Adduct Compounds $(MCl_5)_2(\beta\text{-}P_4Ch_4)$ with M = Nb, Ta and Ch = S, Se

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Dedicated to Professor Otto J. Scherer on the occasion of his 75th birthday

Adduct compounds of the general composition $(MCl_5)_2(\beta\text{-}P_4Ch_4)$, M = Nb, Ta and Ch = S, Se, were obtained from solutions of M_2Cl_{10} and P_4Ch_3 in CS_2 / *n*-hexane. The compounds are isotypic with $(NbCl_5)_2(\beta\text{-}P_4S_4)$, crystallizing in the monoclinic space group $P\,2_1/n$ (no. 14) with $Z = 4$. The lattice constants are $a = 6.304(2)$, $b = 13.071(3)$, $c = 26.552(6)$ Å, $\beta = 93.74(3)^\circ$, $V = 2183(1)$ Å^3 for $(TaCl_5)_2(\beta\text{-}P_4S_4)$, $a = 6.360(2)$, $b = 13.322(3)$, $c = 26.710(6)$ Å, $\beta = 93.81(3)^\circ$, $V = 2258(1)$ Å^3 for $(TaCl_5)_2(\beta\text{-}P_4Se_4)$, and $a = 6.334(2)$, $b = 13.267(6)$, $c = 26.583(7)$ Å, $\beta = 93.71(3)^\circ$, $V = 2229(2)$ Å^3 for $(NbCl_5)_2(\beta\text{-}P_4Se_4)$. The adduct molecules consist of two MCl_5 units which are linked with two of the basal phosphorus atoms of the central $\beta\text{-}P_4Ch_4$ cage.

Key words: Phosphorus Selenide, Phosphorus Sulfide, Niobium Pentachloride, Tantalum Pentachloride, Crystal Structure

Introduction

Most phosphorus chalcogenides consist of single cage-like molecules. Among these, P_4S_3 and P_4Se_3 show the lowest content of chalcogen. They can be produced very easily, and their chemistry – especially their coordination chemistry – is well-investigated [1].

By contrast, the cages of $\beta\text{-}P_4S_4$ and $\beta\text{-}P_4Se_4$ still could not be crystallized as binary phases; they have only been characterized *via* solution NMR spectroscopy. There is experimental evidence that these molecules either decompose upon heating or even in solution ($\beta\text{-}P_4S_4$) [2] or polymerize forming chains of catenated molecules ($\beta\text{-}P_4Se_4$) [3 – 5]. However, these $\beta\text{-}P_4Ch_4$ phosphorus chalcogenide cages can be found in several quaternary adduct compounds, such as $(CuI)_3(\beta\text{-}P_4Se_4)$ [6], $(CuI)_3(\beta\text{-}P_4S_4)$ [7], $(CuBr)_3(\beta\text{-}P_4Se_4)$ [8], and $(NbCl_5)_2(\beta\text{-}P_4S_4)$ [9], where metal atoms are coordinated to phosphorus atoms of the cages.

In the last decades, particularly Blachnik and co-workers contributed to the understanding of the chemistry of phosphorus chalcogenides. Starting from the results of their investigations on derivatives and adducts of these compounds, the behavior of related phosphorus cages towards d^0 metal halides are now to be examined in detail.

First experiments with P_4S_{10}, a cage compound with phosphorus totally saturated by sulfur, led to products of the type $(M_2Cl_{10})(P_4S_{10})_2$, M = Nb, Ta [10]. Subsequently, the reaction of P_4S_3 and P_4Se_3 with M_2Cl_{10}, as described in ref. [9], was looked at more closely. First results of these investigations – the formation and crystal structures of $(TaCl_5)_2(\beta\text{-}P_4S_4)$, $(TaCl_5)_2(\beta\text{-}P_4Se_4)$ and $(NbCl_5)_2(\beta\text{-}P_4Se_4)$, which are isotypic with $(NbCl_5)_2(\beta\text{-}P_4S_4)$ [9] – are reported here. The characterization of adduct compounds of sulfur-rich cages with MCl_5 (M = Nb, Ta) is described in ref. [11].

