DOI: 10.1002/ejic.200900581

Syntheses, Structures and Theoretical Investigations of $[Li(thf)_4]_2[Ti_2Cu_8S_4(SPh)_{10}]$ and $[Ti_2Ag_6S_6Cl_2(PPh\mathit{i}Pr_2)_6]$

Heino Sommer,[a] Nedko Drebov,[b] Andreas Eichhöfer,[c] Reinhart Ahlrichs,*[b] and Dieter Fenske*[a,c]

Keywords: Copper / Cluster compounds / Density functional calculations / Titanium / Sulfur

The reaction of CuOAc (OAc = acetate) with $TiCl_4$·2thf and LiSPh in thf leads to the formation of tiny deep-red crystals of $[Li(thf)_4]_2[Ti_2Cu_8S_4(SPh)_{10}]$. The silver/titanium cluster complex $[Ti_2Ag_6S_6Cl_2(PPh\mathit{i}Pr_2)_6]$ was synthesized by the reaction of $TiCl_4$·2thf with $AgPhCO_2$ and $S(SiMe_3)_2$ in the presence of $PPh\mathit{i}Pr_2$. The crystal structures of the compounds were determined by X-ray analysis of single crystals. Additionally, theoretical investigations were performed to assign the proper chlorine/sulfur atomic positions and to rationalize the bonding situation in **1** and **2**.

Introduction

Titanium thiolate complexes have not been investigated in great detail; nonetheless, there has been some interest in this area due to their suitability as precursors for the formation of thin films by CVD techniques (CVD = chemical vapour deposition). For example, TiS films were obtained by gas-phase decomposition of $Ti(S\mathit{t}Bu)_4$ under relatively mild conditions.[1] The first well-characterized titanium thiolate was reported in 1987 with bulky aryl substituents, $[Li(OEt_2)_3][Ti(S\text{-}2,4,6\text{-}\mathit{i}Pr_3C_6H_2)_4]$.[2] Several other known examples like $[Li(C_4H_8O)_4][Ti_2(SPh)_9]$,[3] $[NMe_2H_2][Ti_2(SMe)_9]$ and $[Ti_3(SMe)_{12}]$ have been isolated only in low yields.[4] The structural analysis of these complexes normally reveals a trigonal distortion of the octahedral coordination around the titanium atoms. In addition, larger cyclopentadienyltitanium/sulfur clusters, such as $[Cp_4Ti_4S_4]$[5] ($Cp = \eta\text{-}C_5H_5$), $[Cp_4Ti_4(\mu_3\text{-}S)_3(\mu_2\text{-}S)_2(\mu_2\text{-}SEt)_2]$, $[Cp_6Ti_6(\mu_3\text{-}S)_4(\mu_3\text{-}O)_4]$[6] and $[Cp_5Ti_5(\mu_3\text{-}S)_6]$,[7] were reported some years ago.

Interest in early–late transition metal heterodimetallic complexes arises for several reasons. The combination of two different metal atoms with an electron-deficient and an electron-rich metal offers the possibility of Lewis acid activation of a substrate molecule bound to the electron-rich metal centre. Thiolato-bridged titanium heretometallic compounds have been reviewed during the last two decades.[8] Examples of well-characterized sulfur-bridged heterodimetallic complexes of titanium and another transition metal are $[Cp_2Ti((CH_3)_2PCH_2CH_2S)_2Cu]PF_6$,[9] $[(Cp_2Ti(SCH_2CH_2CH_2S)_2TiCp_2)Ag]BPh_4$,[10] $[CpTi(SCH_2CH_2CH_2S)_2Cu]_n$ and $[CpTi(SCH_2CH_2S)_2CuPMe_3]$.[11] The authors suggested that the short Ti–Cu distance (Ti–Cu 280.3 pm) in $[(Cp_2Ti(SCH_2CH_3)_2TiCp_2)CuL]PF_6$ (L = PPh_3 and $P(C_6H_{11})_3$) is consistent with $Cu(d^{10})\rightarrow Ti(d^0)$ dative interactions.[12] Other authors propose that the resultant highly electron-deficient titanium centres in early–late transition metal heterodimetallic cubane-type compounds such as $[Cp_2Ti_2Cu_2(\mu_3\text{-}S)_4(PPh_3)_2]$[13] or $[Cp_2Cp^*_2Ti_2Ru_2(\mu_3\text{-}S)_4]$[14] seem to be stabilized by M→Ti dative bonds, as indicated by the relatively short M–Ti distances.

Recently we reported several studies by a combined approach of experiment and theory.[15] In these cases the X-ray investigation provided structural data, but an unequivocal assignment of atoms was not possible, e.g., for chlorine and sulfur; this ambiguity was resolved by DFT calculations. In continuation of earlier work, we now report the syntheses and crystal structures of the mixed titanium(IV)/coin metal complexes $[Li(thf)_4]_2[Ti_2Cu_8S_4(SPh)_{10}]$ (**1**) and $[Ti_2Ag_6S_6Cl_2(PPh\mathit{i}Pr_2)_6]$ (**2**). Theoretical investigations, described after the discussion of the experiments, were performed for **1** and **2** to comment on the proposed $d^{10}\rightarrow d^0$ interactions.

