copper(I) complexes were then reacted with phosphorus and nitrogen donor ligands in methanol, which resulted in the formation of complexes $[(RO)_2PS_2]Cu \cdot nL$ [$n = 2, L = P(C_6H_5)_3$ and $n = 1, L = C_{12}H_8N_2$] in 1:2 molar ratio. These compounds have been characterized by elemental analysis, molecular weight determination, magnetic moment, electronic, IR, and NMR (1H , ^{13}C and ^{31}P) spectroscopic measurements. Square planar geometry for the copper(II) complexes and tetrahedral geometry for the copper(I) complexes are suggested.

Key words: Dithiophosphates; Phosphordithioates, Phosphorous compounds, sulfur ligands.

INTRODUCTION

Dialkylphosphonates $[(RO)_2PO]$, dialkylthiophosphonates $[(RS)_2PO]$, dialkyldithiophosphates $[(OR)_2PS_2]$, and *O,O'*-alkylenedithiophosphates $[OGOPS_2]$ are important phosphorus-sulfur containing ligands and have attracted wide attention in academia in particular for providing various bonding aspects with metals and metalloids¹⁻⁴. A variety of complexes have been reported in which the dithiophosphate ligands behave, normally, in a bidentate manner⁵⁻¹¹. However, some compounds with less common monodentate linkages have also been described^{12, 13}. It is pertinent to mention that these dithiophosphato derivatives find extensive applications in various fields, like agriculture¹⁴⁻¹⁶, industries¹⁷⁻¹⁸, analytical studies¹⁹⁻²⁰, lubrication industries²¹ and plastic industries²²⁻²³. They also show biological activity *i.e.* antitumor properties²⁴. Amongst the 3d metals copper occupies an interesting position, acting like a bridge between main group and transition metals. The chemistry of copper(II) and copper(I) complexes with 1, 1'-dithio ligands is well-established in the literature²⁵⁻²⁹. It has a strong tendency to form covalent bonds with soft ligands (such as P and S donor atoms)²⁹. The *O,O'*-dialkyldithiophosphato derivatives of copper(II) and copper(I) have been described and the equilibrium between the two types of derivatives has also been studied.²⁸ Recently, the synthesis and characterization of ditolyldithiophosphates added a new development in the area of dithiophosphate chemistry³⁰⁻³¹. These new ditolyldithiophosphate ligands appear to be potential chelating ligands to the metals, metalloids and nonmetals akin to the dialkyl- and alkylenedithiophosphate ligands. Some metal complexes with the ditolyl/dibenzyl dithiophosphate ligands have also been reported^{23, 32-39}. Some ditolyldithiophosphates have also demonstrated important applications which are highlighted in literature use as rubber vulcanizers⁴⁰, heat and light stabilizers⁴¹, polymerization catalysts⁴², and acaricides⁴³. Keeping the view of interesting applications of the dithiophosphates in general and paucity of work on copper dithiophosphates, it is

thought worthy to investigate the chemistry of ditolyldithiophosphates, particularly, with copper. We report herein on the synthesis and characterization of new copper(II) and copper(I) dithiophosphates corresponding $[(RO)_2PS_2]_2Cu$ (**1-4**), $[(RO)_2PS_2]Cu$ (**5-8**), $[(RO)_2PS_2]Cu.nL$ ($n = 2, L = P(C_6H_5)_3$ (**9-12**) and $n = 1, L = C_{12}H_8N_2$ (**13-16**); $R = o-, m-$ or $p-CH_3C_6H_4-$ or $C_6H_5CH_2-$).

EXPERIMENTAL SECTION

Methanol and dichloromethane were dried by the standard method prior to their use. Sodium salt of *O,O'*-ditolyl/dibenzyl dithiophosphoric acid have been prepared by the literature method²⁹⁻³⁰. IR spectra were recorded in KBr pellets in the range of 4000–400 cm^{-1} on a Perkin Elmer-557 spectrophotometer. The NMR (1H , ^{13}C and ^{31}P) spectra were recorded in $CDCl_3$ on a Bruker DRX 500 (120 MHz) using trimethylsilane, $(CH_3)_3Si$ as internal reference for 1H and ^{13}C and 85% H_3PO_4 as external reference for ^{31}P NMR. The NMR and UV-Vis studies were conducted at Sophisticated Analytical Instrumentation Faculty (SAIF) University of Panjab, Chandigarh and Indian Institute of Integrative Medicine (IIIM), Jammu. Sulfur was estimated as barium sulfate according to the Messenger's method and copper was estimated as gravimetrically as copperdipyridinedithiocyanate, $[Cu(C_5H_5N)_2(SCN)_2]$ (dark green). Elemental analyses (C, H and N) and magnetic susceptibility were conducted using a Leco CHNS-932 analyzer and by VSM (vibrational sample magnetometer) method, respectively, at Central Drug Research Institute (CDRI), Lucknow.

Synthesis of complexes

Synthesis of $[(o-CH_3C_6H_4O)_2PS_2]_2Cu$ (**1**)

An aqueous solution of $CuSO_4 \cdot 5H_2O$, (0.56 g, 2.50 mmol) was added dropwise to the aqueous solution of sodium phosphodithioate, $(o-CH_3C_6H_4O)_2PS_2Na$, (1.50 g, 4.50 mmol) at the room temperature. The color of the reaction mixture changed immediately to dark brown. The dark brown precipitates were separated by filtration on sintered glass crucible (G-4), which was given several washing first with water followed by ethanol. Finally, the complex was dried at 90 °C for 2-3 hours, which afforded the complex $[(o-CH_3C_6H_4O)_2PS_2]_2Cu$ (**1**) as brown powder in 93% (1.89 g, 2.77 mmol) yield.

Similar methodology was applied for the complexes **2-4** using stoichiometric weights.

