DOI: 10.1002/zaac.200900266

Ring-shaped $[(TiCl_2)(1,3\text{-}P_2S_8)]_2$ Molecules Containing Uncommon $[P_2S_8]^{2-}$ Anions

Diana Hoppe[a] and Arno Pfitzner*[a]

Dedicated to Professor Martin Jansen on the Occasion of His 65th Birthday

Keywords: Titanium; Chlorine; Ring molecules; Thiophosphates; Polysulfides

Abstract. Intensely red, moisture-sensitive crystals of $[(TiCl_2)(1,3\text{-}P_2S_8)]_2$ were obtained by the reaction of $TiCl_4$ and P_4S_{10} at room temperature. The crystal structure determination revealed molecules formally consisting of two units of the anion $[1,3\text{-}P_2S_8]^{2-}$ connected with two $[TiCl_2]^{2+}$ cations resulting in the ring-shaped $[(TiCl_2)(1,3\text{-}P_2S_8)]_2$. The thiophosphate $[1,3\text{-}P_2S_8]^{2-}$ forms a six-membered ring and has a rather uncommon constitution among the multitude of anionic phosphorus sulfides and selenides.

Introduction

The reaction of hard Lewis-acids such as transition metal halides with d^0 configuration with Lewis-bases such as phosphorus sulfides and selenides was systematically investigated in order to study the interaction modes between the reactants and the type of the resulting Lewis-acid/base adducts [1]. Our attention was especially focused on the group 5 metal halides, especially Nb_2Cl_{10} and Ta_2Cl_{10}, leading to several phosphorus sulfide and selenide adducts [2]. In the course of these investigations we also checked whether $TiCl_4$ is capable of forming such adducts. The formation of $TiCl_4$ adducts with Lewis-bases was observed before, and especially the cage-like S_4N_4 molecule showed a variety of possibilities to connect with the metal chloride. For example, $[(TiCl_4)(S_4N_4)]_2$ molecules have been observed and structurally characterized earlier [3, 4]. Organophosphanes can also act as electron donors towards titanium, e.g., in $[(TiCl_4)(Ph_3P)]$ or $[(TiCl_4)(Ph_3PCh)]$ (Ch = O, S) [5, 6].

From this starting point, different phosphorus sulfides with more or less cage-like molecular shape, such as P_4S_3, β-P_4S_5, α-P_4S_7 or P_4S_{10}, were used as Lewis-bases. These have different phosphorus and sulfur atoms within the cages which can act as possible coordination sites, and α-P_4S_7 and P_4S_{10} furthermore exhibit terminal sulfur atoms as possible coordination sites. These cages should be able to act as Lewis-bases similar as found for other metal halides (see for example [7–10]). Herein we present $[(TiCl_2)(1,3\text{-}P_2S_8)]_2$ which was obtained en route from $TiCl_4$ and P_4S_{10} in CS_2 at room temperature. However, it is no adduct of P_4S_{10} but instead a fragmentation product of the phosphorus sulfide cage.

Experimental Section

Synthesis

$TiCl_4$ (*Merck-Schuchardt*, > 99 %) was purified by distillation from copper powder according to [11]. P_4S_{10} was obtained by heating red phosphorus (*Hoechst*, ultrapure) and sulfur (*Alfa Aesar*, 99.9995 %) in stoichiometric amounts to 300 °C for three days and slowly cooling down to ambient temperature [12, 13]. The phosphorus sulfide was used without further purification, after the absence of by-products was checked via solution NMR spectroscopy.

$[(TiCl_2)(1,3\text{-}P_2S_8)]_2$: $TiCl_4$ (0.3 mL, 2.6 mmol) was solved in carbon disulfide (2.3 mL, *Aldrich*, > 99 %), which was dried beforehand by distillation from P_4O_{10} in Schlenk flasks. Finely ground P_4S_{10} (1.2 g. 2.6 mmol) was added together with carbon disulfide (2 mL); the mixture was covered with *n*-hexane (1 mL, *Acros*, 95 %, dried with Na_2SO_4, distilled). Soon the solution showed an orange color. Small, intensely red, rhombic crystals formed, mostly grown onto yellow crystals of P_4S_{10} after some days. All reactions were performed under inert atmosphere.