[a] Institut für Anorganische Chemie, Universität Karlsruhe, Engesserstr. 15, 76131 Karlsruhe, Germany
Fax: +49-721-608-8440
E-mail: dieter.fenske@chemie.uni-karlsruhe.de
[b] Institut für Physikalische Chemie, Universität Karlsruhe, Fritz-Haber-Weg 4, 76131 Karlsruhe, Germany
E-mail: reinhart.ahlrichs@chemie.uni-karlsruhe.de
[c] Institut für Nanotechnologie, Forschungszentrum Karlsruhe, Postfach 3640, 76021 Karlsruhe, Germany

Results and Discussion

The reaction of CuOAc (OAc = acetate) with $TiCl_4$·2thf and LiSPh in thf leads to the formation of deep red crystals in low yields (Scheme 1). Due to virtually identical X-ray structure factors of chlorine and sulfur, the X-ray structural

analysis only reveals the formula $[Li(thf)_4]_2[Ti_2Cu_8X_4(SPh)_{10}]$ (X = Cl and/or S), whereas the exact structural formula $[Li(thf)_4]_2[Ti_2Cu_8S_4(SPh)_{10}]$ of **1** was determined with the help of electronic structure calculations (see below). In addition, ESI-TOF mass spectrometry was applied.[16] However, the ESI-TOF mass spectra indicated a decomposition of **1** in solution, and only $Cu_x(SPh)_y^{z-}$ fragments {e.g., $[Cu(SPh)_2]^-$, $[Cu_2(SPh)_3]^-$ and $[Cu_4(SPh)_6]^{2-}$} could be clearly verified. The formation of **1** is most easily rationalized by assuming a cleavage of S–C and S–Si bonds. This has been observed repeatedly in the syntheses of silver sulfide clusters.[17]

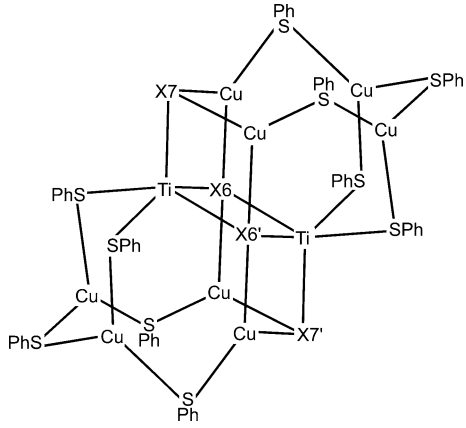
$$TiCl_4{\cdot}2thf + CuOAc + 5\,LiSPh \xrightarrow{thf} [Li(thf)_4]_2[Ti_2Cu_8S_4(SPh)_{10}]\ (\mathbf{1})$$

$$TiCl_4{\cdot}2thf + 3\,AgPhCO_2 + 3\,S(SiMe_3)_2 \xrightarrow[thf]{3\,PPh_2iPr} [Ti_2Ag_6S_6Cl_2(PPh_2iPr)_6]\ (\mathbf{2})$$

Scheme 1.

Treatment of $TiCl_4{\cdot}2thf$ with $AgPhCO_2$, a phosphane (PPh_2iPr) and $S(SiMe_3)_2$ in a molar ratio of 1:3:3:3 at room temperature gives rise to orange-coloured crystals of $[Ti_2Ag_6S_6Cl_2(PPh_2iPr)_6]$ (**2**).

Compound **1** crystallizes in the triclinic space group ($P\bar{1}$). As a result of the single-crystal X-ray diffraction analysis the molecular structure can be refined to structural formula $[Li(thf)_4]_2[Ti_2Cu_8X_4(SPh)_{10}]$ (X = Cl, S; Scheme 2). However, the X-ray method does not allow to discriminate between chlorine and sulfur atoms because of virtually identical X-ray structure factors, and the bond lengths for M–S and M–Cl (M = Ti, Cu) are also very similar. This problem has been discussed previously.[15b] Provided that all X are Cl^-, the titanium atoms would have a formal oxidation state +II, whereas all X occupied by S^{2-} would lead to a formal assignment of Ti^{4+} always assuming a +1 charge for copper.



Scheme 2.

In the crystallographic structure of compound **1** four atomic positions (X6, X6′, X7 and X7′) were left unassigned (X). DFT calculations were carried out for the anion part $[Ti_2Cu_8X_4(SPh)_{10}]^{2-}$ (X = Cl, S), considering different distributions of sulfur and chlorine atoms amongst these X atomic positions: four sulfur, four chlorine.[18] The so constructed structures of C_i symmetry were structurally optimized, as described in the Experimental Section. In Table 1 and Figure 1 we compare computed with experimental bond lengths. The result is clear-cut: only X = S yields an actually very satisfying agreement, the largest deviation for bond lengths (Ti–Cu, Ti–X and Cu–X) of $[Ti_2Cu_8S_4(SPh)_{10}]^{2-}$ is only 6 pm (Figure 2), even for the relatively

Table 1. Selected geometric parameters [pm].

