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Reactions of silver thiolates with bidentate phosphanes

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ABSTRACT

A series of reactions of different silver thiolates, AgSR (R = Mes (mesityl), Nph (naphthyl), Cy (cyclohexyl)), with bidentate phosphanes was performed yielding a bunch of new compounds, which were characterized by single crystal X-ray diffraction.

Depending on the nature of the thiolate and the phosphane the solid state structure of the products varies from discrete complexes or clusters to a 3-dimensional coordination network. The mesityl group favors the formation of trinuclear units which are then linked in one, e.g. $[Ag_3(SMes)_3(dpph)_2]$ (**5**), two, e. g. $[Ag_3(SMes)_3$ $(dpppt)_2]$ (**4**), or three dimensions $[Ag_3(SMes)_3(dppb)_2]$ (**3**), via the phosphanes. With naphthyl and cyclohexyl groups mostly clusters are formed which are either isolated with some phosphanes in their ligand sphere, e.g. $[Ag_{12}(SCy)_{12}(dpppt)_2]$ (**13**), or additionally linked by the phosphanes to form 1-dimensional chains, e.g. $[Ag_{12}(SCy)_{12}(dppo)]$ (**17**).

1. Introduction

Since many years we are investigating the syntheses and structures of metal-rich cluster compounds of the transition metals [1,2]. These are compounds consisting of a metal chalcogenide core which is surrounded by a shell of tertiary phosphane ligands. The ligands inhibit the formation of the thermodynamically favored binary phases of the metal chalcogenides. This means that this class of substances can be seen as intermediates in the formation of the solid state chalcogenides. For the preparation three methods have been proved.

The first one is the reaction of phosphane complexes of transition metal halides (or pseudo halides) with silylated chalcogen compounds $E(SiMe_3)_2$ and $RE'SiMe_3$ (E, E′ = S, Se or Te), respectively. In organic solvents polynuclear clusters stabilized by PR_3 (R = org. group) are formed, e.g. $[Co_7S_6Cl_2(PPh_3)_5]$ [3], $[Ni_{32}S_{24}(PPh_3)_{10}]$ [4] and $[Cu_{70}Se_{35}(PEt_3)_{20}]$ [5]. Driving force in these reactions is the formation of trimethylsilylhalide (Me_3SiX, X = halogen).

A variation of this method is the *in situ* formation of phosphane complexes by adding the phosphane to a suspension (or solution) of the metal halide in an organic solvent. Addition of silylated chalcogen derivatives yields the final cluster compounds. The composition of the product strongly depends on the reaction conditions. Solvent, reaction temperature and especially the tertiary phosphane play a decisive role for the structure of the isolated cluster. Also by using different stoichiometric amounts of the reactants one can influence the structure of the product. In this respect the second method has the advantage that one can further manipulate the syntheses by variation of the phosphane to halide ratio. However the structure of the *in situ* formed phosphane complexes stays unknown.

The third method uses metal thiolates (MSR; M = Cu, Ag; R = org. group) instead of halides. Also in this case reactions with $S(SiMe_3)_2$ in the presence of mono- or bidentate phosphanes lead to polynuclear compounds. Normally these clusters consist of a metal sulfide core surrounded by a metal thiolate shell. In some cases the phosphanes are incorporated into the ligand shell (e.g. $[Cu_{136}S_{56}(SCH_2C_4H_3O)_{24}(dpppt)_{10}]$ [6] or $[Ag_{320}(StBu)_{60}S_{130}(dppp)_{12}]$ [7]) but one can also isolate compounds without phosphanes ligands (e.g. $[Ag_{344}S_{124}(StBu)_{96}]$ [8]). Nevertheless the presence of the phosphane is essential for the cluster formation indicating a template effect.

Taking into account the complex compositions it is remarkable how reproducible these reactions are as long as one strictly keeps the desired reaction conditions (solvent, temperature, ratio of the reactants). In most cases also the yields are very high and only rarely mixtures of different products crystallize.

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Especially in the field of copper or silver chalcogenides a huge number of clusters containing several hundreds of metal atoms could be synthesized and characterized by single crystal X-ray diffraction. For the synthesis of these very large clusters the third method with thiolates as starting materials and the use of bidentate phosphanes (e.g. $Ph_2P–X–PPh_2$; $X = C_6H_4$, $CH_2–C_6H_4–CH_2$, $(CH_2)_n$, $n = 1–12$) turned out to be very applicable. The first step in these reactions must be the formation of metal thiolate phosphane complexes which then react with $S(SiMe_3)_2$ to give the final metal-rich clusters. The one with the highest number of metal atoms isolated so far has the composition $[Ag_{490}S_{188}(StC_5H_{11})_{114}]$ [7].