Synthesis of $[(o-CH_3C_6H_4O)_2PS_2]Cu$ (**5**)

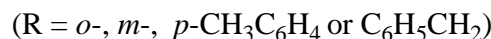
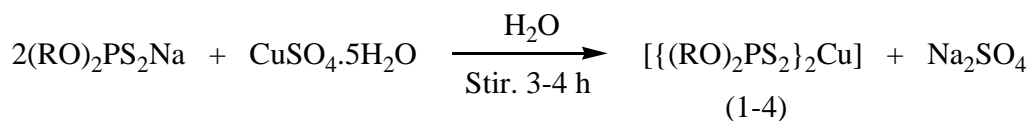
$[(o-CH_3C_6H_4O)_2PS_2]Cu$ (**5**) (0.58 g, 0.85 mmol) was dissolved in 30 ml dichloromethane than added methanol dropwise with constant stirring. White precipitates were formed immediately, which were filtered using a funnel fitted with G-4 sintered disc. The residue was washed with ethanol several times followed by drying for 3 hours at 60 °C, which afforded $[(o-CH_3C_6H_4O)_2PS_2]Cu$ (**5**) as white powder in 89% (0.52 g, 1.40 mmol) yield. The complexes **6-8** were synthesized using similar methodology.

Synthesis of $[(o-CH_3C_6H_4O)_2PS_2]Cu \cdot 2P(C_6H_5)_3$ (**9**)

A dichloromethane solution (10 ml) of triphenylphosphine, $P(C_6H_5)_3$, (0.28 g, 1.00 mmol) was added dropwise to a dichloromethane solution (20 ml) of the copper(I) ditolyldithiophosphate, $[(o-CH_3C_6H_4O)_2PS_2]Cu$ (0.20 g, 0.50 mmol) (**5**) with constant stirring at the room temperature. The contents were stirred for 3 hrs which resulted in the formation of white precipitates. The precipitates were filtered using a funnel fitted with G-4 sintered glass disc and washed 3-4 times with distilled water followed by drying for two hours at 60 °C. The complex $[(o-CH_3C_6H_4O)_2PS_2]Cu \cdot 2P(C_6H_5)_3$ was obtained as white powder in 92% (0.44 g, 0.50 mmol) yield. The complexes **10-16** were synthesized using similar methodology. The relevant synthetic and analytical data for all the complexes (**1-16**) are given in Table 1.

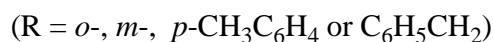
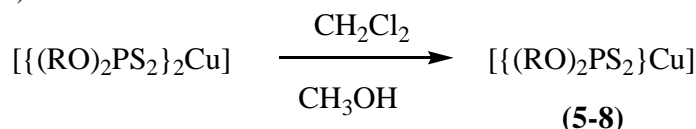
RESULTS AND DISCUSSION

Reaction of $CuSO_4 \cdot 5H_2O$ with the sodium phosphordithioate, $(RO)_2PS_2Na$ ($R = o-, m-$ or $p-CH_3C_6H_4-$ or $C_6H_5CH_2-$), are facile due to the anionic nature of the dithiophosphate nucleophile but the contents were stirred for 3-4 hours just for the sake of completion of the reaction. The copper(II) complexes $[(RO)_2PS_2]_2Cu$ (**1-4**) were obtained as dark brown powder in 90-93% yield by the reaction of $(RO)_2PS_2Na$ with $CuSO_4 \cdot 5H_2O$ in 2:1 molar stoichiometry in water (**Scheme. 1**).



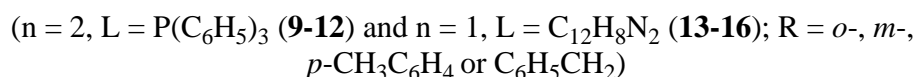
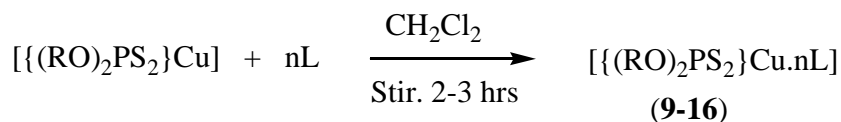
Scheme 1. Synthesis of $[(\text{RO})_2\text{PS}_2]_2\text{Cu}$ (1-4).

Copper(II) complexes (1-4) were reduced to copper(I) complexes corresponding to $[(\text{RO})_2\text{PS}_2]\text{Cu}$ (5-8) by a facile reaction with methanol in dichloromethane. The copper(I) complexes (5-8) were obtained as yellowish powder in 87-88% yield (Scheme. 2).



Scheme 2. Synthesis of $[(\text{RO})_2\text{PS}_2]\text{Cu}$ (5-8).

Copper(I) complexes (5-8) were reacted with phosphorus and nitrogen ligands in order to see the coordinative unsaturation around the copper atom. The reactions of the complexes (5-8) with the donor ligands in 1:2 and 1:1 were proceeded in a facile manner in dichloromethane and afforded the adducts of the composition $[(\text{RO})_2\text{PS}_2]\text{Cu} \cdot n\text{L}$ [$n = 2$, $\text{L} = \text{P}(\text{C}_6\text{H}_5)_3$ (9-12) and $n = 1$, $\text{L} = \text{C}_{12}\text{H}_8\text{N}_2$ (13-16) (Scheme. 3)]. The complexes with triphenylphosphine were white while those with 1, 10-phenanthroline were red.



Scheme 3. Synthesis of $[(\text{RO})_2\text{PS}_2]\text{Cu} \cdot n\text{L}$ [$n = 2$, $\text{L} = \text{P}(\text{C}_6\text{H}_5)_3$ (9-12) and $n = 1$, $\text{L} = \text{C}_{12}\text{H}_8\text{N}_2$ (13-16)].