	Bond lengths, experimentally determined	Bond lengths, computed[a] $[Ti_2Cu_8Cl_4(SPh)_{10}]^{2-}$ bp/def2-SV(P)	bp/def2-TZVP	$[Ti_2Cu_8S_4(SPh)_{10}]^{2-}$ bp/def2-SV(P)	bp/def2-TZVP
Ti1–μ_2-S1	245.36(13)	247.6	247.0	246.4	**247.6**
Ti1–μ_2-S2	247.74(12)	247.5	248.5	249.8	**250.3**
Ti1–μ_4-S6	240.24(11)	265.9	260.9	240.3	**240.7**
Ti1–μ_4-S6′	238.42(14)	268.2	263.7	241.4	**240.6**
Ti1–μ_3-S7	223.70(10)	245.9	242.7	226.5	**226.8**
Cu1–μ_2-S4	220.84(12)	232.7	228.1	226.2	**223.2**
Cu1–μ_4-S6	230.73(10)	247.5	245.1	231.7	**230.0**
Cu2–μ_2-S3	220.57(12)	227.1	223.9	226.7	**224.0**
Cu2–μ_4-S6′	228.15(10)	234.3	231.4	233.7	**231.4**
Cu2–μ_3-S7	224.99(10)	255.7	254.9	230.6	**226.0**
Cu3–μ_2-S4	224.17(10)	229.8	228.6	229.0	**226.4**
Cu3–μ_2-S5	225.09(11)	229.8	228.6	229.0	**226.0**
Cu3–μ_2-S1	229.74(9)	235.2	233.6	236.5	**233.8**
Cu4–μ_2-S5	225.26(12)	233.1	229.6	230.7	**226.6**
Cu4–μ_2-S3	227.44(12)	239.7	235.2	231.7	**229.4**
Cu4–μ_2-S2	228.47(10)	233.7	230.6	232.1	**230.7**
Ti1···Ti1′	339.07(17)	292.1	297.7	344.6	**337.5**
Ti1···Cu1′	278.85(12)	294.9	297.0	283.9	**282.7**
Ti1···Cu2′	277.68(12)	292.3	295.2	279.4	**279.7**
Cu1···Cu2	288.19(10)	239.5	243.7	271.7	**287.9**
Cu3···Cu4	277.11(10)	256.0	263.9	263.4	**274.3**

[a] For the sake of completeness we document results for def2-TZVP as well as for the smaller def2-SV(P) basis set. It should be noted that the deviations larger than 6 pm (def2-TZVP) occur only for not directly bonded atom pairs.

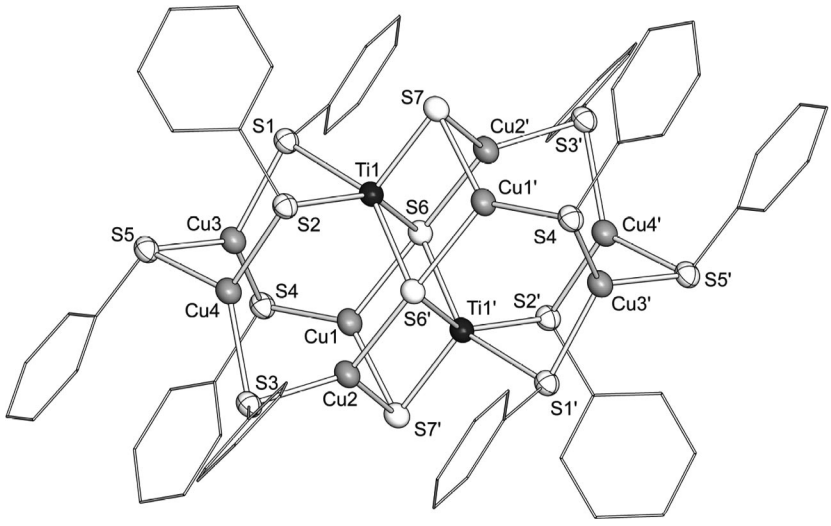


Figure 1. Molecular structure of the $[Ti_2Cu_8S_4(SPh)_{10}]^{2-}$ dianion in the crystal structure (50% ellipsoids).

weak bonds like Ti1–Ti1′, Ti1–Cu1′, Ti–Cu2′ and Cu3–Cu4. The computed structure was proven by vibrational analysis to represent a minimum on the potential energy surface. With X = S, titanium has a formal oxidation state of +IV, that is a d^0 electronic configuration.

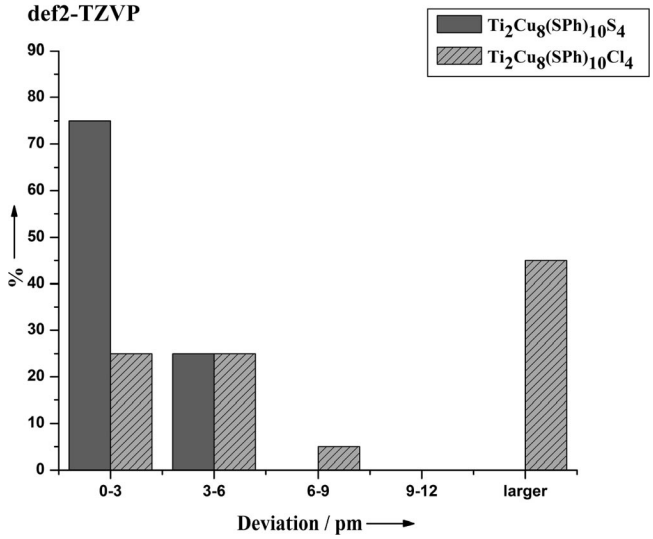


Figure 2. Histograms showing statistics of deviations [pm] between experimental and computed interatomic distances of **1** for all X = Cl and X = S, respectively. The column height gives the percentage of cases with deviations indicated on the abscissa. For both cases M–X and M–M distances up to $1.05\,r_{M-X(M)}$ are considered, where $r_{M-X(M)}$ is the sum of corresponding covalence radii.