In literature one can find only very rare structural data about silver thiolates. From powder diffraction data of a series of *n*-alkyle thiolates ($AgS(CH_2)_nCH_3$, $n = 2, 3, 5, 7$) and aryle thiolates ($AgSC_6H_4$-X, X = H, F, Cl, Br, CH_3, OCH_3) Dance et al. concluded that these compounds consist of layers where the silver and sulfur atoms form honeycomb-like sheets which are separated by the organic substituents [9]. Corrigan and co-workers were able to grow single crystals of one analogous selenium compound ($AgSeC_6H_5$). Its solid state structure shows a distorted honeycomb-like arrangement of the metal atoms with μ4-bridging selenium atoms above and below the silver layer [10]. For $AgS(C(CH_3)(C_2H_5)_2)$ with a more bulky organic group a 1-dimensional chain structure was determined in solid state [11], whereas AgSCy forms cyclic $(AgSCy)_{12}$ molecules (an earlier paper by Hesse and co-workers [12] interpreted the crystallographic data for AgSCy also as a chain structure but Dance [13] insisted that there are significantly shorter Ag–S distances within the $(AgSCy)_{12}$ cycles (~2.45 Å) compared to secondary interactions between silver and sulfur atoms of neighboring $(AgSCy)_{12}$ molecules (~2.81 Å). With sterically highly demanding thiolates discrete complexes $(AgSR)_n$ with $n = 3, 4, 8$ could be crystallized [14]. The silver salt of *N*,*N*-dimetylcysteamine has a 1-dimensional polymeric structure with a cylindrical Ag–S core which is surrounded by an organic shell, where some of the cysteamine groups act as bidentate ligands by additional coordination via the nitrogen atoms [15]. Furthermore there is a limited number of isolated silver thiolate clusters with additional phosphane ligands: $[Ag_4(SPh_4)(PPh_3)_4]$ [16], $[Ag_4(StBu)_4(PnPr_3)_2]$ [17], $[Ag_6(StBu)_6(PiPr_3)_2]$ [17], $[Ag_6(SC_6H_4\text{-}Cl)_6(PPh_3)_5]$ [18], $[Ag_8(SMeEt_2)_8(PPh_3)_2]$ [19] $[Ag_{14}(StBu)_{14}(PPh_3)_4]$ [19], $[Ag_8H_4(S(CH)(CH_3)COO)_6(PPh_3)_6]$ [20] and $[Ag_6(SC_6H_4\text{-}Me)(dppm)_4](PF_6)_2$ [21].

In this paper we want to have a closer look at the first step of the formation of the previously described giant clusters starting from thiolates by just investigating the reaction behavior of different silver thiolates with various bidentate phosphanes without $S(SiMe_3)_2$ as a source for naked sulfide dianions.

2. Experimental

2.1. General

All experiments were performed under an atmosphere of purified nitrogen using standard Schlenk technique. Toluene were heated to reflux over sodium/benzophenone and distilled under a nitrogen atmosphere. *n*-Hexane was dried with $LiAlH_4$. The bidentate phosphanes dppm, dppe, dpppt, dppox and dppfc were purchased from Aldrich, Alfa Aesar or Merck; dpph and dppo were synthesized from $KPPh_2$ and 1,6-dibromohexane or 1,8-dibromooctane, respectively [22]. The silver thiolates were synthesized from silver nitrate and the corresponding thiols following the preparation method for Ag*St*Bu [23].

IR spectra of all compounds were recorded with samples as KBr pellets with a Perkin–Elmer Spectrum GX FTIR system. The following abbreviations are used for the IR data: very strong (vs), strong (s), medium (m), weak (w), very weak (vw) and broad (br). Elemental analyses were performed with an Elementar VarioEL V2.10 instrument.

2.2. X-ray structure determination

Data were collected with a STOE IPDS II or STOE STADI VARI diffractometer by using Mo Kα ($\lambda = 0.71073$ Å) or Cu Kα ($\lambda = 1.54178$ Å) at low temperature. Structure solution and refinement against F^2 were carried out with the SHELXS and SHELXL algorithms [24] using the program OLEX 2.1 [25]; molecular drawings were performed with Diamond 3.2i [26].