The complexes (1-16) are soluble in chloroform, benzene and dichloromethane and insoluble in *n*-hexane and carbon tetrachloride. These complexes were decomposed in the temperature range of 145-165 °C at atmospheric pressure. The elemental analyses (C, H, N, S and Cu) were found consistent with the molecular composition of these complexes.

IR spectra

IR spectra (4000-200 cm^{-1}) of these complexes are interpreted on basis of earlier reports^{28, 30, 44}. All the complexes copper (II) and copper(I) have shown the presence strong band in the region 1140-1170 cm^{-1} and 990-1030 cm^{-1} due to $\nu(\text{P})\text{-O-C}$ and $\nu\text{P-O-(C)}$ stretching vibrations, respectively. The bands in the regions 550-560 cm^{-1} and 658-679 cm^{-1} are ascribed to $\nu(\text{P-S})$ and $\nu(\text{P=S})$ symmetrical and unsymmetrical vibrations. All the complexes of copper(II) and copper(I) have depicted a shift of 10-30 cm^{-1} for $\nu(\text{P=S})$ compared to the parent dithio ligand, which is suggestive of bidentate mode of chelation. Appearance of a new band in the region 370-386 cm^{-1} may be assigned to $\nu(\text{Cu-S})$ vibrations; this supports the complexation between the copper and ligand. The IR spectra of the adducts (9-16) have showed all the bands observed in the parent copper-dithiophosphates and bands characteristic of donor

ligands ($[P(C_6H_5)_3]$ and $N_2C_{12}H_8$) in addition to the bands in the region 408-410 and 470-475 cm^{-1} , which may be assigned to $\nu(Cu-P)$ and $\nu(Cu-N)$ bonding modes, respectively. The IR spectral values of the complexes are given in Table 2.

¹H NMR spectra

The ¹H NMR spectra of these derivatives show a marginal upfield shift for all characteristic resonance signals compared to the parent dithiophosphate moieties. The chemical shifts for $-CH_3$ (tolyl ring) and $-CH_2$ (benzyl ring) were observed as singlet in the region 2.2-2.3 and 4.5-4.8 ppm whereas the chemical shift for the tolyl and benzyl ring protons were appeared as multiplet in the region 6.6-7.1 ppm and 7.0-7.4 ppm, respectively, with their usual splitting patterns. There were two resonances for the ring protons of *para* complexes whereas four resonances were observed for *ortho* and *meta* derivatives. The chemical shifts for aromatic protons of triphenylphosphine moiety in the complexes **9-12** were observed in the region 7.2-8.9 ppm as multiplet. The complexes **13-16** have shown the characteristic resonances for phenyl protons of 1,10-phenanthroline moiety in the 7.2-9.1 ppm. The detail ¹H NMR spectral data are summarized in the Table 3.

³¹P NMR spectra

In proton decoupled ³¹P NMR spectra of these complexes exhibited a singlet in each case with characteristic downfield shift of ~14-19 ppm, which is commensurate with the bidentate nature of the dithiophosphate moieties⁴⁵. The ³¹P chemical shift of these complexes was observed in the region 85.6-95.7 ppm for all the complexes. The occurrence of singlet in all the cases is due to chemically equivalent nature of phosphorus atom in the molecule. Similarly the presence of a separate peak in the region -4.2 to -4.6 ppm confirms the presence of PPh_3 moiety in the complexes (**9-12**). The ³¹P NMR spectral data of all the compounds are summarized in Table 3.

¹³C NMR spectra

The ¹³C NMR spectra of few representative complexes (**1, 3, 6, 8, 10, 12, 13 and 15**) did not show any appreciable deviation in the chemical shift value of the carbon nuclei present in the parent moieties compared to the parent dithio moiety. The chemical shift for methyl ($-CH_3$) and methylene ($-CH_2$) carbon occurred in the range 17.4-20.6 ppm and 61.0-61.8 ppm, respectively. The carbon nuclei of phenyl ring ($-C_6H_5$ and $-C_6H_4$) have displayed their resonance in the region 114.1-141.2 ppm. The chemical shift for C-O and C-(CH_3) carbon in *ortho*-ditolyldithiophosphato derivatives (**1** and **13**) was found in the range of 148.2-148.3 ppm and 124.0-124.2 ppm. However, the chemical shift for C-O and C-(CH_3) carbon in *meta*- and *para*-ditolyldithiophosphato derivatives (**3, 6, 10 and 15**) were found in the region 152.6-154.4 ppm and 114.1-115.2 ppm^{30, 32-39}. The downfield and upfield swing in the chemical shift of C-O and C-(CH_3) carbon in *meta*- and *para*- derivatives may be attributed to the presence of hydrogen interactions in between proton attached to *ortho*- carbon of one tolyl ring with the oxygen atom of the other tolyl ring while in *ortho*- derivatives C-O and C-(CH_3) have shown the chemical shift in their normal region, hence, no hydrogen interactions in such cases. The chemical shift for the C-(CH_2) carbon in complexes (**8** and **12**) was observed in the range 141.1-142.2 ppm. The ¹³C NMR spectra of the addition complexes exhibited the signals of the carbon nucleus of the donor moieties in addition to the characteristic chemical shifts indicated above. The aryl carbon nuclei of the triphenylphosphine moiety in the complexes (**10, 12**) and the phenanthroline moiety in the complexes (**13, 15**) resonated at 122.0-149.0 ppm and 120.0-150.0 ppm, respectively. All the chemical shift values are given in the Table 4.