A view of the centrosymmetric molecular structure of the dianion in **1** is shown in Figure 1. All titanium atoms are coordinated by five sulfur atoms in a distorted square-pyramidal geometry. The μ_4-S^{2-} atoms S6 and S6′ bridge two Ti (Ti1, Ti1′) atoms and two Cu (Cu1, Cu2′) atoms fairly symmetrically with Ti–S bonds (238.4–247.7 pm) significantly longer than those in the apical position (Ti1–S7 223.7 pm) of the distorted square-based pyramidal geometry. All copper atoms are coordinated by three sulfur atoms (220.6–230.7 pm) in a distorted trigonal-planar fashion (S–Cu–S 359.62–360°). The μ_2-S–Ti bonds (Ti1–S1 245.4, Ti1–S2 247.7 pm) are in the range of those which were found in $[CpTi(SCH_2CH_2S)_2CuPMe_3]$.[11] The nonbonding Ti–Ti distance (338.4 pm) is comparable to that found in Ti_2-$[O_2CNtBu\text{-}3,5\text{-}C_6H_3Me_2]_4(NtBu\text{-}3,5\text{-}C_6H_3Me_2)_2$.[19] Recently, a short Ti–Ti bond of 259.4 pm was determined in $[Ti_2(\eta^2\text{-hpp})_2(\eta^2\text{-hpp})Cl_2]$ (hpp = 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine).[20] The Ti–Cu distances range from 277.7 to 278.8 pm and are insignificantly shorter than the discussed Ti–Cu distances in $[Ti_2Cu_2S_4Cp_2(PPh_3)_2]$.[13] Nonbonding Cu–Cu distances (288.2–294.4 pm) compare with those found in other Cu clusters.[21] In $[Li(thf)_4]^+$ the lithium atom is connected to four thf molecules (Li–O 190.1–195.5 pm) oriented in a tetrahedral fashion (104.8–113.9°).

Compound **2** crystallizes in the monoclinic space group $P2_1/c$ with two molecules and two dme molecules in the unit cell. The molecular structure of **2** is a distorted Ti_2Ag_6 cube with μ_4-S^{2-} ligands (Figure 3). The titanium atoms are coordinated tetrahedrally by one chlorine atom and three sulfur atoms. Ti–S bond lengths are in the range of Ti–S distances reported before and discussed above. The terminal Ti–Cl bond (228.3 pm) is similar to that in $[TiCu_3S_3Cl(PEt_3)_4]$.[22] All Ag atoms assume a tetrahedral geometry, formed by a phosphane ligand and three S^{2-} atoms. The Ag–S bond lengths and the Ag–Ag distances fall within the ranges typical for sulfido-bridged silver clusters.[23] The cluster core of **2** is structurally analogous to $[Ni_8S_6Cl_2(PPh_3)_6]$[24] $[Co_8S_6(SPh)_8]^{4-}$,[25] $[Fe_8S_6I_8]^{3-}$,[26] and $[Ti_2Cu_6S_6Cp_2(PEt_3)_6]$.[22] Compound **2** and the isostructural $[Ti_2Cu_6S_6Cp_2(PEt_3)_6]$ contain 112 valence electrons and represent a rare example of chloro(sulfido)titanium complexes without cyclopentadienyl ligands. The core structure of **2** is identical to the one of $[Cp_2Ti_2Cu_6S_6(PEt_3)_6]$ described by Komuro.[22] In an analogous way, it can be viewed as an $[Ag_6S_6]^{6-}$ prismane, which is capped at each of the two Ag_3S_3 hexagonal chairs by Ti–Cl units.