Experimental Section

Synthesis

The phosphorus chalcogenides P_4Ch_3 were prepared beforehand from the elements at 300 °C and subsequently recrystallized from CS_2 (P: Hoechst, ultra-high grade; S: Alfa Aesar, 99.9995 %; Se: Alfa Aesar, 99.999+ %; CS_2: Aldrich, > 99 %, distilled over P_4O_{10}). Phosphorus and sulfur were heated in 1 : 1 ratio to 330 °C and then rapidly cooled down to ambient temperature to obtain a solidified melt which is a mixture of different phosphorus sulfides [12, 13].

Table 1. Crystallographic data and details of the structure refinement for $(TaCl_5)_2(\beta\text{-}P_4S_4)$, $(TaCl_5)_2(\beta\text{-}P_4Se_4)$, and $(NbCl_5)_2(\beta\text{-}P_4Se_4)$.

Formula	$Cl_{10}Ta_2P_4S_4$	$Cl_{10}Ta_2P_4Se_4$	$Cl_{10}Nb_2P_4Se_4$
M_r	968.58	1156.16	980.08
Crystal system		— monoclinic —	
Space group		— $P2_1/n$, no. 14 —	
Z	4	4	4
T, K	293(2)	293(2)	293(2)
a, Å	6.304(2)	6.360(2)	6.334(2)
b, Å	13.071(3)	13.322(3)	13.267(6)
c, Å	26.552(6)	26.710(6)	26.583(7)
β, deg	93.74(3)	93.81(3)	93.71(3)
V, Å^3	2183(1)	2258(1)	2229(2)
D_{calcd}, g·cm^{-3}	2.95	3.40	2.92
Size, mm^3	0.20×0.14×0.07	0.14×0.10×0.07	0.34×0.06×0.06
2θ Range	4.4° – 51.6°	4.3° – 51.0°	3.1° – 58.4°
hkl Range	$-7 \le h \le 7$	$-7 \le h \le 7$	$-8 \le h \le 7$
	$-16 \le k \le 15$	$-16 \le k \le 16$	$-18 \le k \le 18$
	$-32 \le l \le 32$	$-32 \le l \le 32$	$-36 \le l \le 36$
Numerical absorption correction		based on an optical description of the crystal shape [17, 18]	
μ (MoK_α), mm^{-1}	11.9	17.58	9.03
F(000), e	1760	2048	1792
Refls. coll.	14498	14666	21017
unique	4166	3993	5951
R_{int} / R_σ	0.029 / 0.025	0.026 / 0.024	0.116 / 0.085
Solution	SHELXS 97 [19], Direct Methods		
Refinement	SHELXL 97 [19], full-matrix least-squares methods on F_o^2; anisotropic displacement parameters		
Parameters	181	181	181
R_1 $[F_o \ge 4\sigma(F_o)]$[a]	0.020	0.020	0.045
R_1 (all F_o)[a]	0.027	0.028	0.078
wR_2 (all F_o)[b]	0.041	0.045	0.109
a / b[b]	0.022 / 0	0.027 / 0	0.046 / 0
GoF[c]	1.01	0.94	0.93
Res. el. dens., e Å^3	+0.70 / −0.52	+0.96 / −0.39	+0.84 / −0.86

[a] $R1 = \sum||F_o| - |F_c|| / \sum|F_o|$; [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$, where $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$; [c] $\mathrm{GoF} = [\sum w(F_o^2 - F_c^2)^2/(n_{obs} - n_{param})]^{1/2}$.