2.3. Syntheses

2.3.1. $[Ag_2(SMes)_2(dppe)_{1.5}]$ (**1**)

AgSMes (77 mg, 0.3 mmol) and dppe (120 mg, 0.3 mmol) were suspended in toluene (20 mL) and boiled for several minutes until most solids were dissolved. After stirring for 3 more hours at room temperature a clear colorless solution from which colorless needles of **1** were obtained within 2 days. Yield: 100 mg (0.045 mmol, 60%). EA: $C_{57}H_{58}Ag_2P_3S_2$ (**1**; 1115.8 g/mol) *Anal.* Calc.: C, 61.35; H, 5.24; S, 5.75. Found: C, 61.65; H, 5.32; S, 5.35%. IR (KBr): 3046 (w), 2914 (w), 1481 (w), 1456 (w), 1432 (m), 1369 (w), 1306 (w), 1174 (w), 1156 (w), 1098 (m), 1055 (m), 1024 (w), 996 (w), 855 (w), 844 (m), 743 (s), 731 (s), 718 (s), 693 (vs), 622 (w), 571(w), 555 (m), 517 (s) cm^{-1}.

2.3.2. $[Ag_3(SMes)_3(dppb)_{1.5}]$ (**2**)

AgSMes (240 mg, 0.93 mmol) and dppb (216 mg, 0.51 mmol) were suspended in toluene (20 mL). After stirring for 3 h at room temperature, the suspension was heated to boiling until all solids dissolved forming clear colorless solution. The hot solution was put in a container with hot water and the whole system was let to cool to room temperature slowly. After 1 day colorless quadrangular plates of **2** (together with a small amount of hexangular plates of **3**) crystallized. EA of hand-picked and vacuum-dried crystals of **2**: $C_{69}H_{75}P_3S_3Ag_3$ (**2**; 1417.1 g/mol) *Anal.* Calc.: C, 58.48; H, 5.33; S, 6.79. Found: C, 58.90; H, 5.55; S, 6.91% (indicating the loss of lattice bound solvent molecules). IR of hand-picked sample of **2** (KBr): 3048 (w), 2911 (w), 1586 (w), 1571 (w), 1482 (w), 1458 (m), 1434 (m), 1369 (w), 1306 (w), 1261 (w), 1173 (w), 1098 (m), 1080 (w), 1056 (m), 1024 (m), 952 (w), 844 (m), 801 (w), 740 (m), 722 (s), 692 (vs), 624 (w), 571 (w), 554 (m), 515 (s) cm^{-1}.

2.3.3. $[Ag_3(SMes)_3(dppb)_2]$ (**3**)

AgSMes (123 mg, 0.48 mmol) and dppb (210 mg, 0.49 mmol) were suspended in toluene (20 mL). After stirring for 1 h at room temperature, the suspension was heated to boiling until all solids dissolved forming clear colorless solution. The hot solution was put into a container with hot water and the whole system was slowly cooled to room temperature slowly. After 1 day colorless hexangular plates of **3** crystallized (together with a small amount of **2**). EA of hand-picked crystals of and vacuum-dried crystals of **3**: $C_{97}H_{103}Ag_3P_4S_3$ ($\mathbf{3}\cdot 2C_7H_8$; 1812.56 g/mol) *Anal.* Calc: C, 64.28; H, 5.73; S, 5.31. Found: C, 63.92; H, 5.85; S, 5.22% (indicating no significant loss of lattice bound solvent molecules). IR of hand-picked sample of **3** (KBr): 3046 (w), 2914 (w), 1481 (m), 1456 (m), 1432 (m), 1369 (w), 1306 (w), 1174 (m), 1156 (w), 1098 (m), 1070 (m), 1055 (m), 1024 (m), 996 (w), 950 (w), 855 (w), 844 (m), 743 (s), 731 (s), 718 (s), 693 (vs), 622 (w), 571 (w), 555 (m), 517 (s) cm^{-1}.

2.3.4. $[Ag_3(SMes)_3(dpppt)_2]$ (**4**)

AgSMes (129 mg, 0.5 mmol) and dpppt (440 mg, 1 mmol) were suspended in toluene (15 mL) and stirred at room temperature for 1 h yielding a clear colorless solution. After layering with *n*-hexane