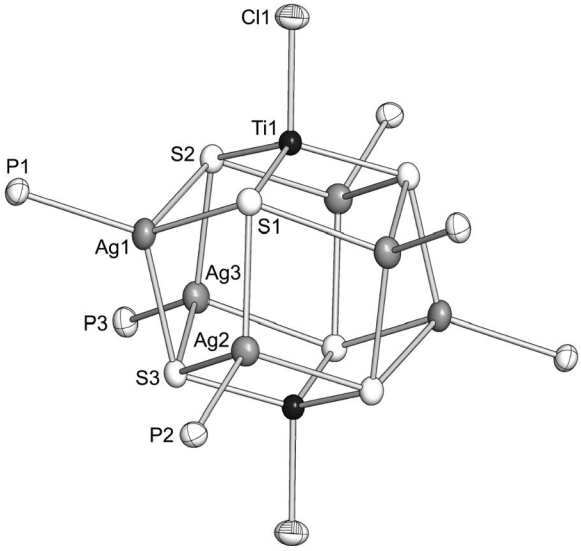


Figure 3. Molecular structure of $[Ti_2Ag_6S_6Cl_2(PPh_iPr_2)_6]$ (50% ellipsoids); phenyl groups and isopropyl groups have been omitted for clarity. Symmetry transformation for generation of equivalent atoms: $-x$, 0.5 + y, 0.5 – z. Selected interatomic distances [pm] and angles [°]; computed distances [pm] in square brackets: Ti1–S1 226.42(10) [228.5], Ti1–S2 225.23(11) [228.2], Ti1–S3′ 225.11(10) [228.3], Ti1–Cl1 228.35(13) [227.1], Ti–Ag 308.87(8) – 310.72(9) [310.6-311.6], Ag1–S2 261.14(10) [263.4], Ag1–S1 261.64(10) [263.3], Ag1–S3 266.38(14) [271.8], Ag2–S2′ 260.26(10) [262.7], Ag–Ag 309.76(6)–327.91(7) [325.1–327.1], Ag–P 242.63(10)–243.77(10) [243.4–244.2]; S–Ti–S 111.47(4)–112.10(4) [111.7–112.0], S–Ag–S 90.75(3)–103.69(3) [91.7–100.7], S–Ti–Cl 106.53(4)–107.54(4) [106.7–107.3], S–Ag–P 114.63(3) 122.85(3) [111.1–128.3], Ag2–Ag1–Ag3 92.58(3) [91.9] Ag3′–Ag2–Ag1 95.42(2) [93.1].

Computed structure parameters for **2** also show close agreement with experimental values for all bond lengths – deviations of 6 pm at most, as for **1**.

Molecular Electronic Structure

We finally comment on the suggested $d^{10}\rightarrow d^0$ dative bonding between Cu (Ag) and Ti atoms. For this purpose we have computed NAO occupations with the following results:

1: Ti $3d^{3.3}$ $4s^{0.3}$ Cu $3d^{9.8}$ $4s^{0.4}$

2: Ti $3d^{3.2}$ $4s^{0.3}$ Ag $4d^{9.9}$ $5s^{0.4}$

This confirms the d^{10} configuration for coinage metal elements, the 3d occupation of titanium is not even close to zero, however. The formal characterisation of Ti as +IV is not connected with a d^0 occupation. This may be unexpected for non-theoreticians, but it is a rather common feature;[15a,15d,27] it is also in agreement with the electronegativity according to Allred and Rochow: Ti 1.32, Cu 1.75, S 2.44,[28] from which one would not expect a pronounced bond polarity. A very similar picture is found for sulfur, where a formal oxidation state –II is connected with occupations around $3s^{1.7}$ $3p^{4.8}$, with variations of 0.15 depending on the actual chemical surrounding in **1** and **2**. These examples show again that formal oxidation states have no direct connection to actual atomic orbital occupations or atomic charges.[29]

We come back to the idea of dative $d^{10}\rightarrow d^0$ bonds, which was proposed on the basis of the relatively short titanium–copper distances (280–302.4 pm)[12,30,31] The idea has been supported by Fenske–Hall MO (FHMO) calculations for $[Cp_2Ti(SH)_2CuPH_3]^+$, which resulted in a small positive Ti–Cu overlap population.[32] Although the authors admit that "bonding cannot be quantitatively assessed with accuracy by FHMO calculations" they consider it as a "qualitative and comparative guide". This is a very weak argument; a Mulliken population analysis for the DFT density of **1** gives a negative overlap population for two basis sets def2-SV(P) and def2-TZVP. We also follow Hoffman et al.[33] and Cotton et al.[34] who, in the context of d^{10}–d^{10} interactions, have pointed out that short distances alone are not an indication for metal–metal bonding. This view has been supported by extensive ab initio calculations of copper complexes with Cu–Cu distances in the range 216–250 pm.[35] Metal–metal distances are of course dominantly determined by attractive Coulomb interactions between metal atom cations and bridging anionic ligands. These comments apply to the Cu–Cu distances in **1** (277.1–288.2 pm). Our results do not provide support for $d^{10}\rightarrow d^0$ dative bonding or d^{10}–d^{10} interaction in **1** and **2**.

Conclusions

We have described preparation, molecular structures and results of DFT treatments of new titanium/transition metal chalcogenolate/chalcogenide cluster complexes. A comparison of measured and computed bond lengths shows virtually perfect agreement.

Experimental Section

General: Investigations were performed under exclusion of water and oxygen in purified N_2; thf (tetrahydrofurane) and dme (1,2-dimethoxyethane) were dried with sodium/benzophenone and were distilled under nitrogen. $TiCl_4$·2thf,[36] LiSPh[37] and $S(SiMe_3)_2$[38] were prepared according to literature procedures. CuCl was washed with HCl, CH_3OH, and diethyl ether to remove traces of $CuCl_2$, and then dried under vacuum. $AgPhCO_2$ was purchased from Sigma Aldrich.