Electronic spectra

The electronic spectra (800-200 nm) of these complexes (**1-4** and **9-16**) interpreted on the basis of the literature reports³⁵⁻³⁶. Electronic spectra were recorded in benzene, which show absorption in the visible and or ultra violet region. The complexes (**1-4**) show the absorption of medium intensity in the range 710-690 nm, 560-540 nm, 400-380 nm and 290-270 nm. The absorption in the range of 710-690 nm and 560-540 nm, may be ascribed to ${}^2B_g \rightarrow {}^2A_g$ and ${}^2B_{1g} \rightarrow {}^2E_g$, respectively, due to *d-d* transitions *i.e.* transition of electrons between the lower energy to higher energy orbital of the copper atom and other transition of weak intensity in the 290-270 nm region assigned to charge-transfer spectra. These transitions suggested that the copper(II) has d^9 configuration. The weak intensity absorption bands which were both spin and orbital forbidden and observed in the region 550-510 nm, 430-400 nm, 300-280 nm and 270-250 nm for the complexes (**9-16**), may be assigned to *d-d* transition, *i.e.* transition of electrons between the lower energy to higher energy orbital of the copper atom. The absorption spectral band in the region 400-380 nm and 290-270 nm for the complexes (**1-4**), and 300-280 nm and 270-250 nm for (**9-16**) complexes, were of weak intensity and ascribed to charge-transfer spectra, which revealed that there is transition between the metal to ligand ($M \rightarrow L$) or ligand to metal ($L \rightarrow M$). The electronic spectral data of the complexes (**1-16**) are given in Table 5.

Magnetic susceptibility data

Room temperature magnetic moment (μ_{eff}) of these complexes (1-4) was found in the range 1.5-1.4 B. M. The magnetic susceptibility is accordance with the low spin only value (1.73 B. M.) and suggested that the copper in these complexes is as Cu(II) *i.e.* having the electronic configuration d^9 . Magnetic moment values also show antiferromagnetic interactions between copper centers of dimeric molecules in the solid state²⁸. This also signifies the geometry around copper(II) atom as tetrahedral. Magnetic moment values of these complexes (1-4) are given in Table 5.

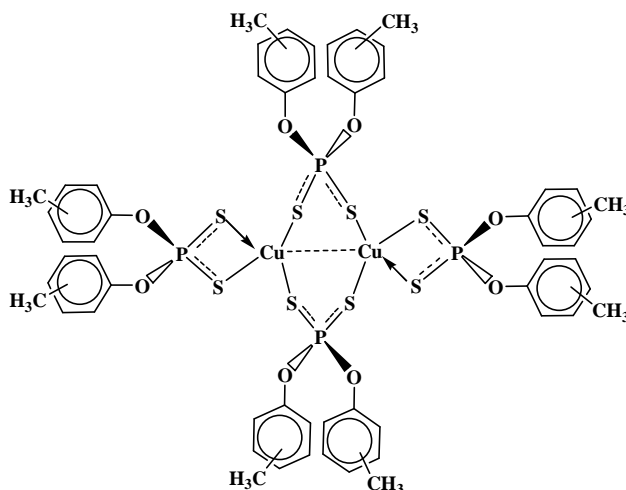
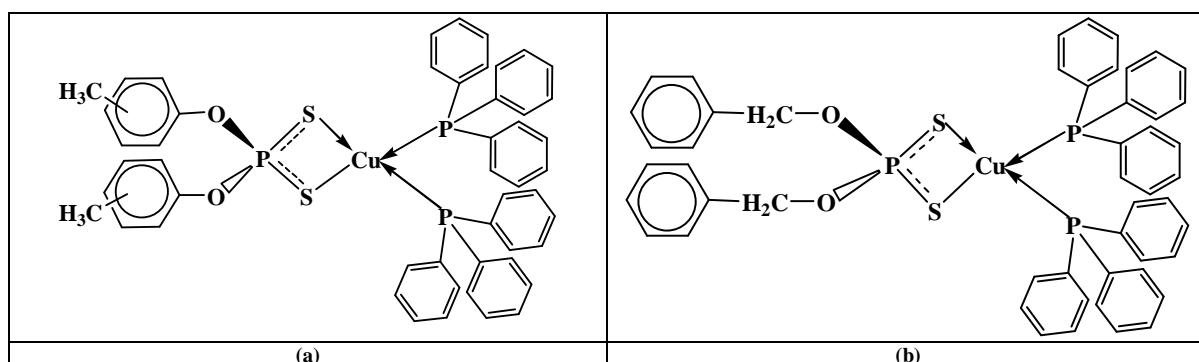
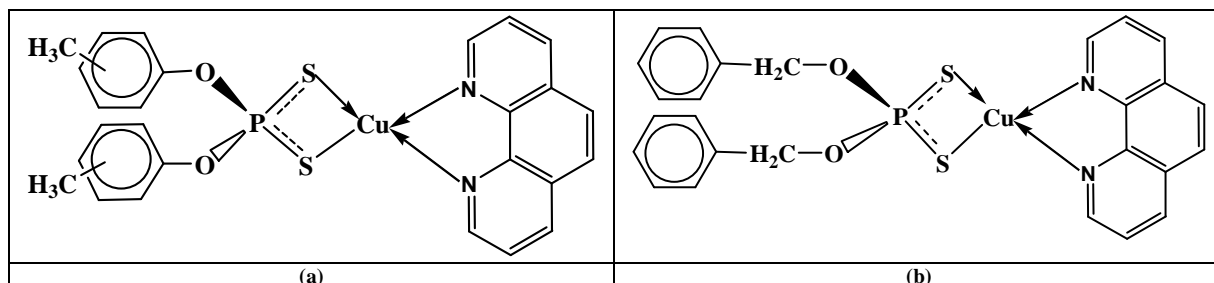
Figure 1a: Proposed geometry for $[\{(\text{CH}_3\text{C}_6\text{H}_4\text{O})_2\text{PS}_2\}\text{Cu}]$ (1-4).Figure 1b: Proposed distorted tetrahedral geometry for the molecules $[\{(\text{CH}_3\text{C}_6\text{H}_4\text{O})_2\text{PS}_2\}\text{Cu}.2\text{P}(\text{C}_6\text{H}_5)_3]$ (9-11) (a) and $[\{(\text{C}_6\text{H}_5\text{CH}_2\text{O})_2\text{PS}_2\}\text{Cu}.2\text{P}(\text{C}_6\text{H}_5)_3]$ (12) (b)Figure 1c: Proposed distorted tetrahedral geometry for $[\{(\text{CH}_3\text{C}_6\text{H}_4\text{O})_2\text{PS}_2\}\text{Cu}.N_2C_{12}H_8]$ (13-15) (a) and $[\{(\text{C}_6\text{H}_5\text{CH}_2\text{O})_2\text{PS}_2\}\text{Cu}.N_2C_{12}H_8]$ (16) (b)