In a typical reaction, about 1 mmol P_4Ch_3 and 1 mmol M_2Cl_{10} were filled into a Schlenk flask (Nb_2Cl_{10}, Ta_2Cl_{10}: H. C. Starck, ultra-high grade). About 2 mL of CS_2 was added and covered with 1.5 mL of *n*-hexane (Alfa Aesar, 99 %, dried). Columnar, intensely colored crystals grew within several days [$(TaCl_5)_2(\beta\text{-}P_4S_4)$: bright greenish yellow; $(TaCl_5)_2(\beta\text{-}P_4Se_4)$: yellow; $(NbCl_5)_2(\beta\text{-}P_4S_4)$: orange; $(NbCl_5)_2(\beta\text{-}P_4Se_4)$: dark red]. These crystals are sensitive to moisture and therefore must be handled under inert conditions.

The products could not be obtained free of by-products due to the preparation procedure (see above) and the difficulty of preparing single-phased $\beta\text{-}P_4Ch_4$ [2, 14, 15].

Table 2. Atom coordinates and equivalent isotropic displacement parameters U_{eq}[a] of $(TaCl_5)_2(\beta\text{-}P_4S_4)$.

Atom	x	y	z	U_{eq} (Å^2)
P(1)	0.0482(2)	0.91117(8)	0.29601(3)	0.0291(2)
P(2)	0.0679(2)	0.84179(8)	0.40126(3)	0.0295(2)
P(3)	0.3047(2)	0.93037(9)	0.35855(4)	0.0349(2)
P(4)	−0.0891(2)	1.08232(9)	0.38120(4)	0.0434(3)
S(12)	−0.0601(2)	0.77795(8)	0.33220(4)	0.0369(2)
S(14)	−0.1621(2)	1.03278(9)	0.30522(4)	0.0404(3)
S(24)	−0.1395(2)	0.95239(9)	0.42769(4)	0.0394(3)
S(34)	0.2510(2)	1.07873(9)	0.38233(4)	0.0483(3)
Ta(1)	0.17931(3)	0.88769(1)	0.200116(5)	0.03029(5)
Cl(10)	0.3271(3)	0.8614(1)	0.12583(4)	0.0643(4)
Cl(11)	0.3606(2)	1.0343(1)	0.22717(5)	0.0561(3)
Cl(12)	−0.1067(2)	0.9902(1)	0.17455(4)	0.0563(3)
Cl(13)	−0.0546(2)	0.7500(1)	0.19958(5)	0.0532(3)
Cl(14)	0.4254(2)	0.7880(1)	0.24852(5)	0.0558(3)
Ta(2)	0.22593(3)	0.70805(1)	0.474223(6)	0.03459(5)
Cl(20)	0.3740(3)	0.6074(1)	0.53601(6)	0.0823(5)
Cl(21)	−0.0722(2)	0.7612(1)	0.51478(4)	0.0502(3)
Cl(22)	0.3887(2)	0.86400(9)	0.49818(4)	0.0497(3)
Cl(23)	0.4790(2)	0.6892(1)	0.41498(5)	0.0579(3)
Cl(24)	0.0133(3)	0.5916(1)	0.42916(6)	0.0631(4)

Table 3. Atom coordinates and equivalent isotropic displacement parameters U_{eq}[a] of $(TaCl_5)_2(\beta\text{-}P_4Se_4)$.

Atom	x	y	z	U_{eq} (Å^2)
P(1)	0.0408(2)	0.90952(9)	0.29386(4)	0.0340(3)
P(2)	0.0597(2)	0.83702(9)	0.40146(4)	0.0354(3)
P(3)	0.2918(2)	0.9206(1)	0.35699(5)	0.0399(3)
P(4)	−0.0961(3)	1.0869(1)	0.38289(5)	0.0489(4)
Se(12)	−0.0800(1)	0.76748(4)	0.32919(2)	0.0445(1)
Se(14)	−0.1817(1)	1.03786(4)	0.30235(2)	0.0464(1)
Se(24)	−0.1577(1)	0.95184(4)	0.43204(2)	0.0456(1)
Se(34)	0.2633(1)	1.07730(4)	0.38351(2)	0.0537(2)
Ta(1)	0.17161(4)	0.89065(2)	0.198370(7)	0.03634(6)
Cl(10)	0.3089(3)	0.8659(2)	0.12330(6)	0.0729(5)
Cl(11)	0.3419(3)	1.0370(1)	0.22420(6)	0.0631(4)
Cl(12)	−0.1211(3)	0.9869(1)	0.17372(6)	0.0632(4)
Cl(13)	−0.0529(3)	0.7525(1)	0.19847(6)	0.0628(4)
Cl(14)	0.4251(3)	0.7955(1)	0.24436(6)	0.0648(4)
Ta(2)	0.21971(4)	0.70446(2)	0.473273(7)	0.04095(6)
Cl(20)	0.3620(4)	0.6030(2)	0.53417(8)	0.0889(6)
Cl(21)	−0.0749(3)	0.7565(1)	0.51420(5)	0.0564(4)
Cl(22)	0.3851(3)	0.8556(1)	0.49862(6)	0.0560(4)
Cl(23)	0.4704(3)	0.6853(1)	0.41475(6)	0.0640(4)
Cl(24)	0.0057(3)	0.5920(1)	0.42804(7)	0.0672(4)

