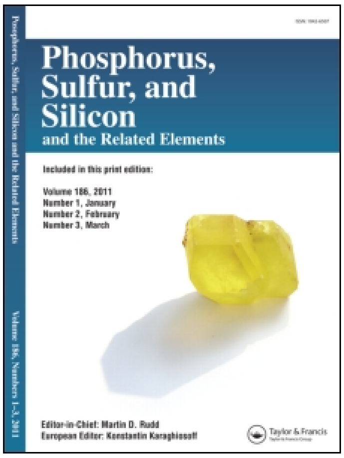

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Competitive Coordination of Metals by Phosphorus and Sulfur in Complexes with Polydentate Ligands Containing P(III)-S Bonds

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A series of complexes of thiophosphites with transition metals has been studied by X-ray single crystal diffraction: $CuHal{\bullet}P(SR)_3$, $CuHal{\bullet}P(SR)_3{\bullet}NCMe$, $CuBr{\bullet}P(SEt)_2NEt_2$, $CuSCN{\bullet}P(SR)_3$, $CpMn(CO)_2{\bullet}P(SR)_3$, $ArCr(CO)_2{\bullet}P(SR)_3$, with Hal = Cl, Br, I and R = Me, Et, Pr, i-Pr, Bu, Ph. Depending on the metal center, substituents R at sulfur, the conditions of reactions and crystal growth, different coordination modes have been observed: "classical" monodentate binding via phosphorus, unusual bidentate mode with participation of both P and S donor atoms of the ambident P – S system, as well as both monodentate and bidentate modes in one complex.

Keywords: Trithiophosphites; bidentate coordination; X-ray diffraction

INTRODUCTION

Trithiophosphites are of great interest as potential ligands in complexes with metals because of their conformational flexibility and the presence of four donor atoms capable of binding metal centers. Thus, different coordination modes may be observed in complexes of trithiophosphites with participation of phosphorus, sulfur or several donor atoms of the same ligand molecule in metal-element bond. Analogous oxygen containing ligands, phosphites, usually form monodentate complexes binding metal centers only via the phosphorus atom [1] similar to phosphines. There are two features of thiophosphites which indicate that their coordination ability might be significantly different in comparison with oxygen analogues. First, phosphorus donor ability decreases in the series phosphines - phosphites - thiophosphites correspondingly with the ionization potential of the phosphorus lone electron pair [2, 3], in trithiophosphites these values for the phosphorus and sulfur atoms being close [3]. Second, the reactivity of phosphites and thiophosphites is significantly different: in phosphites only phosphorus is an active reaction center, while in thioanalogues there are two competitive active reaction centers in the ambident P - S system [4].

The aim of the present paper is to analyze factors determining the coordination modes realized in the complexes. of trithiophosphites with transition metals on the basis of the X-ray single crystal diffraction data.

RESULTS AND DISCUSSION

So far there are few publications on the structure of thiophosphite complexes [5-9]. "Classical" monodentate coordination with formation of the M -P bond was realized in complexes with iron and manganese dicarbonyl [5-7]. Similar structure we observed for analogous chromium compounds (Figure).

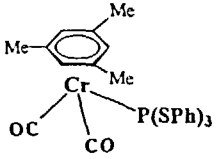
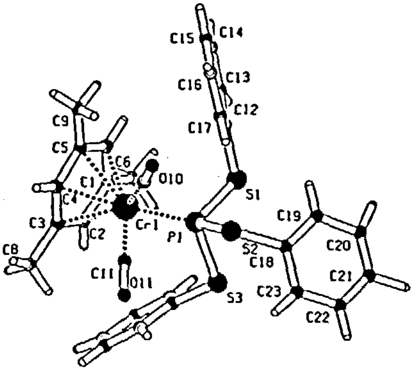
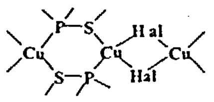


FIGURE Molecular structure of ArCr(CO)$_2$·P(SR)$_3$

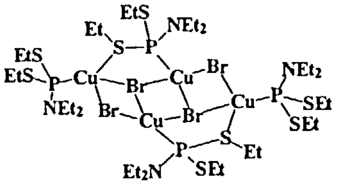


The first example of the bidentate coordination with participation of both P and S donor atoms of the ambident P - S system was found in the series of isostructural complexes of $(EtS)_3P$ with copper (I) halides (Hal = Cl, Br, I) [8, 9]. A polymeric chain with alternating 6- and 4-membered cycles was observed in crystals.



The elongation of the alkyl substituent at sulfur does not change the coordination type in complexes $(PrS)_3P{\cdot}CuHal$ and $(BuS)_3P{\cdot}CuHal$. Bidentate coordination appeared to be preserved in complexes with copper (I) rhodanide. The polymeric chain is formed in crystals with alternating 6- and 8-membered cycles, the SCN anion binding Cu via both S and N atoms. However, such coordination appeared to be not stable enough to stand recrystallization of the $(EtS)_3P \cdot CuSCN$ complex in acetonitrile. In this case a ligand exchange was observed with the cleavage of both Cu - P and Cu - S coordination bonds and formation of the complex $CuSCN \cdot NCMe$.

As a whole in a series of above complexes the Cu - P bond is much stronger than Cu - S with average bond distances being equal to 2.213 and 2.386 Å respectively, thus we never observed monodentate complexes of thiophosphites with M - S coordination bond. In case of active solvents it is the M - S bond which is broken first, as it was observed while recrystallization of the $(i\text{-}PrS)_3P \cdot CuBr$ complex in acetonitrile. Monodentate binding mode via phosphorus was found in crystals after recrystallization, one molecule of acetonitrile being included into the coordination sphere of copper. As to P-S bonds in bidentate complexes of thiophosphites, additional sulfur coordination with Cu (I) results in *significant elongation (by 0.05 Å) of the P - SCu bond in comparison with the* average value for the rest two P - S bonds equal to 2.078 Å.



The most interesting tetrameric structure was observed for $CuBr \cdot P(SEt)_2NEt_2$ with both mono- and bidentate coordination modes in one crystal and two unequivalent Cu atoms, one including the P, S, two Br atoms into coordination sphere and the second forming coordination bonds with the phosphorus and three Br atoms.

CONCLUSIONS

The system of coordination bonds in $(RS)_3P$ metal complexes is very labile, the coordination mode being determined by substituents R at sulfur, type of metal, conditions of reactions and crystal growth. Monodentate via the phosphorus atom, bidentate via both P and S atoms of the ambident system, as well as these both coordination modes in one compound are observed. Comparing the geometry of trithiophosphites realized in complexes with the structure of "free" ligands, we observed the overall tendency of increasing their conformational flexibility.

EXPERIMENTAL

The X-ray single diffraction data for all complexes were measured on a "Enraf-Ninus" CAD4 automatic diffractometer using graphite-monochromated Mo K_α radiation using routine methods described in [9]. The details of experiments and structural data will be published elsewhere.

ACKNOWLEDGEMENT

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