Table 1: Synthetic and analytical data of copper(I) and copper(II) (*o*-, *m*- or *p*-ditolyl)/dibenzylidithiophosphates

S. No.	Reactants (g mmol)		Molar Ratio	Complex (physical state)	M.W. Found (Calc.)	Yield (%)	Analysis (%) Found (Calcd.)				
	LNa	CuSO ₄ /L*					C	H	N	S	
1.	1.50 (4.50)	0.56 (2.25)	2:1	[{(o-MeC ₆ H ₄ O) ₂ PS ₂] ₂ Cu] (Brown powder)	1358.65 (682.27)	85	49.28 (49.29)	4.10 (4.14)	--	18.79 (18.80)	9.28 (9.31)
2.	1.32 (4.00)	0.50 (2.00)	2:1	[{(m-MeC ₆ H ₄ O) ₂ PS ₂] ₂ Cu] (Brown powder)	--	83	49.25 (49.29)	4.13 (4.14)	--	18.76 (18.80)	9.30 (9.31)
3.	1.50 (4.50)	0.56 (2.25)	2:1	[{(p-MeC ₆ H ₄ O) ₂ PS ₂] ₂ Cu] (Brown powder)	1355.54 (682.27)	85	49.26 (49.29)	4.11 (4.14)	--	18.78 (18.80)	9.27 (9.31)
4.	1.33 (4.00)	0.50 (2.00)	2:1	[{(C ₆ H ₄ CH ₂ O) ₂ PS ₂] ₂ Cu] (Brown powder)	--	81	49.27 (49.29)	4.13 (4.14)	--	18.75 (18.80)	9.29 (9.31)
5.	1.32 (4.00)	--	--	[{(o-MeC ₆ H ₄ O) ₂ PS ₂ Cu] (Creamish powder)	--	80	45.08 (45.09)	3.76 (3.78)	--	17.15 (17.20)	17.02 (17.04)
6.	0.58 (1.50)	--	--	[{(m-MeC ₆ H ₄ O) ₂ PS ₂ Cu] (Creamish powder)	1483.78 (372.91)	78	45.05 (45.09)	3.74 (3.78)	--	17.19 (17.20)	17.00 (17.04)
7.	0.43/1.60	--	--	[{(p-MeC ₆ H ₄ O) ₂ PS ₂ Cu] (Creamish powder)	--	78	45.07 (45.09)	3.77 (3.78)	--	17.18 (17.20)	17.03 (17.04)
8.	0.58/1.50	--	--	[{(C ₆ H ₄ CH ₂ O)PS ₂ Cu] (Creamish powder)	1485.08 (372.91)	72	45.06 (45.09)	3.75 (3.78)	--	17.17 (17.20)	17.01 (17.04)
9.	0.20/0.50	0.28/1.00	1:2	[{(o-MeC ₆ H ₄ O) ₂ PS ₂ Cu.2P(C ₆ H ₅) ₃] (White powder)	890.67 (897.48)	75	42.90 (66.91)	4.92 (4.94)	--	7.10 (7.15)	7.03 (7.08)
10.	0.20/0.50	0.28/1.00	1:2	[{(m-MeC ₆ H ₄ O) ₂ PS ₂ Cu.2P(C ₆ H ₅) ₃] (White powder)	--	74	42.88 (66.91)	4.89 (4.94)	--	7.14 (7.15)	7.06 (7.08)
11.	0.20/0.50	0.28/1.00	1:2	[{(p-MeC ₆ H ₄ O) ₂ PS ₂ Cu.2P(C ₆ H ₅) ₃] (White powder)	887.05 (897.48)	75	42.86 (66.91)	4.93 (4.94)	--	7.12 (7.15)	7.05 (7.08)
12.	0.20/0.50	0.28/1.00	1:2	[{(C ₆ H ₄ CH ₂ O) ₂ PS ₂ Cu.2P(C ₆ H ₅) ₃] (White powder)	--	72	42.89 (66.91)	4.90 (4.94)	--	7.11 (7.15)	7.04 (7.08)
13.	0.15/0.40	0.22/0.80	1:1	[{(o-MeC ₆ H ₄ O) ₂ PS ₂ Cu.N ₂ C ₁₂ H ₈] (Red powder)	--	73	56.45 (56.46)	3.97 (4.01)	5.01 (5.06)	11.55 (11.59)	11.47 (11.49)
14.	0.20/0.50	0.28/1.00	1:1	[{(m-MeC ₆ H ₄ O) ₂ PS ₂ Cu.N ₂ C ₁₂ H ₈] (Red powder)	542.07 (553.11)	74	56.42 (56.46)	3.98 (4.01)	5.05 (5.06)	11.58 (11.59)	11.46 (11.49)
15.	0.15/0.40	0.22/0.80	1:1	[{(p-MeC ₆ H ₄ O) ₂ PS ₂ Cu.N ₂ C ₁₂ H ₈] (Red powder)	--	75	56.46 (56.46)	3.99 (4.01)	5.02 (5.06)	11.56 (11.59)	11.45 (11.49)
16.	0.50/1.30	0.26/1.30	1:1	[{(C ₆ H ₄ CH ₂ O) ₂ PS ₂ Cu.N ₂ C ₁₂ H ₈] (Red powder)	546.73 (553.11)	71	56.44 (56.46)	4.00 (4.01)	5.04 (5.06)	11.57 (11.59)	11.48 (11.49)