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

Other solvents or mixtures of solvents showed to be not as suitable for the formation of these adducts as the solvent combination described. Apparently, the highly different solubilities of the reactants in CS_2 and in *n*-hexane are important for crystallization. Furthermore, CS_2 is supposed to form adducts with the metal halides M_2Cl_{10} [16] giving mono- or bidentate complexes of MCl_5 units which may result in a better accessibility of the metal atoms for coordination by other ligands as compared to the dimeric molecules.

Similar experiments with other halides such as MBr$_5$ emphasized their increased sensitivity towards reducing agents like phosphorus chalcogenides. The formation of, *e. g.*, MBr$_4$, P$_4$$Ch_3Br_2$ and PBr$_3$ is observed.

Crystal structure determination

Single-crystal X-ray structure analysis was performed using suitable crystals of the adducts. Data were collected on a Stoe IPDS-I or on a Stoe IPDS-II imaging plate diffractometer. Crystallographic data are summarized in Table 1. Data were numerically corrected for absorption after refinement of a description of the crystal shape with the X-SHAPE program suite [17, 18]. Direct Methods revealed the positions of the atoms which were then subsequently refined including anisotropic displacement parameters for all atoms [19] (Tables 2 – 4). A re-determination of the crystal structure of (NbCl$_5$)$_2$(β-P$_4$S$_4$) [9] was also performed for a better comparability of the data (see below).

Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-informationsdienste.de/en/DB/icsd/depot_anforderung.html) on quoting the deposition numbers CSD-420094 ((TaCl$_5$)$_2$-(β-P$_4$S$_4$)), CSD-420093 ((TaCl$_5$)$_2$(β-P$_4$Se$_4$)), CSD-420095 ((NbCl$_5$)$_2$(β-P$_4$Se$_4$)), and CSD-420096 (redetermination of (NbCl$_5$)$_2$(β-P$_4$S$_4$)).

Results and Discussion

Crystals of (MCl$_5$)$_2$(β-P$_4$$Ch_4$), M = Nb, Ta and Ch = S, Se, can be obtained from solutions of P$_4$$Ch_3$ (only with niobium) or a phosphorus sulfide mixture and the metal halides in CS$_2$ / n-hexane. The mechanism of this adduct formation is still unknown [9]. In the case of the niobium-containing adducts, presumably the reduction of the metal from Nb(V) to Nb(IV) and an oxidative chlorination of phosphorus are involved (see also ref. [20]), this view being supported by ^{31}P NMR signals of by-products such as PCl$_3$ and α-P$_4$$Ch_3Cl_2$ in the reaction solution. As already stated [9], there is no evidence for the existence of free β-P$_4$$Ch_4$ molecules in solution.

Crystals of the four compounds (NbCl$_5$)$_2$(β-P$_4$S$_4$), (TaCl$_5$)$_2$(β-P$_4$S$_4$), (TaCl$_5$)$_2$(β-P$_4$Se$_4$) and (NbCl$_5$)$_2$(β-P$_4$Se$_4$) are isotypic and contain separated molecules, which consist of two MCl$_5$ units linked to a β-P$_4$$Ch_4$ cage *via* two basal P atoms (Fig. 1).

