

Nb₂Cl₁₀(P₄S₁₀)₂: A Co-Crystal of Nb₂Cl₁₀ and P₄S₁₀

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Dedicated to Professor Hans Georg von Schnering on the Occasion of his 75th Birthday

Abstract. Red moisture-sensitive crystals of Nb₂Cl₁₀(P₄S₁₀)₂ were obtained from a solution of P₄S₁₀ and Nb₂Cl₁₀ in CS₂. Nb₂Cl₁₀(P₄S₁₀)₂ crystallises in the space group $P\bar{1}$ with $a = 9.577(2)$, $b = 10.894(2)$, $c = 11.477(2)$ Å, $\alpha = 71.40(1)$, $\beta = 68.14(1)$, $\gamma = 67.58(1)^\circ$; $V = 1005.2(3)$ Å³, $Z = 2$. In the crystal structure molecules of P₄S₁₀ and Nb₂Cl₁₀ are arranged similar to the packing of the ions in the CaF₂ structure type. A comparison of the Raman spectrum of Nb₂Cl₁₀(P₄S₁₀)₂ with spectra of the corresponding reactants indicates that no significant bonds are present

between both components of the title compound. Therefore, Nb₂Cl₁₀(P₄S₁₀)₂ has to be considered as a co-crystal of the starting materials. Ta₂Cl₁₀(P₄S₁₀)₂ is isotopic with Nb₂Cl₁₀(P₄S₁₀)₂, the lattice constants are $a = 9.643(3)$, $b = 10.963(3)$, $c = 11.572(4)$ Å; $\alpha = 71.54(2)$, $\beta = 68.11(2)$, $\gamma = 67.61(2)^\circ$.

Keywords: Phosphorus sulphide; Niobium chloride; Tantalum chloride; Crystal structure; Raman spectroscopy

Introduction

The stabilisation of pnictogen-, chalcogen- and pnictogen chalcogenide molecules by metal halides has been studied intensively during the last years. Because of its structural flexibility, copper(I) iodide proved to be especially suited to act as a matrix for the synthesis of new molecules of group 5 and group 6 elements [1]. Several compounds like (CuI)₃β-P₄S₄ [2], (CuI)₃β-P₄Se₄ [3], (CuI)₂P₈Se₃ [4], and (CuI)P₄Se₄ [5] arose from these investigations. They contain neutral phosphorus chalcogenide molecular structures that are still unknown from the binary systems. For instance the hypothetical β-cage of P₄Se₄, which is structurally analogous to the As₄S₄ molecules in *pararealgar* [6], was found in (CuI)₃β-P₄Se₄ [3]. Two similar coordination compounds were found for NbCl₅. Inspired by the compounds (NbCl₅)₂β-P₄S₄ and (NbCl₅)₂P₄Se₃ [7] we carried out first experiments starting from Nb₂Cl₁₀ and Ta₂Cl₁₀, respectively, to elucidate the existence of related compounds systematically. These studies should provide information about the coordination behaviour of a phosphorus chalcogenide cage where phosphorus is completely saturated by chalcogen (sulphur in this case) in presence of MCl₅ or M₂Cl₁₀ ($M = \text{Nb, Ta}$) as prospective coordination partner. The compounds M₂Cl₁₀(P₄S₁₀)₂ resulted, which can be considered as co-crystals of neutral P₄S₁₀ and M₂Cl₁₀ molecules.

Experimental

Synthesis

Nb₂Cl₁₀(P₄S₁₀)₂ was obtained from the binary phases in organic solvents. P₄S₁₀ was synthesised from phosphorus (Hoechst, ultra high grade) and sulphur (chempur, 99.999 %) by heating stoichiometric mixtures to 400 °C followed by slow cooling [8]. According to [7] 206 mg (0.46 mmol) of the sulphide P₄S₁₀ and 500 mg (0.92 mmol) Nb₂Cl₁₀ (HC Starck, 99.999 %) were filled under an argon atmosphere into a Schlenk flask and covered with 2 ml of dry CS₂ (Aldrich, >99 %) as well as 1.5 ml of dry *n*-hexane (Aldrich, >99 %). The mixture was kept at room temperature under an argon atmosphere. Small, red, moisture-sensitive crystals formed after several days.