L = *o*-, *m*-, *p*-CH₃C₆H₄- or C₆H₅CH₂; Me = CH₃; *L = 2P(C₆H₅)₃ (9-12) and C₁₂H₈N₂ (13-16)

Table 2. IR spectral data cm⁻¹ of copper(II) and copper(I) ditolyl- and dibenzylidithiophosphates

S. No.	v(P)-O-C	vP-O-(C)	vP=S	vP-S	vCu-S	**vCu-N/ vCu-P
1.	1170, s	992, s	661, s	554, m	370, m	--
2.	1170, s	993, s	671, s	556, m	380, m	--
3.	1170, s	994, s	657, s	556, m	375, m	--
4.	1145, s	997, s	658, s	556, m	378, m	--
5.	1155, s	990, s	651, s	560, m	384, m	--
6.	1140, s	998, s	679, s	560, m	377, m	--
7.	1158, s	995, s	658, s	554, m	374, m	--
8.	1164, s	996, s	658, s	555, m	380, m	--
9.	1164, s	1030, s	667, s	556, m	381, m	408, m
10.	1165, s	1029, s	665, s	550, m	379, m	409, m
11.	1167, s	1030, s	663, s	553, m	386, m	410, m
12.	1150, s	1028, s	661, s	553, m	375, m	409, m
13.	1160, s	999, s	671, s	553, m	378, m	470, m
14.	1165, s	996, s	677, s	552, m	374, m	473, m
15.	1160, s	998, s	674, s	558, m	378, m	470, m
16.	1155, s	991, s	663, s	550, m	380, m	475, m

s = sharp, m = medium, b = broad

S. No. of the complexes is according to Table 1.

Table 3. ¹H and ³¹P NMR spectral data of copper(II) and copper(I) ditolyl- and dibenzylidithiophosphates (ppm)

S. No.	¹ H NMR	Donor moiety	³¹ P NMR Dithio (PPh ₃)	
1.	2.2, s, 12H (-CH ₃); 7.0, d, [H(2)]; 6.9, t, [H(3)]; 7.1, t, [H(4)]; 6.6, d, [H(5)]	--	90.6, s	--
2.	2.3, s, 12H (-CH ₃); 7.1, s, [H(1)]; 6.9, t, 1H, [H(3)]; 7.0, t, [H(4)]; 6.6, d, [H(5)]	--	95.7, s	--
3.	2.2, s, 12H (-CH ₃); 6.9, d, [H(1,5)]; 7.1, d, [H(2,4)]	--	85.6, s	--
4.	4.5, s, 8H(-CH ₂); 7.0-7.4, m, 8H(-C ₆ H ₅)	--	93.6, s	--
5.	2.2, s, 6H (-CH ₃); 7.0, d, [H(2)]; 6.9, t, [H(3)]; 7.1, t, [H(4)]; 6.6, d, [H(5)]	--	89.6, s	--
6.	2.2, s, 6H (-CH ₃); 7.1, s, [H(1)]; 6.9, t, 1H, [H(3)]; 7.0, t, [H(4)]; 6.6, d, [H(5)]	--	88.6, s	--
7.	2.2, s, 6H (-CH ₃); 6.9, d, [H(1,5)]; 7.1, d, [H(2,4)]	--	89.6, s	--
8.	4.7, s, 4H(-CH ₂); 7.0-7.4, m, 8H(-C ₆ H ₅)	--	94.1, s	--
9.	2.2, s, 6H (-CH ₃); 7.0, d, [H(2)]; 6.9, t, [H(3)]; 7.1, t, [H(4)]; 6.6, d, [H(5)]	7.5-8.9, m, 30H, (PPh ₃)	86.8, s	-4.2, s
10.	2.2, s, 6H (-CH ₃); 7.1, s, [H(1)]; 6.9, t, 1H, [H(3)]; 7.0, t, [H(4)]; 6.6, d, [H(5)]	7.3-7.8, m, 30H, (PPh ₃)	90.8, s	-4.6, s
11.	2.2, s, 6H (-CH ₃); 6.9, d, [H(1,5)]; 7.1, d, [H(2,4)]	7.2-8.6, m, 30H, (PPh ₃)	86.8, s	-4.0, s
12.	4.8, s, 4H(-CH ₂); 7.0-7.4, m, 8H(-C ₆ H ₅)	7.2-8.0, m, 30H, (PPh ₃)	91.8, s	-4.5, s
13.	2.2, s, 6H (-CH ₃); 7.0, d, [H(2)]; 6.9, t, [H(3)]; 7.1, t, [H(4)]; 6.6, d, H(5)]	7.3-8.9, m, 8H, (N ₂ C ₁₂ H ₈)	89.5, s	--
14.	2.3, s, 6H (-CH ₃); 7.1, s, [H(1)]; 6.9, t, 1H, [H(3)]; 7.0, t, [H(4)]; 6.6, d, [H(5)]	7.3-9.1, m, 8H, (N ₂ C ₁₂ H ₈)	88.3, s	--
15.	2.2, s, 6H (-CH ₃); 6.9, d, [H(1,5)]; 7.1, d, [H(2,4)]	7.3-9.0, m, 8H, (N ₂ C ₁₂ H ₈)	92.7, s	--
16.	4.5, s, 4H(-CH ₂); 7.0-7.4, m, 8H(-C ₆ H ₅)	7.2-8.9, m, 8H, (N ₂ C ₁₂ H ₈)	88.8, s	--

s = singlet, *m* = multiplet, *t* = triplet
S. No. of the complexes is according to Table 1.