Crystal Structure Determination

X-ray diffraction data collection of a single crystal of $[(TiCl_2)(1,3\text{-}P_2S_8)]_2$ was performed with a four-circle diffractometer *Gemini R* (Oxford Diffraction), using graphite-monochromated Cu-K_α radiation (λ = 1.54184 Å). The raw-data were corrected for background, polarization and Lorentz factors using the program package *CrysAlis*^{Pro} [14]. The description of the crystal shape was optimized by using sets of reflections that are equivalent in the Laue class $2/m$. Furthermore numerical absorption corrections were applied.

Crystal structure solution and refinement against F_o^2 were performed with the SHELX-97 program package [15]. Anisotropic displacement parameters were used for description of all atoms. The title compound crystallizes in the space group $P2_1/n$ with lattice parameters of a = 6.610(2) Å, b = 12.593(2) Å, c = 15.478(3) Å, β = 91.86(3)° and Z = 2. The structure refinement converged to R_1 ($F_o > 4\,\sigma(F_o)$) = 0.050,

---

* Prof. Dr. A. Pfitzner
E-Mail: arno.pfitzner@chemie.uni-regensburg.de
[a] Institut für Anorganische Chemie
Universität Regensburg
Universitätsstr. 31
93040 Regensburg, Germany

Table 1. Crystallographic data and details of the structure refinement for $[(TiCl_2)(1,3\text{-}P_2S_8)]_2$.

Formula	$Cl_4Ti_2P_4S_{16}$ ($Cl_2TiP_2S_8$)
Molar mass /g·mol^{-1}	874.48
Crystal system, space group	monoclinic, $P2_1/n$ (No. 14)
Number of formula units, Z	2
Temperature, T /K	293(2)
Lattice parameters from single crystal data /Å	
a	6.610(2)
b	12.593(2)
c	15.478(3)
β	91.86(3)
Cell volume, V /Å^3	1287.7(5)
Calculated density, ρ_{calc} /g·cm^{-3}	2.26
Crystal size /mm	0.25 × 0.15 × 0.10
Diffractometer	Gemini R, Oxford Diffraction, graphite monochromator, Cu-K_α radiation (λ = 1.54184 Å)
Range of data collection /2θ	11.4–100.9 °
	$-6 \leq h \leq 5$
	$-12 \leq k \leq 11$
	$-15 \leq l \leq 15$
Absorption correction	numerical with optical description of the crystal shape [14]
Absorption coefficient μ(Cu-K_α) /mm^{-1}	23.58
No. of reflections collected (independent)	3072 (1344)
R_{int}, R_σ	0.077, 0.063
Structure solution	SHELXS 97 [15], direct methods
Structure refinement	SHELXL 97 [15], full-matrix least-squares method, refinement on F_o^2; anisotropic displacement parameters for all atoms
No. of refined parameters	118
No. of restraints	0
Residual electron density /e·Å^{-3}	+ 0.55 / – 0.43
$R1$ (I_o>2σ(I_o))	0.050
$R1$ (all I_o)	0.063
$wR2$ (all I_o)	0.145
GooF	1.14

wR_2 (all data) = 0.145, *GooF* = 1.14. Table 1 summarizes the results of the single crystal structure analysis of $[(TiCl_2)(1,3\text{-}P_2S_8)]_2$. Details of the crystal structure investigations are available from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: +49-7247-808-666, E-Mail: crysdata@fiz-karlsruhe.de) referring to number CSD-420670, name of the authors and citation of the paper.