Ta₂Cl₁₀(P₄S₁₀)₂ was synthesised similarly using 664 mg (0.92 mmol) Ta₂Cl₁₀ (strem, 99.9 %) and 206 mg (0.46 mmol) P₄S₁₀. The resulting pale yellow crystals are also moisture-sensitive.

Crystal structure determination

Suitable crystals for X-ray structure analysis were handled in an argon-filled glove box; they were isolated from the reactant mixture and filled into sealed glass capillaries to prevent decomposition due to the moisture sensitivity. Data collection was performed using a four-circle diffractometer Xcalibur S with MoK_α radiation. A numerical absorption correction of the intensities was applied. The structure was solved by direct methods and refined against F^2 with anisotropic displacement parameters for all atoms using the SHELX-97 programme package [9]. Table 1 summarises the results of

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Table 1 Crystallographic data and details of the structure refinement for Nb₂Cl₁₀(P₄S₁₀)₂.

Formula		NbCl ₅ P ₄ S ₁₀
Molar mass in g·mol ⁻¹		714.72
Crystal system, space group		triclinic, <i>P</i> $\bar{1}$ (No. 2)
Number of formula units	<i>Z</i>	2
Temperature in °C	<i>T</i>	293(2)
Lattice parameters in Å resp. °	<i>a</i>	9.577(2)
from single crystal data	<i>b</i>	10.894(2)
	<i>c</i>	11.477 (2)
	α	71.40(1)
	β	68.14(1)
	γ	67.58(1)
Cell volume in Å ³	<i>V</i>	1005.2(3)
Calculated density in g·cm ⁻³	ρ_{calc}	2.36
Crystal size in mm		0.20 × 0.19 × 0.11
Diffractometer		four-circle diffractometer (Xcalibur S, Oxford)
		graphite monochromator
		MoK α radiation (λ = 0.71073 Å)
Range of data collection	<i>2</i> θ	7.0° – 50.6°
		–11 ≤ <i>h</i> ≤ 8
		–13 ≤ <i>k</i> ≤ 12
		–13 ≤ <i>l</i> ≤ 12
Absorption correction		numerical with optical description of the crystal shape [10]
Absorption coefficient in mm ⁻¹	μ (MoK α)	2.60
No. of reflections collected (independent)		6587 (3563)
	<i>R</i> _{int} , <i>R</i> _{σ}	0.044, 0.071
Structure solution		SHELXS 97 [9], direct methods
Structure refinement		SHELXL 97 [9], full-matrix least-squares method, refinement on <i>F</i> _o ² ;
		anisotropic displacement parameters
No. of refined parameters		181
Residual electron density in e·Å ⁻³		+ 0.98 / – 0.44
	<i>R</i> ₁ (<i>F</i> _o > 4 σ (<i>F</i> _o))	0.058
	<i>R</i> ₁ (all <i>F</i> _o)	0.088
	<i>wR</i> ₂ (all <i>F</i> _o)	0.132
	<i>Goodness of fit</i>	1.03
Weighting parameters	<i>a</i> , <i>b</i>	0.06, 0

the single crystal structure analysis of Nb₂Cl₁₀(P₄S₁₀)₂. Further details of the crystal structure investigation are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (Fax: (+49) 7247-808-666, e-mail: crysdata@fiz-karlsruhe.de) referring to number CSD-416095, name of the authors and citation of the paper.

Ta₂Cl₁₀(P₄S₁₀)₂ was also analysed by X-ray diffraction. It is isotypic to the title compound and crystallises in the space group *P* $\bar{1}$ with a slightly enlarged unit cell (lattice parameters *a* = 9.643(3), *b* = 10.963(3), *c* = 11.572(4) Å; α = 71.54(2), β = 68.11(2), γ = 67.61(2)°). All crystals examined were systematically twinned and thus no satisfying structure refinement could be achieved so far.

Raman spectroscopy

Raman measurements were performed on a LabRam spectrometer (Jobin Yvon; single stage device with notch filter; HeNe laser, λ = 632.817 nm; CCD detection system). Single crystals of Nb₂Cl₁₀(P₄S₁₀)₂ were analysed in various orientations.