Table 4. ¹³C NMR spectral data of copper(I) and copper(II) ditolyl/benzylidithiophosphates in CDCl₃ (ppm)

S. No.	-CH ₃ /CH ₂	C-O	C-O*	C-(ortho)	C-(meta)	C-(para)	C-(CH ₃ /CH ₂)	Donor moiety
1.	20.6	148.2	--	124.5	127.6, 129.0	134.5	124.2	--
3.	20.6	--	154.0	120.5	130.0	--	115.2	--
6.	17.4	--	154.4	121.4, 123.9	125.8	132.5	115.0	--
8.	61.8	--	--	127.3	128.6	127.7	141.2	--
10.	18.8	--	152.6	120.6, 120.7	129.7	133.2	114.1	126.0-137.0
12.	61.0	--	--	123.4	128.7	126.0	141.1	122.0-149.0
13.	20.2	148.3	--	124.9	127.0, 130.0	134.8	124.0	124.5-145.7
15.	20.3	--	153.4	122.8	129.1	--	115.2	120.0-150.0

* = hydrogen bonded oxygen
S. No. of the complexes is according to Table 1.

Table 5. Magnetic moment (B. M.) and UV-Vis. (cm⁻¹) data of copper dithiophosphates

S. No.	Magnetic moment (B. M)	Absorption (in cm ⁻¹)	Tentative assignments
1.	1.5	14084 18518 25641 35714 } }	${}^2B_g \rightarrow {}^2A_g$ } <i>d-d</i> transition ${}^2B_{1g} \rightarrow {}^2E_g$ } Charge transfer
2.	1.4	14285 18181 25000 34482 } }	${}^2B_g \rightarrow {}^2A_g$ } <i>d-d</i> transition ${}^2B_{1g} \rightarrow {}^2E_g$ } Charge transfer
3.	1.5	14492 17857 26315 37037 } }	${}^2B_g \rightarrow {}^2A_g$ } <i>d-d</i> transition ${}^2B_{1g} \rightarrow {}^2E_g$ } Charge transfer
4.	1.4	14084 18182 25641 35714 } }	${}^2B_g \rightarrow {}^2A_g$ } <i>d-d</i> transition ${}^2B_{1g} \rightarrow {}^2E_g$ } Charge transfer
13.	--	18518 24390 35714 38461 } }	${}^2B_g \rightarrow {}^2A_g$ } <i>d-d</i> transition ${}^2B_{1g} \rightarrow {}^2E_g$ } Charge transfer
14.	--	12182 23809 35714 39215 } }	${}^2B_g \rightarrow {}^2A_g$ } <i>d-d</i> transition ${}^2B_{1g} \rightarrow {}^2E_g$ } Charge transfer
15.	--	19607 23256 35714 40000 } }	${}^2B_g \rightarrow {}^2A_g$ } <i>d-d</i> transition ${}^2B_{1g} \rightarrow {}^2E_g$ } Charge transfer
16.	--	18518 25000 35714 39215 } }	${}^2B_g \rightarrow {}^2A_g$ } <i>d-d</i> transition ${}^2B_{1g} \rightarrow {}^2E_g$ } Charge transfer

S. No. of the complexes is according to Table 1.

CONCLUSION

³¹P NMR chemical shift was obtained as singlet, describing equivalent nature of the phosphorus atom of the dithio moiety in addition to bidentate mode of bonding with copper(I) atom. Molecular weight determination showed that these compounds are tetrameric in nature. Considering other analytical data like elemental analysis, IR, ¹H, ³¹P NMR and in conjunction with the literature reports^{22-29, 35-36} we conclude a tetra-coordinated environment exists around copper(I) atom (Figure 1a.) whereas molecular weight measurement shows monomeric nature of copper(I) adducts. So, a distorted tetrahedral geometry around copper nucleus has been proposed (Figure 1b-c). The distortion from the regular tetrahedron can be interpreted in terms of steric hindrance of triphenyl phosphine and phenanthroline and the bidentate nature of dithiophosphate group.

Copper(II) complexes are dimeric as indicated by molecular weight determination. Considering the analytical results obtained from IR, NMR (¹H, ¹³C and ³¹P), electronic spectra and magnetic moments along with the literature reports,^{35,36} four coordinated square planer environment may be postulated for copper(II) complexes.

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REFERENCES

- [1] J. R. Wasson, G. M. Woltermann and H. J. Stocklosa, *Top. Curr. Chem.*, **1973**, **35**, 65
- [2] B. P. S. Chauhan, G. Srivastava and R. C. Mehrotra, *Coord. Chem. Rev.*, **1984**, **55**, 207.
- [3] H. P. S. Chauhan, *Coord. Chem. Rev.*, **1998**, **173**, 1.
- [4] I. Haiduc, *Rev. Inorg. Chem.*, **1981**, **3**, 353.
- [5] S. K. Pandey, G. Srivastava and R. C. Mehrotra, *Synth. React. Inorg. Met.-Org. Nano Met. Chem.*, **1989**, **19**, 795.

