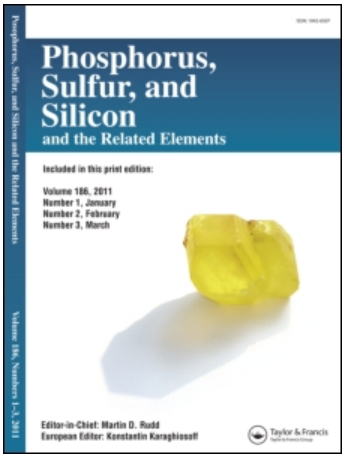

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Batyeva, Elvira , Kursheva, Lidiya , Frolova, Liliya and Dunaev, Victor(1997) 'New Sulfur and Phosphorus Containing Metal Complexes on the Basis of Trithiophosphites. Synthesis and Properties', Phosphorus, Sulfur, and Silicon and the Related Elements, 120: 1, 373 — 375
To link to this Article: DOI: 10.1080/10426509708545555
URL: http://dx.doi.org/10.1080/10426509708545555

hosphorus, Sulfur, and Silicon, 1997, Vol. 120 & 121, pp. 373-375
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NEW SULFUR AND PHOSPHORUS CONTAINING METAL COMPLEXES ON THE BASIS OF TRITHIOPHOSPHITES. SYNTHESIS AND PROPERTIES.

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Abstract New sulfur- and phosphorus containing metal complexes have been obtained by means of reactions of trialkyl- and triaryltrithiophosphites with transition metal halides . Their reactions with proton containing and carbonyl compounds have been studied.

Key words trialkyltrithiophosphite, triaryltrithiophosphite, transition metal halides, complex,

Reactions of trialkyl- and triaryltrithiophosphites with transition metal halides were conducted for synthesizing a series of novel transition metal complexes with trithiophosphite ligands with the following general formula: R'R"PSR* MX, where R'=R"=SR, R=Alk , Ph; M=Cu(I), Cu(II), Pd, Pt; X=Cl,Br,I. They were examined by X-rays to investigate possible binding modes of potentially polydentate ligands to study their properties[1,2].

Thus, by varying the reaction conditions, the nature and oxidation state of the central metal atom, the nature or the size of substituents at the sulfur or phosphorus atoms in a ligand we were able to prepare complexes with different types of coordination. A bidentate coordination mode via both phosphorus and sulfur atoms with the formation of polymeric chains along the x-axis is realized in complexes of copper(I) monohalides with trialkyltrithiophosphite . The same type of coordination occurs in triphenyltrithiophosphite with different structural features available .

Such a mode of coordination via sulfur atoms along with the phosphorus atom of a P-S ambident system is the first example of bidentate coordination for thioderivatives of P^{III} acids as amides and esters have the usual mode of binding via the phosphorus atom.

The additional coordination of sulfur atoms results in the elongation of P-S and S-C bonds by 0.04-0.06 Å as compared to other P-S and S-C bonds. Besides the lengthening of the Cu-P bond (0.035 Å) in the phenyl complex as compared to the alkyl complex was revealed. Thus, these structural peculiarities must result in a higher reactivity of complexes as compared to "free" thiophosphites and make reactions which do not proceed with thiophosphite possible.

Indeed, the P-S bond of these complexes has been found to be easily ruptured in alcoholysis and aminolysis in contrast to noncoordinated thiophosphites, which react with alcohols only in severe reaction conditions and do not react with amines at all. Thus, the interaction of copper complexes with ethanol is followed by the substitution of thioalkyl groups and results in diethylphosphite as a final product.

$$\underset{\text{(a, b)}}{(RS)_3P^*CuX} + 3\ EtOH \xrightarrow[78^oC]{EtOH} [(RO)_3P^*CuX + 3\ EtSH] \xrightarrow[-\ Et_2S]{EtOH} (RO)_2POH$$

a)R=Et, n-Pr; X=Br; b) R=Ph; X=Cl

The unexpected formation of diethylphosphite may be due to the presence of mercaptane in the reaction medium and its following interaction in situ with the intermediate substitution product - triethylphosphite complex, resulting in the end phosphorylated product. This scheme was confirmed by the model reaction of triethylphosphite complex with mercaptane.

Reaction of complexes (a) and (b) with diethylamine in accordance with the NMR ^{31}P data proceeds readily with the substitution of thiogroups by amido groups at the phosphorus atom and the formation of phosphorane (δ_P=3 ppm, J_{P-H}=549 Hz)

$$(RS)_3P^*CuX + R_2NH \longrightarrow (R_2N)P(SR)_2{}^*CuX + RSH \xrightarrow{R_2NH}$$

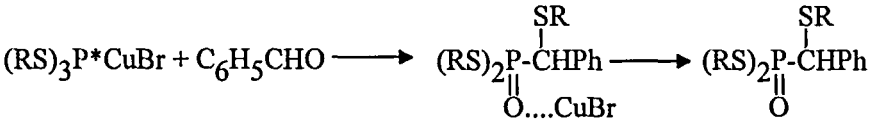
$$(R_2N)_2PSR^*CuX + RSH \xrightarrow{R_2NH} (R_2N)_3P^*CuX + RSH \xrightarrow{R_2NH}$$

$$(R_2N)_3\overset{+}{P}H\overset{-}{N}R + CuX^*R_2NH \longrightarrow (R_2N)_3PHNR_2$$

R=Et, Ph; X= Cl, Br

It should be noted that the reactions above proceed more easily in case of phenyl complex.

Meanwhile reactions of "free' trialkyltrithiophosphites with aldehydes take place only at high temperatures or in the presence of acid catalists[3] we have found that the reactions of the triethyltrithiophosphite copper bromide complex easily occurs with benzaldehyde even at room temperature resulting in the formation of an addition product - S,S-diethylthiobenzylphosphonate (δ_P = 66 ppm)



Thus, a study of the properties of new types of phosphorus and sulfur containing complexes on the basis of trialkyl- and triaryltrithiophosphites has shown that the reaction with the rupture of the P- S bond and the formation of substitution or addition products at the phosphorus atom takes place in any case.

ACKNOWLEDGEMENT

The authors wish to express their sincere thanks to Prof. R. Schmutzler for his assistance in conducting these investigations.

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