These central cages can formally be derived from the structure of a P$_4$ tetrahedron by first inserting chalcogen atoms into all three bonds of one phosphorus atom. The P$_4$$Ch_3$ molecule thus obtained features one apical and three basal phosphorus atoms. Secondly a fourth chalcogen atom is inserted into the P$_3$ basis of the molecule, leading to the β-type cage of P$_4$$Ch_4$. Two stereochemically identical phosphorus atoms are present which are both connected to the metal atoms of the MCl$_5$ units. Considering the resulting coordination sphere of niobium and tantalum, five chlorine atoms and a phosphorus atom form distorted octahedra around the metal atoms. Thus, the dimeric M_2Cl$_{10}$ molecules are split up into MCl$_5$ monomers, and the free coordination site at the metal atom is occupied by phosphorus which is acting as an electron pair donor towards the d^0 metal chloride Lewis acid. The coordination could possibly also take place *via* the apical

Table 4. Atom coordinates and equivalent isotropic displacement parameters U_{eq}[a] of (NbCl$_5$)$_2$(β-P$_4$Se$_4$).

Atom	x	y	z	U_{eq} (Å^2)
P(1)	0.0419(3)	0.9105(1)	0.29357(5)	0.0368(3)
P(2)	0.0611(2)	0.8372(1)	0.40140(5)	0.0366(3)
P(3)	0.2933(3)	0.9213(1)	0.35704(5)	0.0412(4)
P(4)	−0.0954(3)	1.0881(1)	0.38283(6)	0.0503(4)
Se(12)	−0.0796(1)	0.76770(5)	0.32885(2)	0.0450(2)
Se(14)	−0.1812(1)	1.03906(5)	0.30216(2)	0.0483(2)
Se(24)	−0.1574(1)	0.95225(6)	0.43203(2)	0.0470(2)
Se(34)	0.2649(1)	1.07849(6)	0.38368(3)	0.0551(2)
Nb(1)	0.17410(9)	0.89148(4)	0.19769(2)	0.0382(1)
Cl(10)	0.3141(4)	0.8656(2)	0.12301(6)	0.0750(6)
Cl(11)	0.3419(4)	1.0382(2)	0.22464(7)	0.0653(5)
Cl(12)	−0.1205(3)	0.9884(2)	0.17357(6)	0.0651(5)
Cl(13)	−0.0535(3)	0.7533(2)	0.19848(7)	0.0645(5)
Cl(14)	0.4252(3)	0.7956(2)	0.24472(7)	0.0679(5)
Nb(2)	0.2215(1)	0.70358(5)	0.47361(2)	0.0429(2)
Cl(20)	0.3626(5)	0.6022(2)	0.53498(9)	0.0935(8)
Cl(21)	−0.0755(3)	0.7571(2)	0.51372(5)	0.0586(5)
Cl(22)	0.3851(3)	0.8565(2)	0.49837(6)	0.0577(4)
Cl(23)	0.4714(3)	0.6857(2)	0.41447(7)	0.0663(5)
Cl(24)	0.0053(4)	0.5924(2)	0.42738(8)	0.0699(5)

[a] U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

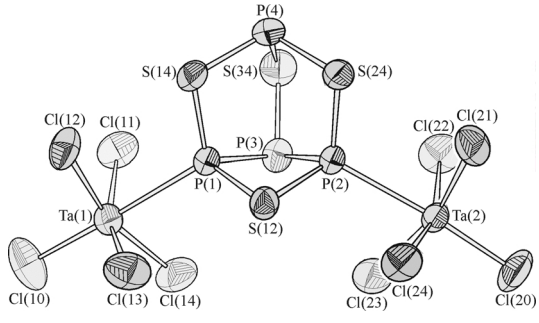

Fig. 1. Molecular structure of (TaCl$_5$)$_2$(β-P$_4$S$_4$) in the crystal (ellipsoids enclose 70 % probability for atomic displacement).