- [6] S. K. Pandey, G. Srivastava and R. C. Mehrotra, *J. Ind. Chem. Soc.*, **1989**, **66**, 558.
- [7] R. Chander, B. L. Kalsotra and S. K. Pandey, *Ind. J. Chem.*, **2004**, **43A**, 1134.
- [8] J. L. Lefferts, K. C. Molloy, J. J. Zuckerman, I. Haiduc, M. Curtui, G. Gutal and D. Rose, *Inorg. Chem.*, **1980**, **19**, 2861.
- [9] R. Chander, B. L. Kalsotra and S. K. Pandey, *Trans. Met. Chem.*, **2003**, **28**, 405.
- [10] U. N. Tripathi, *Phosphorus, Sulfur Silicon Relat. Elem.*, **2000**, **159**, 47.
- [11] U. N. Tripathi, P. P. Bipin, R. Mirza and A. Chaturvedi, *Pol. J. Chem.*, **1999**, **73**, 1751.
- [12] P. S. Shetty and Q. Fernando, *J. Am. Chem. Soc.*, **1970**, **92**, 3964.
- [13] K. C. Molloy, M. B. Hossain, D. V. Helm, J. J. Zuckerman and I. Haiduc, *Inorg. Chem.* **1980**, **18**, 3507.
- [14] A. Mihailovski, US Pat. No. 4071545/1978 (*Chem. Abstr.* **1978**, **88b**, 170295j).
- [15] J. Kanazawa, H. Kubo and R. Sato, *Agric. Biol. Chem.*, **1965**, **29**, 43.
- [16] A. Kumar, S. Kour, M. S. Hundal and S. K. Pandey, *J. Chem. Crystallogr.*, **2012**, **42**, 299.
- [17] H. H. Farmer, B. W. Malone and H. F. Tompkins, *Lubric (Eng)*, **1967**, **23**, 57.
- [18] C. L. Stewart, US Pat. No. 20010604/2002 (*Chem. Abstr.*, **2002**, **138**, 41800).
- [19] K. Hayashi, Y. Sasaki, S. Tagashira, Y. Soma and S. Kato, *Anal. Sci.*, **1986**, **105**, 237529d.
- [20] A. Shishkov and D. Atanasova, *Nauchi. Tr. Plovdivski. Univ.*, **1982**, **19**, 265 (*Chem. Abstr.*, 1983, **98**, 190813).
- [21] H. So, Y. C. Lin and G. S. Chang, *Wear*, **1993**, **166**, 17.
- [22] B. Kim, R. Mourhatch and P. B. Aswath, *Wear*, **2010**, **268**, 579.
- [23] S. C. Bajja, *Synth. React. Inorg. Met.-Org. Chem.*, **2011**, **41**, 746.
- [24] D. S. A. Chaturvedi and R. K. Upadhyay, *E- J. Chem.*, **2011**, **8(S1)**, S113.
- [25] K. Xu, W. Ding and Y. Chen, *J. Chem. Crystallogr.*, **2004**, **34**, 665.
- [26] D. Rusanova, K. E. Christensen, I. Person, K. J. Pike, O. N. Antzutkin, X. Zou, R. Dupree, and W. Forsling, *J. Coord. Chem.*, **2007**, **60**, 517.
- [27] M. J. Hutchings, G. J. Moody and J. D. R. Thomas, *Analyst*, **1987**, **112**, 601.
- [28] U. N. Tripathi, R. Bohra, G. Srivastava and R. C. Mehrotra, *Polyhedron*, **1992**, **11**, 1187.
- [29] B. J. Liaw, T. S. Lobana, Y. W. Lin, J. C. Wang and C. W. Liu, *Inorg. Chem.*, **2005**, **44**, 9921.
- [30] A. Kumar, K. R. Sharma and S. K. Pandey, *Phosphorus, Sulfur Silicon Relat. Elem.*, **2007**, 182, 1023.
- [31] J. E. Drake, C. L. B. McDonald, A. Kumar, S. K. Pandey and R. Ratnani, *J. Chem. Crystallgr.*, **2005**, **35**, 447.
- [32] B. Gupta, S. Magotra and S. K. Pandey, *Monatsh. Chem.*, **2008**, 139, 747.
- [33] B. Gupta, K. Kumar and S. K. Pandey, *Synth. React. Inorg. Met-Org. Nano Met. Chem.*, **2009**, **39**, 559.
- [34] D. Kumar, B. Gupta and S. K. Pandey, *Int. J. Chem.*, **2012**, **1**, 247.
- [35] S. Kour, B. Gupta, R. Chander and S. K. Pandey, *Main Group Met. Chem.*, **2009**, **32**, 195.
- [36] S. Sharma, S. Magotra and S. K. Pandey, *Phosphorus, Sulfur Silicon Relat. Elem.*, **2009**, **184**, 2140.
- [37] A. Kumar, D. Kumar and S. K. Pandey, *Synth. React. Inorg. Met-Org. Nano Met. Chem.*, **2007**, **37**, 697.
- [38] K. R. Sharma, D. Kumar and S. K. Pandey, *J. Coord. Chem*, **2008**, **61**, 1811.
- [39] A. Kumar, K. Kumar and S. K. Pandey, *Pol. J. Chem.*, **2009**, **83**, 2097.
- [40] J. A. McCleverty, R. S. Z. Kowalaski, N. A. Bailey, R. Mulvaney and D. A. O' Cleirigh, *J. Chem. Soc. Dalton Trans.*, 1983 **4**, 627.
- [41] D. A. Akhmedzade and N. F. Dzhanikbekov, *Azer. Khim. Zh.*, 1979, **4**, 118 (*Chem. Abstr.*, **1980**, **92**, 23431e).
- [42] N. N. Glebova, O. K. Sharaev, E. I. Tinyakova and B. A. Dolgoplosk, *Petrochem. Synth.*, **1995**, **37**, 1145 (*Chem. Abstr.* **1996**, **125**, 143371g).
- [43] F. Yuan, Y. Haung and Q. Xie, *App. Orgomet. Chem.*, **2002**, **16**, 660.
- [44] S. P. Sovilj, V. M. Leovac and D. M. Minic, *Pol. J. Chem.*, **2000**, **74**, 945.
- [45] C. Glidewell, *Inorg. Chim. Acta.*, **1977**, **25**, 159.