1: CuOAc (36 mg, 0.3 mmol) and $TiCl_4$·2thf (100 mg, 0.3 mmol) were suspended in thf (20 mL). To the yellow suspension a solution of LiSPh (175 mg, 1.5 mmol) in thf (10 mL) was added dropwise. An immediate change from yellow to violet was observed. After 1 d of stirring, the solution turned deep-red. The solution afforded after three weeks tiny deep-red crystals of $[Li(thf)_4]_2[Ti_2Cu_8S_4(SPh)_{10}]$ in low isolated yield (less than 20% based on titanium). Attempts to improve the yield by stoichiometric reactions [molar ratio 1:4:2:5 of $TiCl_4$·2thf/CuOAc/$S(SiMe_3)_2$/LiSPh] failed to give crystalline **1**. IR (KBr): $\tilde{\nu}$ = 413.1 (w), 452.6 (m), 573.1 (w), 689.1 (m), 739.1 (m), 802.6 (s), 1022.9 (s), 1039.9 (s), 1082.9 (s), 1094.8 (s), 1261.9 (s), 1436.8 (m), 1453.2 (m), 1475.5 (m), 1577.3 (m), 1627.3 (br.), 2871.4 (m), 2963.9 (m), 3050.0 (w) cm^{-1}.

Table 2. Crystal data.

	1	**2**
Empirical formula	$C_{92}H_{114}O_8Cu_8Li_2S_{14}Ti_2$	$C_{72}H_{114}Ag_6Cl_2P_6S_6Ti_2$
Molecular mass	2414.67	2352.02
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a [Å]	13.002(3)	13.999(3)
b [Å]	13.430(3)	24.099(5)
c [Å]	16.484(3)	17.096(3)
α [°]	68.02(3)	
β [°]	74.74(3)	109.93(3)
γ [°]	70.09(3)	
V [Å]	2479.1(9)	5422.1(19)
Z	1	2
$\delta_{calcd.}$ [g cm^{-3}]	1.617	1.539
μ(Mo-K_α) [mm^{-1}]	2.178	1.499
F(000)	1236	2544
T [K]	180(2)	180(2)
$2\theta_{max}$ [°]	54	51
Measured reflecions	16640	37191
Unique reflecions	9659	10215
Refined parameters	669	534
R_{int}	0.0650	0.1081
GOOF	1.050	0.989
Residual electron density [e Å^{-3}]	0.779/–1.091	0.758/–0.963
R_1 [$I > 2\sigma(I)$][a]	0.0487	0.0361
wR_2 (all data)[b]	0.1491	0.0880

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

2: $TiCl_4$·2thf (200 mg, 0.6 mmol) and $AgPhCO_2$ (411 mg, 1.8 mmol) were suspended in dme (20 mL), and $PPhiPr_2$ (0.35 mL, 1.8 mmol) was added to the yellowish suspension. After 1 h of stirring, the mixture became clear, and $S(SiMe_3)_2$ (0.38 mL, 1.8 mmol) was added to give a deep-red solution. Within several hours, **2** crystallized as orange blocks in a yield of 88%. $C_{72}H_{114}Ag_6Cl_2P_6S_6Ti_2$ (2171.81): calcd. C 39.82, H 5.29, S 8.5; found C 39.92, H 4.95, S 8.71. IR (KBr): $\tilde{\nu}$ = 2954.7 (s), 2925.8 (m), 2893.8 (m), 2866.4 (m), 1820.5 (w), 1735.3 (w), 1865.4 (w), 1570.5 (m), 1459.1 (m), 1434.1 (s), 1379.6 (w), 1361.4 (w), 1315.6 (w), 1292.24 (w), 1239.73 (m), 1106.3 (m), 1024.4 (s), 1000.4 (w), 924.1 (w), 881.6 (m), 853.2 (w), 756.9 (s), 703.9 (s), 629.3 (m), 518.8 (s), 431.3 (s), 411.0 (s) cm^{-1}.

Crystallography: Crystals suitable for single-crystal X-ray diffraction were taken directly from the reaction solution of the compounds and then selected in perfluoroalkylether oil. Single-crystal X-ray diffraction data of **1** and **2** were collected by using graphite-monochromatized Mo-K_α radiation (λ = 0.71073 Å) with a STOE IPDS II (Imaging Plate Diffraction System). The structures were solved with the direct-methods program SHELXS of the SHELXTL PC suite of programs, and were refined with the use of the full-matrix least-squares program SHELXL.[39] Molecular diagrams were prepared by using DIAMOND 3.1d.[40] All atoms of the cluster molecule **1** were refined with anisotropic displacement parameters with exception of the H atoms. The hydrogen atoms of $[Ti_2Cu_8S_4(SPh)_{10}]^{2-}$ were located in the difference-Fourier map and subsequently refined with C–H distances of 0.905–1.069, whereas the H atoms of $[Li(thf)_4]^+$ were calculated in fixed positions. The Ag, Cl, P, S, Ti, and C atoms of the cluster molecule in **2** were refined with anisotropic displacement parameters, whereas O and C atoms of the solvent molecules were refined isotropically. In addition, split positions were calculated for the oxygen atoms O1, O3 and O4 of the dme molecules; H atoms were calculated in fixed positions for **2**. For all data sets a numerical absorption correction was applied[41] (Table 2). CCDC-736700 (**1**) and CCDC-736701 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

DFT Calculations: Quantum chemical calculations were carried out with TURBOMOLE[42] to assign the proper atomic positions and to investigate the chemical bonding in **1** and **2**. Because of the large number of atoms in these compounds (up to 208 atoms) we chose the BP86 functional,[43] which has proved reliable in previous similar treatments.[15a] To be on the safe side we used an extended def2-TZVP basis[44] for heavier atoms; only for the Ph groups was the smaller SV(P) basis[45] selected. We applied the m4 multiple grid for numerical evaluations of the exchange-correlation term[43b,46] and the efficient MARI-J technique (multipole-accelerated resolution of identity approximation for the inter-electronic Coulomb term J).[46] All structure parameters were optimized in C_i symmetry by means of analytical gradients using redundant internal coordinates.[47] X-ray geometries served as a start where possible, only a few H atoms of Ph had to be assigned proper positions by hand. Dianion **1** was treated with the COSMO solvent model[48] by using a small value for the dielectric constant, ε = 20. Molecular electronic atom charges are discussed in terms of NPA (natural population analysis).[49]

Acknowledgments

We gratefully acknowledge financial support by the DFG Center for Functional Nanostructures, the Forschungszentrum Karlsruhe and the Fonds der Chemischen Industrie.