Results and Discussion

The crystal structure determination of the product obtained from the reaction of $TiCl_4$ and P_4S_{10} revealed ring-shaped C_{2h} symmetrical molecules of the composition $[(TiCl_2)_2(P_2S_8)_2]$ displayed in Figure 1. Table 2 displays the atomic coordinates and anisotropic displacement parameters are listed in Table 3. Corresponding bond lengths and bonding angles are summarized in Table 4. The molecular formula shows that these rings consist of two components: two thiophosphate ions $[P_2S_8]^{2-}$ exhibiting a central six-membered ring $[P_2S_4]^{6+}$ are linked via two terminating sulfide ions per phosphorus atom to two $[TiCl_2]^{2+}$ ions resulting in an octahedral environment for the titanium atom. It is quite difficult to distinguish between sulfur and chlorine by X-ray diffraction. However, the use of copper radiation and the observed distances of the anions to titanium and phosphorus helped to assign sulfur and chlorine to the anion positions and to obtain a reasonable structure model. A closer inspection of the literature shows that the molecular anion $[1,3\text{-}P_2S_8]^{2-}$ was already observed in $[(PPh_4)_2(1,3\text{-}P_2S_8)]$ described by *Gruber* and *Müller* [16] and $[(AsPh_4)_2(1,3\text{-}P_2S_8)]$ described by *Dimitrov* et al. [17]. With a sequence of three adjacent sulfur atoms within the six-membered ring, it is a quite uncommon variant of $[P_2S_8]^{2-}$, whereas the anion $[1,4\text{-}P_2Q_8]^{2-}$ (Q = S, Se) containing two Q–Q dumb-bells is well-known from different investigations [18–21]. They exhibit middle-sized members of a series of ring-shaped thio- and selenophosphates $[P_xQ_y]^{n-}$ (x = 2–4, y = 6–10, n = 2–5) [18, 22]. In addition, chains of two or more sulfur atoms can be found in different (phosphorus) polysulfides (see for example [23, 24]). The formation of $[P_2S_8]^{2-}$ and thiophosphates in general from highly sulfurized phosphorus species is an established way of synthesis, see for example refs. [25, 26]. Alternatively, these polysulfide molecules can be obtained from alkali metal polysulfides and white phosphorus or phosphorus trichloride, as for example described in ref. [16].

The six-membered $[1,3\text{-}P_2S_8]^{2-}$ rings in the title compound have a chair conformation as in $[(PPh_4)_2(1,3\text{-}P_2S_8)]$, see Figure 2. In the case of $[1,3\text{-}P_2S_8]^{2-}$ other conformations, e.g., the boat or twist form, would lead to rather unfavorable arrangements not at least because of steric hindrance due to the vicinity of the PS_4 tetrahedra. Therefore these are not likely to be realized.

P–S bonds to sulfur atoms being situated in equatorial *exo*-position of the P_2S_8 rings are slightly longer (2.00 Å) than

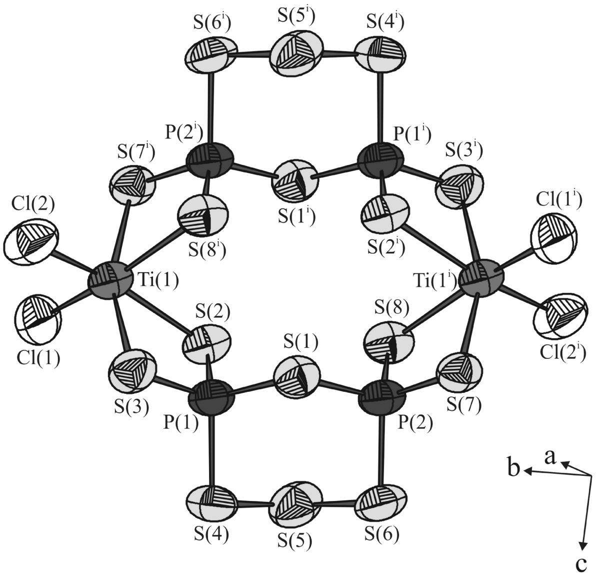

Figure 1. One molecule of $[(TiCl_2)(1,3\text{-}P_2S_8)]_2$. Ellipsoids enclose 70 % probability for atomic displacement. Phosphorus: dark gray; sulfur: light gray; titanium: medium gray; chlorine: white.

