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Supramolecular copper halide networks using the coordinative flexibility of the *cyclo*-P_2S_3 middle deck in $(C_5Me_5)_2Mo_2P_2S_3$: Phosphorus versus sulfur coordination

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ABSTRACT

Reaction of solutions of $[Cp^*_2Mo_2P_2S_3]$ (**1**; $Cp^* = \eta^5\text{-}C_5Me_5$) in CH_2Cl_2 with solutions of CuHal (Hal = Cl, Br, I) in CH_3CN gave after slow diffusion the novel coordination polymers $[Cp^*_2Mo_2P_2S_3(CuCl)_4]$ (**2**), $[Cp^*_2Mo_2P_2S_3(CuBr)_3]$ (**3**) and $[Cp^*_2Mo_2P_2S_3(CuI)_3]$ (**4**). The products were characterized by elemental analysis, ^{31}P magic angle spinning (MAS) NMR spectroscopy and single-crystal X-ray crystallography. The solid-state structures of **2** and **3** are composed of two-dimensional polymeric networks, whereas that of **4** contains parallel stacks of one-dimensional ribbons. In all cases the planar *cyclo*-P_2S_3 middle deck of the organometallic building block **1** provides one or two P atoms of the PS dumbbells along with the singly bridging sulfur atom as coordination sites for the various copper halide subunits. The assignment of P atoms follows from the correlation of ^{31}P MAS NMR spectra with X-ray crystallographic data. In all compounds the distribution of main group atoms in the *cyclo*-P_2S_3 middle deck is different from that previously found in the starting material **1**.

1. Introduction

Organometallic E_n ligand complexes (E = P, As, Sb) represent a versatile class of building blocks in supramolecular chemistry [1]. Oligomers and polymers have been formed starting from organometallic P_n-ligand complexes, like $[(C_5H_5)_2Mo_2(CO)_4P_2]$ [2] and $[Cp^*FeP_5]$ [3] (Scheme 1) and various Cu(I) or Ag(I) salts. The formation of spheric aggregates from $[Cp^*FeP_5]$ and CuCl under carefully controlled diffusion conditions is an exciting aspect in the chemistry of nanoclusters derived from C_{60} or C_{80} [4].

On the other hand, the aggregation of S- or Se-organic compounds with copper halides has also been reported recently [5]. The development of bifunctional S, N containing organic linkers allows the construction of organic–inorganic hybrid materials with new and interesting properties [6]. However, little is known on the simultaneous connection of phosphorus and sulfur atoms by metal centers in coordination polymers. To our knowledge the only exception is the interaction of Ag^+ with S and P atoms of two different P_4S_3 cage molecules [7]. Nevertheless, one may expect organometallic complexes with functional P and S sites to be suitable candidates for supramolecular chemistry, in which phosphorus and sulfur atoms may either compete for coordination sites or may both coordinate.

Heterodiatomic EQ ligands of the heavier group 15 elements P, As, Sb (E) and group 16 elements S, Se, Te (Q) are interesting research objects for they can only be stabilized within the coordination sphere of metal complexes [8]. The observed coordination modes include terminally bonded ligands, as in complexes with $M_3(\mu_3\text{-EQ})$ [9] or $M(\eta^1\text{-EQ})$ fragments [10], and bridging ligands, as in $M_2(\eta^2\text{-EQ})$ units [9a,11]. A particular property of pairs of η^2-AsS or η^2-AsSe bridges is their pronounced tendency for dimerization [12]. This dimerization process, which is susceptible to small changes of the electronic situation within the substrate complexes, creates tetraatomic As_2S_2 and As_2Se_2 ligands [12]. Recently, we have established the coexistence of two η^2-PS ligands and a singly bridging sulfur ligand within the dimolybdenum tripledecker complex $[Cp^*_2Mo_2(\mu,\eta^{2:2}\text{-PS})_2S]$ (**1**; $Cp^* = \eta^5\text{-}C_5Me_5$). The resulting *cyclo*-P_2S_3 middle deck serves as a P-donor upon addition of Lewis-acidic metal carbonyls, e.g., $W(CO)_5$, giving rise to an unexpected rearrangement within the middle deck [13,14].