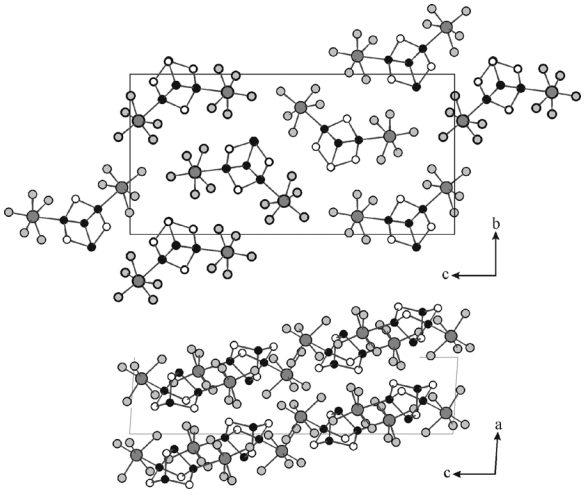

Fig. 2. Projection of the crystal structure of $(TaCl_5)_2(\beta\text{-}P_4S_4)$ in (100) (above) and (010) (below). Black: phosphorus; white: sulfur; grey: chlorine; dark grey: tantalum. Above: Molecules with atoms highlighted with a thicker outline are shifted by +1/2 in a compared to other molecules. Below: The stacking of layers of molecules is shown.

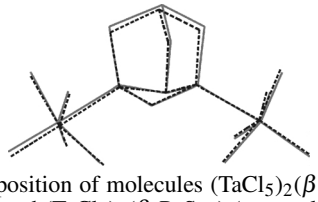

Fig. 3. Superposition of molecules $(TaCl_5)_2(\beta\text{-}P_4S_4)$ (black dashed lines) and $(TaCl_5)_2(\beta\text{-}P_4Se_4)$ (grey solid lines). Due to the larger atomic radius of selenium the molecules differ slightly in their size and orientation.

phosphorus atom, the third basal phosphorus atom or even the chalcogen atoms present, but neither of these alternatives could be observed so far. For a discussion, see also [11].

The maximum molecular symmetry (C_s) is not preserved in the crystal structure due to the packing of the molecules in the crystal. The molecules show a slightly curved shape allowing them to be packed most favorably forming layers with a "herring bone" pattern parallel to the (101) plane (Fig. 2). By this means rather short intermolecular distances between chalcogen atoms and chlorine atoms result in [010] as described in ref. [9] [$(NbCl_5)_2(\beta\text{-}P_4S_4)$: 3.32 Å; $(TaCl_5)_2(\beta\text{-}P_4S_4)$: 3.35 Å; $(NbCl_5)_2(\beta\text{-}P_4Se_4)$: 3.30 Å; $(TaCl_5)_2(\beta\text{-}P_4Se_4)$: 3.32 Å].

Bond lengths and bond angles of the niobium- compared to the tantalum-containing compounds are equal within the triple standard deviations, see Tables 5 – 7.

Table 5. Bond lengths (Å) in $(TaCl_5)_2(\beta\text{-}P_4S_4)$.

Bond		Distance	Bond		Distance
P(1)	– P(3)	2.255(2)	Ta(1)	– Cl(10)	2.262(1)
	– S(12)	2.123(2)		– Cl(11)	2.320(1)
	– S(14)	2.095(2)		– Cl(12)	2.313(1)
P(2)	– P(3)	2.253(2)		– Cl(13)	2.326(1)
	– S(12)	2.125(2)		– Cl(14)	2.344(1)
	– S(24)	2.101(2)		– P(1)	2.745(1)
P(3)	– S(34)	2.074(2)	Ta(2)	– Cl(20)	2.257(1)
P(4)	– S(14)	2.135(2)		– Cl(21)	2.332(1)
	– S(24)	2.136(2)		– Cl(22)	2.351(1)
	– S(34)	2.143(2)		– Cl(23)	2.325(2)
				– Cl(24)	2.310(1)
				– P(2)	2.748(1)

Table 6. Bond lengths (Å) in $(TaCl_5)_2(\beta\text{-}P_4Se_4)$.