Table 2. Atom coordinates and equivalent isotropic displacement parameters $U_{eq}$$^{a)}$ of $[(TiCl_2)(1,3\text{-}P_2S_8)]_2$.

Atom	x	y	z	U_{eq} /Å^2
Ti(1)	0.2227(2)	0.7628(1)	0.03447(8)	0.0467(6)
Cl(1)	0.0909(4)	0.9121(2)	0.0843(2)	0.0688(8)
Cl(2)	0.5282(4)	0.8310(2)	0.0134(1)	0.0680(8)
P(1)	0.1105(4)	0.5911(2)	0.1669(1)	0.0481(7)
P(2)	–0.1020(4)	0.3507(2)	0.1358(1)	0.0470(7)
S(1)	0.1771(3)	0.4317(2)	0.1360(1)	0.0497(7)
S(2)	–0.0876(3)	0.6612(2)	0.0870(1)	0.0493(7)
S(3)	0.3760(4)	0.6658(2)	0.1582(1)	0.0579(7)
S(4)	0.0238(4)	0.5881(2)	0.2958(1)	0.0647(8)
S(5)	–0.2479(4)	0.5125(2)	0.2714(1)	0.0690(8)
S(6)	–0.1943(4)	0.3527(2)	0.2639(1)	0.0627(8)
S(7)	–0.0243(3)	0.2037(2)	0.1008(1)	0.0488(7)
S(8)	–0.3111(3)	0.4039(2)	0.0519(1)	0.0516(7)

a) U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Tensor coefficients $U_{ij}$$^{a)}$ /Å^2 of the anisotropic displacement parameters in $[(TiCl_2)(1,3\text{-}P_2S_8)]_2$, $T = 20$ °C.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ti(1)	0.050(1)	0.051(1)	0.0392(8)	0.0007(8)	0.0077(7)	0.0054(7)
Cl(1)	0.092(2)	0.046(1)	0.070(2)	0.001(1)	0.018(1)	–0.006(1)
Cl(2)	0.056(2)	0.090(2)	0.059(1)	–0.014(1)	0.005(1)	0.016(1)
P(1)	0.059(2)	0.051(2)	0.035(1)	0.002(1)	0.008(1)	0.004(1)
P(2)	0.055(2)	0.051(2)	0.035(1)	0.006(1)	0.010(1)	0.005(1)
S(1)	0.050(2)	0.051(2)	0.049(1)	0.007(1)	0.008(1)	0.002(1)
S(2)	0.051(2)	0.055(2)	0.043(1)	0.005(1)	0.009(1)	0.008(1)
S(3)	0.060(2)	0.065(2)	0.048(1)	–0.009(1)	–0.007(1)	0.013(1)
S(4)	0.095(2)	0.065(2)	0.035(1)	–0.001(2)	0.013(1)	–0.003(1)
S(5)	0.085(2)	0.059(2)	0.066(2)	0.010(1)	0.032(1)	0.006(1)
S(6)	0.096(2)	0.051(2)	0.043(1)	0.010(1)	0.028(1)	0.010(1)
S(7)	0.062(2)	0.042(1)	0.042(1)	0.010(1)	0.006(1)	0.0057(9)
S(8)	0.053(2)	0.055(2)	0.048(1)	0.014(1)	0.007(1)	0.004(1)

a) Coefficients U_{ij} of the anisotropic displacement factor tensor of the atoms are defined by $\exp[-2\pi^2(h^2a^*2U_{11} + ... + 2hka^*b^*U_{12} + ...)]$.

Table 4. Selected bond lengths and angles in $[(TiCl_2)(1,3\text{-}P_2S_8)]_2$.