In this work, we report on the synthesis of novel supramolecular networks from the triple-decker complex **1** and copper(I) halides via simultaneous coordination through phosphorus and sulfur. The structural characterization of the products requires combination of X-ray crystallography and solid-state ^{31}P MAS NMR spectroscopy as a tool for the unequivocal assignment of the positions of the main group elements.

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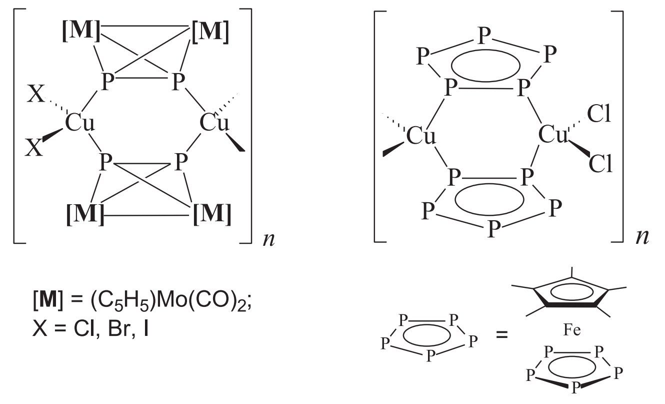


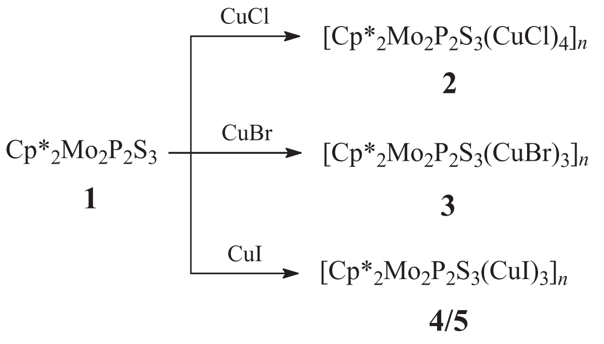
Scheme 1. Building principle of 1D polymeric structures generated from $[(C_5H_5)_2Mo_2(CO)_4P_2]$ and $[Cp^*FeP_5]$, respectively, and various copper halides.

2. Results

2.1. Reaction of **1** with CuHal (Hal = Cl, Br, I)

Reaction of two equivalents of the corresponding Cu(I) halide with one equivalent of **1** gave the novel polymers **2–5** (Scheme 2). Red needles or prisms were obtained after slow diffusion of ether into a mixture of CuHal in MeCN and **1** in CH_2Cl_2. Precipitation of undefined amorphous brown powders during the diffusion processes often may reduce the yields. As cyclovoltammetry of **1** in CH_2Cl_2 reveals a reversible one-electron oxidation at +0.19 V it cannot be excluded that the formation of side-products is due to the easy oxidizability of **1**. After removal of crystalline **2** the mother liquor was investigated by means of ^{31}P MAS NMR spectroscopy after evaporation of the solvent showing that the formation of other polymers of still unknown nature has also to be considered (see below). In one case it has been possible to isolate a few crystals of $[Cp^*_2Mo_2P_2S_3(CuI)_3(CH_2Cl_2)]_n$ (**5**), which is isostructural with polymer **3** (Fig. S1). Compounds **4** and **5** can only be distinguished crystallographically.

Compounds **2–5** are sparingly soluble in polar solvents, e.g., acetonitrile, and insoluble in dichloromethane or toluene. The composition was determined by single-crystal X-ray diffraction analysis and elemental analyses. Positive electrospray ionization (PI-ESI) mass spectra of **2–4** in acetonitrile exhibit similar fragmentation patterns, which indicate complete depolymerization under the action of the coordinating solvent. The largest fragments are peaks corresponding to $[(Cp^*_2Mo_2P_2S_3)_2Cu_2Hal]^+$ (Hal = Cl, Br) and $[(Cp^*_2Mo_2P_2S_3)_2Cu]^+$, respectively, in the case of **4**. The ^{31}P NMR spectra of **2** and **3** in CH_3CN exhibit one signal each at 61.1 and 61.6 ppm, respectively (Table 1). This observation excludes halogen dependence of the chemical shift. As solid-state NMR spectroscopy provides proof for inequivalent P atoms (see below), one may assume dynamic processes in solution equilibrating the phosphorus resonances, e.g., association–dissociation under the influence of the coordinating solvent. However, these cannot be studied because of the poor solubility of the compounds what prevents recording of spectra at low temperatures. Compound **4** is not sufficiently soluble for NMR spectroscopy at room temperature and after application of ultra-sound.