Bond		Distance	Bond		Distance
P(1)	– P(3)	2.249(2)	Ta(1)	– Cl(10)	2.264(2)
	– Se(12)	2.271(1)		– Cl(11)	2.313(2)
	– Se(14)	2.240(1)		– Cl(12)	2.319(2)
P(2)	– P(3)	2.250(2)		– Cl(13)	2.330(2)
	– Se(12)	2.269(1)		– Cl(14)	2.335(2)
	– Se(24)	2.251(2)		– P(1)	2.747(1)
P(3)	– Se(34)	2.216(2)	Ta(2)	– Cl(20)	2.258(2)
P(4)	– Se(14)	2.279(2)		– Cl(21)	2.336(2)
	– Se(24)	2.276(2)		– Cl(22)	2.351(2)
	– Se(34)	2.288(2)		– Cl(23)	2.320(2)
				– Cl(24)	2.311(2)
				– P(2)	2.752(1)

Table 7. Bond lengths (Å) in $(NbCl_5)_2(\beta\text{-}P_4Se_4)$.

Bond		Distance	Bond		Distance
P(1)	– P(3)	2.249(2)	Nb(1)	– Cl(10)	2.252(2)
	– Se(12)	2.270(2)		– Cl(11)	2.309(2)
	– Se(14)	2.236(2)		– Cl(12)	2.322(2)
P(2)	– P(3)	2.242(2)		– Cl(13)	2.333(2)
	– Se(12)	2.267(2)		– Cl(14)	2.335(2)
	– Se(24)	2.248(2)		– P(1)	2.745(2)
P(3)	– Se(34)	2.213(2)	Nb(2)	– Cl(20)	2.254(2)
P(4)	– Se(14)	2.273(2)		– Cl(21)	2.332(2)
	– Se(24)	2.275(2)		– Cl(22)	2.353(2)
	– Se(34)	2.284(2)		– Cl(23)	2.314(2)
				– Cl(24)	2.312(2)
				– P(2)	2.758(2)

Going from the sulfur- to the selenium-containing compounds, the central cage expands, but the orientational shift of the adduct molecules is negligible (Fig. 3).

Since crystallographic data of the β-type of P_4Ch_4 molecules are not available to date, a comparison of the naked $\beta\text{-}P_4Ch_4$ cages with MCl_5-linked cages is not possible though it might be especially interesting to examine in which way the cage structures change upon metal halide addition. Compared to other metal halide-containing compounds such as $(CuI)_3(\beta\text{-}P_4Se_4)$

[6], in $(MCl_5)_2(\beta\text{-}P_4Se_4)$ the bond lengths P(1)–Se(14) and P(2)–Se(24) are shortened, whereas the bonds P(4)–Se(14), P(4)–Se(24) and P(4)–Se(34) are clearly elongated. In the analogous sulfur-containing compounds, only the P–S bond lengths of the apical phosphorus atom change significantly from about 2.10 Å in $(CuI)_3(\beta\text{-}P_4S_4)$ [7] to about 2.13 Å in $(MCl_5)_2(\beta\text{-}P_4S_4)$. This certainly has to be attributed to the different coordination of the cages to copper, niobium and tantalum, respectively. In $(CuI)_3(\beta\text{-}P_4Ch_4)$ two basal phosphorus atoms and the apical phosphorus atom are bonded to copper, whereas in $(MCl_5)_2(\beta\text{-}P_4Ch_4)$ only two basal phosphorus atoms are coordinating to niobium or tantalum. The formation of the dative bond to the metal d^0 atoms seems to weaken the basicity of the apical phosphorus atom in particular. Sterical hindrance by the bulky MCl_5 moieties has also to be taken into account when discussing possible reasons for this systematic difference between the d^{10} and the d^0 metal adducts.

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