Atoms			distance /Å	atoms			distance /Å
P(1)	–S(1)		2.113(3)	Ti(1)	–Cl(1)		2.220(3)
	–S(2)		1.980(3)		–Cl(2)		2.228(3)
	–S(3)		2.000(3)		–S(2)		2.572(3)
	–S(4)		2.094(3)		–S(3)		2.462(3)
P(2)	–S(1)		2.108(3)		–S(7)		2.470(3)
	–S(6)		2.094(3)		–S(8)		2.566(3)
	–S(7)		2.001(3)	S(4)	–S(5)		2.057(4)
	–S(8)		1.983(3)	S(5)	–S(6)		2.046(3)
Cl(1)	–Ti(1)–	Cl(2)	95.3(1)	S(2)	–P(1)–	S(3)	108.2(1)
Cl(1)	–Ti(1)–	S(3)	107.8(1)	S(2)	–P(1)–	S(4)	114.0(1)
Cl(2)	–Ti(1)–	S(3)	87.3(1)	S(3)	–P(1)–	S(4)	109.9(1)
Cl(1)	–Ti(1)–	S(7)	86.9(1)	S(2)	–P(1)–	S(1)	114.9(1)
Cl(2)	–Ti(1)–	S(7)	105.60(9)	S(3)	–P(1)–	S(1)	104.1(1)
S(3)	–Ti(1)–	S(7)	159.7(1)	S(4)	–P(1)–	S(1)	105.3(1)
Cl(1)	–Ti(1)–	S(8)	166.4(1)				
Cl(2)	–Ti(1)–	S(8)	90.9(1)	S(8)	–P(2)–	S(7)	108.4(1)
S(3)	–Ti(1)–	S(8)	84.52(9)	S(8)	–P(2)–	S(6)	113.5(1)
S(7)	–Ti(1)–	S(8)	79.75(8)	S(7)	–P(2)–	S(6)	110.7(1)
Cl(1)	–Ti(1)–	S(2)	89.1(1)	S(8)	–P(2)–	S(1)	115.4(1)
Cl(2)	–Ti(1)–	S(2)	166.9(1)	S(7)	–P(2)–	S(1)	102.5(1)
S(3)	–Ti(1)–	S(2)	79.61(9)	S(6)	–P(2)–	S(1)	105.9(1)
S(7)	–Ti(1)–	S(2)	86.88(9)				
S(8)	–Ti(1)–	S(2)	87.43(9)				
P(2)	–S(1)–	P(1)	105.8(1)	S(6)	–S(5)–	S(4)	108.3(2)
P(1)	–S(2)–	Ti(1)	84.3(1)	S(5)	–S(6)–	P(2)	97.0(1)
P(1)	–S(3)–	Ti(1)	86.9(1)	P(2)	–S(7)–	Ti(1)	86.4(1)
S(5)	–S(4)–	P(1)	95.6(1)	P(2)	–S(8)–	Ti(1)	84.2(1)

bond lengths to sulfur atoms in the axial positions (1.98 Å). *Gruber* and *Müller* already observed this fact in $(PPh_4)_2[1,3\text{-}P_2S_8]$. The distances d(P–S) and d(S–S) within the rings amount to 2.10 and 2.05/2.06 Å, respectively, and are in the typical range found for phosphorus sulfides (sulfur within the cage as for example in β-P_4S_5 [27]) or elemental sulfur, e.g., α-S_8 or γ-S_8 [28–31]. A slight elongation of the bond lengths d(P–S1) between phosphorus and the bridging sulfur atom S1 as compared to d(P1–S4) and d(P2–S6) is to be mentioned.

Keeping in mind that the compound consists of isolated neutral molecules the formula has to read $[(TiCl_2)(1,3\text{-}P_2S_8)]_2$.