[1] M. Bochmann, I. Hawkins, L. M. Wilson, *J. Chem. Soc., Chem. Commun.* **1988**, 344–345.
[2] G. A. Sigel, P. P. Power, *Inorg. Chem.* **1987**, *26*, 2819–2822.
[3] C. Puke, K. Schmengler, K. Kirschbaum, O. Conrad, D. M. Giolando, *Acta Crystallogr., Sect. C* **2000**, *56*, e542.

[4] W. Stüer, K. Kirschbaum, D. M. Giolando, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1981–1982.
[5] F. Bottomley, P. N. Keizer, P. S. White, *J. Am. Chem. Soc.* **1988**, *110*, 141.
[6] A. V. Firth, D. W. Stephan, *Inorg. Chem.* **1997**, *36*, 1260–1262.
[7] F. Bottomley, G. O. Egharevba, P. S. White, *J. Am. Chem. Soc.* **1985**, *107*, 4354.
[8] D. W. Stephan, *Coord. Chem. Rev.* **1989**, *95*, 41–107; N. Wheatley, P. Kalck, *Chem. Rev.* **1999**, *99*, 3379–3419; D. W. Stephan, T. T. Nadasdi, *Coord. Chem. Rev.* **1996**, *147*, 147–208.
[9] K. Matsuzaki, H. Kawaguchi, P. Voth, K. Noda, S. Itoh, H. D. Takagi, K. Kashiwabara, K. Tatsumi, *Inorg. Chem.* **2003**, *42*, 5320–5329.
[10] T. T. Nadasdi, D. W. Stephan, *Organometallics* **1992**, *11*, 116–122.
[11] T. T. Nadasdi, D. W. Stephan, *Inorg. Chem.* **1994**, *33*, 1532–1538.
[12] T. A. Wark, D. W. Stephan, *Inorg. Chem.* **1987**, *26*, 363–369.
[13] T. Amemiya, S. Kuwata, M. Hidai, *Chem. Commun.* **1999**, 711–712.
[14] T. Nagano, S. Kuwata, Y. Ishii, M. Hidai, *Organometallics* **2000**, *19*, 4176–4178.
[15] a) R. Ahlrichs, A. Eichhöfer, D. Fenske, K. May, H. Sommer, *Angew. Chem.* **2007**, *119*, 8402–8405; *Angew. Chem. Int. Ed.* **2007**, *46*, 8254–8257; b) R. Ahlrichs, A. Eichhöfer, D. Fenske, O. Hampe, M. M. Kappes, P. Nava, J. Olkowska-Oetzel, *Angew. Chem.* **2004**, *116*, 3911–3915; *Angew. Chem. Int. Ed.* **2004**, *43*, 3823–3827; c) R. Ahlrichs, C. E. Anson, R. Clerac, D. Fenske, A. Rothenberger, M. Sierka, S. Wieber, *Eur. J. Inorg. Chem.* **2004**, 2933–2936; d) H. Sommer, A. Eichhöfer, N. Drebov, R. Ahlrichs, D. Fenske, *Eur. J. Inorg. Chem.* **2008**, 5138–5145.
[16] We are grateful to Dr. O. Fuhr for the measurement of the ESI-TOF mass spectra. The mass spectra were taken with a time-of-flight (TOF) mass spectrometer (Bruker Daltonics, MicroTOF-QII) equipped with an electrospray ion source (off axis sprayer). The solutions were sprayed at typical flow rates of about 180 μL/h and nebulized by using dry nitrogen. The desolvation glass capillary was heated to 180 °C. For all ion signals observed the charge state was immediately evident from their isotopomere splitting, and assignment to an ionic species was unequivocally confirmed by comparison with the computed isotopic distribution.
[17] a) D. Fenske, C. E. Anson, A. Eichhöfer, O. Fuhr, A. Ingendoh, C. Persau, C. Richert, *Angew. Chem.* **2005**, *117*, 5376–5381; *Angew. Chem. Int. Ed.* **2005**, *44*, 5242–5246; b) C. E. Anson, A. Eichhöfer, I. Issac, D. Fenske, O. Fuhr, P. Sevillano, C. Persau, D. Stalke, J. Zhang, *Angew. Chem.* **2008**, *120*, 1346–1351; *Angew. Chem. Int. Ed.* **2008**, *47*, 1326–1331.
[18] We further investigated different combinations of two sulfur and two chlorine atoms, but these cases can be excluded, since they lead to very poor agreement with the experimental bond lengths.
[19] A. Mendiratta, C. C. Cummins, F. A. Cotton, S. A. Ibragimov, C. A. Murillo, D. Villagrán, *Inorg. Chem.* **2006**, *45*, 4328–4330.
[20] F. A. Cotton, S. A. Ibragimov, C. A. Murillo, P. V. Poplaukhin, Q. Zhao, *J. Mol. Struct.* **2008**, *890*, 3–8.