Scheme 2.

Table 1
^{31}P NMR chemical shifts of **1**–**4** and coupling constants $^{31}P–^{63/65}Cu$ (*J* in Hz).

Compound	δ (ppm)(C_6H_6 solution)	δ (ppm)(solid-state)
1 [13,14]	−38.6[a]	−34.2, −36.8
2	61.1[b]	55.2 (1463), 41.4 (1806)
3	61.6[b]	59.1 (1500), 50.5
4	–	58, 42 (1450)[c]

[a] C_6D_6.
[b] CH_3CN.
[c] Estimated values because of superposition with a second compound.

2.1.1. Crystal structure of 2D-$[(Cp^*_2Mo_2P_2S_3)(CuCl)_4]_n$ (**2**)

Compound **2** crystallizes in the triclinic space group $P\bar{1}$. The structure may be described by a two-dimensional polymeric network consisting of triple-decker-like $[Cp^*_2Mo_2P_2S_3]$ units and 1D ribbons of hexameric Cu_6Cl_6 ladders, which alternate with eight-membered $Cu_4Cl_2S_2$ rings (Fig. 1). The latter are formed by interaction of the singly bridging sulfur atoms from two opposed *cyclo*-P_2S_3 middle decks, copper (Cu4) from two of the Cu_6Cl_6 ladders and terminal CuCl units (Cu1, Cl4). By this way, the resulting directed Cu_8Cl_8 substructures serve as *pseudo* one-dimensional backbones, which are linked by the organometallic building blocks **1** via their front- and back-side coordination sites. The front-side of the central middle deck is defined by the phosphorus atoms P1 and P2 of two PS dumbbells [d(P–S)$_{mean}$ 2.059 Å] (Table 2). This assignment follows from the ^{31}P MAS NMR spectrum (see below). The back-side of the middle deck is represented by the singly bridging sulfur S1, which provides both lone pairs for coordination of Cu1 and Cu4, thus connecting two adjacent Cu_8Cl_8 fragments. The result of this interaction is a hexameric Cu_6Cl_6 ladder bearing two pendant CuCl units. Such an arrangement is unique in the coordination chemistry of copper halides. In addition, no example has been found in the Cambridge Structural Database for compounds containing Cu_6Cl_6 ladders, but two examples are given for Cu_6I_6 steplike hexamers [6a,15].

In the resulting *pseudo* one-dimensional chain nearly linearly coordinated copper (Cu1) alternates with tetracoordinated copper atoms (Cu2, Cu3, Cu4), each bearing three chloride ligands. The

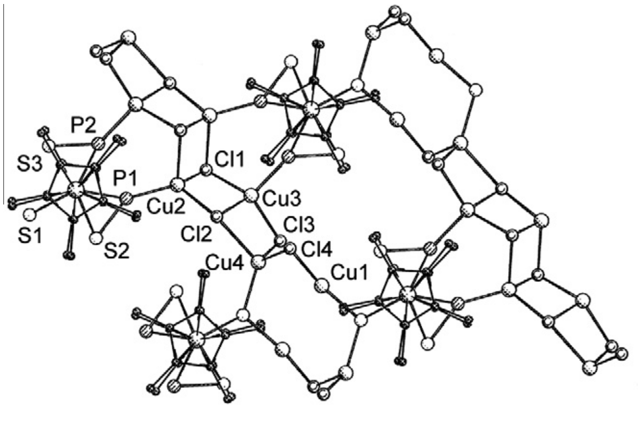


Fig. 1. Section of the structure of **2**; projection on the *b*/*c* plane, H atoms omitted.