Titanium tends to have an octahedral environment. Lewis-base coordinated $TiCl_4$ requires two more ligands for this coordination, thus oligomeric or even polymeric chain- (ligands at opposite sides of the octahedron) or ring-shaped (ligands at same side) complexes can result. This is realized for example in the two forms of $[(TiCl_4)(S_4N_4)]_2$: the α-form consists of ring-shaped molecules, comparable to the molecules presented here, whereas the β-form consists of $[(TiCl_3Cl_{2/2})(S_4N_4)]_2$ dimers [4]. A similar situation is also found in the chain-like polymers of $[(CuCl_2)(S_4N_4)]$ [32]. For $[TiCl_2]^{2+}$, four ligands are necessary to complete the octahedral environment – in case of $[(TiCl_2)(1,3\text{-}P_2S_8)]_2$, four-dentate ligands are available. The terminal sulfur atoms forming the bonds to titanium are situ-

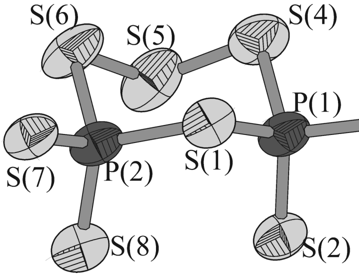

Figure 2. Presentation of the $[1,3\text{-}P_2S_8]^{2-}$ ion within the molecule. Axial P–S bond lengths are slightly shorter than equatorial bond lengths.

ated at the same side of the P_2S_8 rings and consequently the formation of a small ring-shaped molecule rather than a large ring or even polymers is favored.

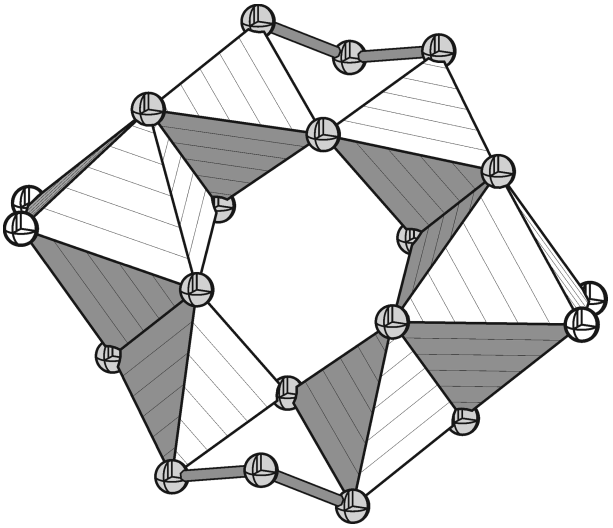

Figure 3. Concatenation of polyhedra within the molecule: $[PS_4]$ tetrahedra share edges with $[TiS_4Cl_2]$ octahedra; two $[PS_4]$ tetrahedral units with common vertex and an additional sulfur atom are forming the $[1,3\text{-}P_2S_8]^{2-}$ ion.

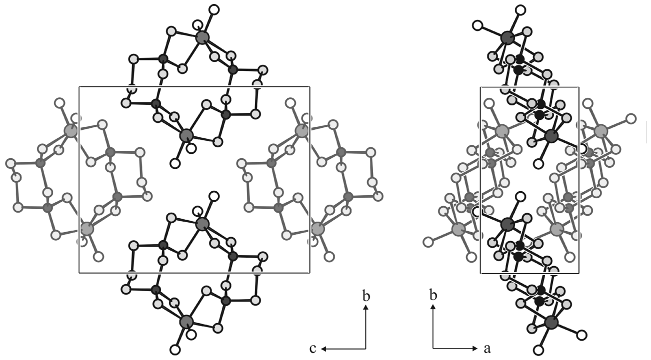

Figure 4. Projections of the unit cell of $[(TiCl_2)(1,3\text{-}P_2S_8)]_2$ along [100] (left side) and [001] direction (right side). Phosphorus is denoted dark gray, sulfur light gray, titanium medium gray, and chlorine white. Molecules which are displayed darker lie closer to the reader.