[21] H. Krautscheid, D. Fenske, G. Baum, M. Semmelmann, *Angew. Chem.* **1993**, *105*, 1364–1367; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1303–1305.
[22] T. Komuro, T. Matsuo, H. Kawaguchi, K. Tatsumi, *Angew. Chem. Int. Ed.* **2003**, *42*, 465–468.
[23] a) D. Fenske, C. E. Anson, A. Eichhöfer, O. Fuhr, A. Ingendoh, C. Persau, C. Richert, *Angew. Chem.* **2005**, *117*, 5376–5381; *Angew. Chem. Int. Ed.* **2005**, *44*, 5242–5246; b) C. E. Anson, A. Eichhöfer, I. Issac, D. Fenske, O. Fuhr, P. Sevillano, C. Persau, D. Stalke, J. Zhang, *Angew. Chem.* **2008**, *120*, 1346–1351; *Angew. Chem. Int. Ed.* **2008**, *47*, 1326–1331.
[24] D. Fenske, J. Hachgenei, J. Ohmer, *Angew. Chem.* **1985**, *97*, 684–686; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 706–709.
[25] G. Christou, K. S. Hagen, J. K. Bashkin, R. H. Holm, *Inorg. Chem.* **1985**, *24*, 1010–1018.
[26] S. Pohl, W. Saak, *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 907–908; S. Pohl, U. Opitz, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 863–864.
[27] S. P. Freidman, V. A. Gubanov, E. Z. Kurmaev, *J. Struct. Chem.* **1981**, *21*, 432–438.
[28] A. L. Allred, E. G. Rochow, *J. Inorg. Nucl. Chem.* **1958**, *5*, 264–268.
[29] An extreme case is MnO_4^-: a formal occupation $3d^0$ has to be compared with computed $3d^{5.9}$.
[30] G. S. White, D. W. Stephan, *Inorg. Chem.* **1985**, *24*, 1499–1503.
[31] T. A. Wark, D. W. Stephan, *Inorg. Chem.* **1990**, *29*, 1731–1736.
[32] R. Rousseau, D. W. Stephan, *Organometallics* **1991**, *10*, 3399–3403.
[33] P. K. Mehrotra, R. Hoffman, *Inorg. Chem.* **1978**, *17*, 2187–2189.
[34] F. A. Cotton, X. Feng, M. Matusz, R. Poli, *J. Am. Chem. Soc.* **1988**, *110*, 7077–7083.
[35] C. Kölmel, R. Ahlrichs, *J. Phys. Chem.* **1990**, *94*, 5536–5542.
[36] L. E. Manzer, *Inorg. Synth.* **1982**, *21*, 135.
[37] R. Köster, G. Seidel, R. Boese, *Chem. Ber.* **1988**, *121*, 1137–1142.
[38] N. Miyoshi, H. Ishii, K. Kondo, S. Murai, N. Sonoda, *Synthesis* **1979**, 300.
[39] G. M. Sheldrick, *SHELXTL, An Integrated System for Solving, Refining, and Displaying Crystal Structures from Diffraction Data*, PC version 5.1, Bruker Analytical X-ray Systems, Karlsruhe, **2000**.
[40] *Diamond 3.1d, Visual Crystal Structure Information System*, Crystal Impact GbR, **2006**.
[41] *X-SHAPE 1.06, Crystal Optimisation for Numerical Absorption Correction Program*, Stoe & Cie GmbH, Darmstadt, **1999**; *X-RED32 1.01, Data Reduction Program*, Stoe & Cie GmbH, Darmstadt, Germany, **2001**.
[42] a) R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, *Chem. Phys. Lett.* **1989**, *162*, 165–169; b) O. Treutler, R. Ahlrichs, *J. Chem. Phys.* **1995**, *102*, 346–354.
[43] a) J. P. Perdew, *Phys. Rev. B* **1986**, *33*, 8822–8824; J. P. Perdew, *Phys. Rev. B* **1986**, *34*, 7406; b) A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098–3100.
[44] F. Weigend, *Phys. Chem. Chem. Phys.* **2006**, *8*, 1057–1065.
[45] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.
[46] a) K. Eichkorn, O. Treutler, H. Ohm, M. Haser, R. Ahlrichs, *Chem. Phys. Lett.* **1995**, *242*, 652–660; b) M. Sierka, A. Hogekamp, R. Ahlrichs, *J. Chem. Phys.* **2003**, *118*, 9136–9148.
[47] M. von Arnim, R. Ahlrichs, *J. Comput. Chem.* **1998**, *19*, 1746–1757.
[48] A. Klamt, G. Schüürmann, *J. Chem. Soc. Perkin Trans. 2* **1993**, 799–805.
[49] A. E. Reed, R. B. Weinstock, F. Weinhold, *J. Chem. Phys.* **1985**, *83*, 735–746.

Received: June 24, 2009
Published Online: August 25, 2009