The octahedra TiS_4Cl_2 are quite distorted, exhibiting angles S–Ti–S of 79.6° and 79.8° respectively, and angles Cl–Ti–Cl of 95.3°, far away from an ideal 90° angle, see also Table 4. This is certainly due to the rigid bite angle of the thiophosphate groups, which exhibit bond angles S–P–S close to the ideal tetrahedral angle, see Table 4. The axial bond angles of the octahedron are 159.7° (S3–Ti1–S7), 166.9° (S2–Ti1–Cl2), and 166.4° (S8–Ti1–Cl1), respectively, and demonstrate the deviation from the ideal octahedral surrounding of Ti^{4+} once more. The distances *d*(Ti–Cl) of 2.22 and 2.23 Å are similar to those in comparable compounds such as $[(TiCl_4)(POCl_3)]_2$ [33], $[(TiCl_4)(S_4N_4)]_2$ [4] and $[(Ti_2Cl_{10})(S_4N_5)]$ [34], but slightly shorter than found in $[(TiSCl_4)(NEt_4)_2]$ [35]. For *d*(Ti–S) values of 2.46 Å, 2.47 Å and 2.57 Å are observed. This is the typical range for distances between titanium and sulfur in binary compounds [36], appropriate examples for comparison admittedly being rare. By contrast a terminal sulfur atom is present in $[(TiSCl_4)(NEt_4)_2]$, and the bond length *d*(Ti–S) only amounts to 2.11 Å.

An alternate description of this dimeric molecule is the condensation of two TiS_4Cl_2 octahedra through two edges formed by sulfur with PS_4 tetrahedra. Two of these tetrahedra share one vertex and are additionally linked by a sulfur atom connecting the fourth vertex, see Figure 3.

The ring molecules are stacked along [100], being slightly inclined relative to the crystallographic (100) plane. The inclination angle alternates along [010] from one stack to the next, thus a fishbone pattern results in the (001) plane. As shown in Figure 4 the stacks of molecules form a rectangular pattern. Shortest intermolecular distances amount to 3.36 Å (between S(3) and S(6)) and 3.47 Å (between S(5) and Cl(1)) resp.

Conclusions

$[(TiCl_2)(1,3\text{-}P_2S_8)]_2$ was obtained by direct reaction of $TiCl_4$ and P_4S_{10}. It forms a ring-shaped molecule of concatenated units formally conceivable as $[TiCl]^{2+}$ and $[1,3\text{-}P_2S_8]^{2-}$.

Obviously, the formation of $[(TiCl_2)(1,3\text{-}P_2S_8)]_2$ from $TiCl_4$ and P_4S_{10} is accompanied by a fragmentation of the phosphorus sulfide framework. To date only the anion $[1,3\text{-}P_2S_8]^{2-}$ was found in the present case, but surely several other products should be formed, and further sulfurization products may be obtained with similar reactants or by variation of the reaction conditions. In fact, $TiCl_4$ seems to be clearly more reactive towards phosphorus sulfides such as P_4S_{10} than other transition metal halides.

Acknowledgement

We gratefully acknowledge the experimental help of students *M. Meier* and *A. Eder*.

References

[1] D. Hoppe, *Phosphorchalkogenid-Molekülverbindungen*, Doctoral Thesis, University of Regensburg **2008**.

[2] D. Hoppe, A. Pfitzner, *Z. Naturforsch.* **2009**, *64b*, 58; D. Hoppe, D.Schemmel, M. Schütz, A. Pfitzner, *Chem. Eur. J.* DOI: 10.1002/chem.200900370.
[3] P. J. Ashley, E. G. Torrible, *Can. J. Chem.* **1969**, *47*, 2587.
[4] U. Thewalt, K. Holl, *Z. Naturforsch.* **1988**, *43b*, 467.
[5] A. D. Westland, L. Westland, *Can. J. Chem.* **1965**, *43*, 426.
[6] W. van der Veer, F. Jellinek, *Recueil Trav. Chim. Pays-Bas* **1966**, *85*, 842.
[7] S. Reiser, G. Brunklaus, J. H. Hong, J. C. C. Chan, H. Eckert, A. Pfitzner, *Chem. Eur. J.* **2002**, *8*, 4228.
[8] H. Nowottnick, K. Stumpf, R. Blachnik, H. Reuter, *Z. Anorg. Allg. Chem.* **1999**, *625*, 693.
[9] A. Biegerl, E. Brunner, C. Gröger, M. Scheer, J. Wachter, M. Zabel, *Chem. Eur. J.* **2007**, *13*, 9270.
[10] J. G. Riess, Coordination and related chemistry of polycyclic tetraphosphorus compounds. In: *Rings, clusters and polymers of the main group elements*, ACS-Symposium Series 232 (Ed.: A. H. Cowley), p. 17–47, American Chemical Society, Washington D. C. **1983**.
[11] G. Brauer, *Handbuch der präparativen anorganischen Chemie*, Ferdinand Enke Verlag, Stuttgart **1960**.
[12] A. Stock, *Ber. der deutschen chemischen Gesellschaft* **1910**, *43*, 150.
[13] R. Blachnik, A. Hoppe, *Z. Anorg. Allg. Chem.* **1979**, *457*, 91.
[14] *CrysAlis*, Version 1.171.27p5 beta, Oxford Diffraction Ltd., Abingdon, United Kingdom **2005**.
[15] G. M. Sheldrick, *SHELX-97*, Program for Crystal Structure Determination, University of Göttingen **1997**.
[16] H. Gruber, U. Müller, *Z. Anorg. Allg. Chem.* **1997**, *623*, 957.
[17] A. Dimitrov, I. Hartwich, B. Ziemer, D. Heidemann, M. Meisel, *Z. Anorg. Allg. Chem.* **2005**, *631*, 2439.
[18] H. Falius, A. Schliephake, D. Schomburg, *Z. Anorg. Allg. Chem.* **1992**, *611*, 141.
[19] J. Zhao, W. T. Pennington, J. W. Kolis, *J. Chem. Soc., Chem. Commun.* **1992**, 265.
[20] P. C. Minshall, G. M. Sheldrick, *Acta Crystallogr., Sect. B* **1978**, *34*, 1378.
[21] P. G. Jones, A. Weinkauf, *Acta Crystallogr., Sect. C* **1991**, *47*, 686.
[22] K. Karaghiosoff, M. Schuster, *Phosphorus Sulfur Silicon Relat. Elem.* **2001**, *168*, 117.
[23] J. Hahn, A. Hopp, A. Borxowsky, *Phosphorus Sulfur Silion* **1992**, *64*, 129.
[24] A. Pfitzner, T. Rödl, to be published.
[25] E. Glatzel, *Z. Anorg. Chem.* **1893**, *4*, 186.
[26] H. W. Roesky, F. N. Tebbe, E. L. Muetterties, *J. Am. Chem. Soc.* **1967**, *89*, 1272.
[27] A. M. Griffin, G. M. Sheldrick, *Acta Crystallogr., Sect. B* **1975**, *31*, 2738.
[28] B. E. Warren, J. T. Burwell, *J. Chem. Phys.* **1935**, *3*, 6.
[29] P. Coppens, Y. W. Yang, R. H. Blessing, W. F. Copper, F. K. Larsen, *J. Am. Chem. Soc.* **1977**, *99*, 760.
[30] D. E. Sands, *J. Am. Chem. Soc.* **1965**, *87*, 1395.
[31] L. K. Templeton, D. H. Templeton, A. Zalkin, *Inorg. Chem.* **1976**, *15*, 1999.
[32] U. Thewalt, *Z. Anorg. Allg. Chem.* **1980**, *462*, 221.
[33] C. I. Brändén, I. Lindqvist, *Acta Chem. Scand.* **1960**, *14*, 726.
[34] J. Eicher, P. Klingelhöfer, U. Müller, K. Dehnicke, *Z. Anorg. Allg. Chem.* **1984**, *514*, 79.
[35] V. Krug, G. Koellner, U. Müller, *Z. Naturforsch.* **1988**, *43b*, 1501.
[36] H. Hahn, B. Harder, *Z. Anorg. Allg. Chem.* **1956**, *288*, 241.

Received: May 11, 2009