Results and discussion

Crystal structure

Nb₂Cl₁₀(P₄S₁₀)₂ consists of independent niobium pentachloride molecules and phosphorus sulphide molecules, see

Figure 1a. The NbCl₅ molecules form dimers similar to both modifications of the binary metal halide, i.e., pairs of two distorted edge-sharing octahedra according to (NbCl_{4/1}Cl_{2/2})₂. The P₄S₁₀ component of Nb₂Cl₁₀(P₄S₁₀)₂ displays adamantane analogous cages which are structurally equal to those in P₄S₁₀ and in P₄O₁₀. The packing of the molecules in the crystal can be described as a heavily distorted CaF₂ type, where Nb₂Cl₁₀ molecules take the positions of calcium cations and P₄S₁₀ molecules those of the fluoride anions, see Figure 1b. Atom coordinates and anisotropic displacement parameters of all atoms are given in Tables 2 and 3.

The bond distances and angles are summarised in Table 4. They agree with those of the binary starting materials within triple standard deviations. Since the phosphorus atoms in P₄S₁₀ are saturated by sulphur there exist no interactions between niobium and phosphorus atoms, see Figure 2, contrary to the situation in adducts formed by NbCl₅ and phosphorus chalcogenides [7], where phosphorus lone electron pairs coordinate to niobium. In the case of (NbCl₅)₂β-P₄S₄ [7] two of the three basal phosphorus atoms coordinate to NbCl₅, in (NbCl₅)P₄Se₃ [7] one basal phosphorus atom of the P₄Se₃ cage is coordinated to NbCl₅. In these compounds niobium pentachloride forms square pyramids. Including the attached phosphorus atom an octahedron results as coordination polyhedron of niobium. One might also expect a coordination of niobium to sulphur of the P₄S₁₀ cage which is for example found in the adduct

Table 2 Atom coordinates and equivalent isotropic displacement parameters U_{eq} ^a of Nb₂Cl₁₀(P₄S₁₀)₂

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq} in Å ²
P(1)	0.0108(2)	0.3282(2)	0.7627(2)	0.0284(5)
P(2)	0.3083(2)	0.3565(2)	0.8423(2)	0.0275(5)
P(3)	0.3858(2)	0.2705(2)	0.5579(2)	0.0277(5)
P(4)	0.3034(2)	0.0435(2)	0.8402(2)	0.0257(4)
S(1)	−0.2086(2)	0.4004(2)	0.7733(2)	0.0435(6)
S(2)	0.0673(2)	0.4341(2)	0.8548(2)	0.0302(5)
S(3)	0.1456(2)	0.3497(2)	0.5693(2)	0.0298(5)
S(4)	0.0630(2)	0.1220(2)	0.8519(2)	0.0297(5)
S(5)	0.3573(3)	0.4534(2)	0.9271(2)	0.0434(6)
S(6)	0.4432(2)	0.3767(2)	0.6491(2)	0.0308(5)
S(7)	0.3585(2)	0.1504(2)	0.9318(2)	0.0306(5)
S(8)	0.5057(3)	0.2902(2)	0.3812(2)	0.0403(5)
S(9)	0.4370(2)	0.0647(2)	0.6468(2)	0.0292(5)
S(10)	0.3499(3)	−0.1439(2)	0.9237(2)	0.0390(5)
Nb(1)	0.04433(8)	0.13346(7)	0.33697(7)	0.0295(2)
Cl(1)	0.1414(2)	0.0130(2)	0.5361(2)	0.0294(4)
Cl(2)	0.2122(2)	−0.0561(2)	0.2561(2)	0.0394(5)
Cl(3)	−0.0772(3)	0.2154(2)	0.1814(2)	0.0440(6)
Cl(4)	−0.1350(2)	0.2905(2)	0.4578(2)	0.0400(5)
Cl(5)	0.2268(3)	0.2432(2)	0.2590(2)	0.0443(5)

^a U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.**Table 3** Tensor coefficients U_{ij} (in Å²)^a of the anisotropic displacement parameters in Nb₂Cl₁₀(P₄S₁₀)₂

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P(1)	0.025(2)	0.027(2)	0.032(2)	−0.0046(9)	−0.0094(9)	−0.007(1)
P(2)	0.030(2)	0.029(2)	0.026(2)	−0.010(1)	−0.0087(9)	−0.0062(9)
P(3)	0.029(2)	0.029(2)	0.024(2)	−0.009(1)	−0.0076(9)	−0.0045(9)
P(4)	0.025(1)	0.023(2)	0.026(2)	−0.0050(9)	−0.0076(9)	−0.0047(9)
S(1)	0.027(2)	0.045(2)	0.056(2)	−0.004(2)	−0.013(2)	−0.014(2)
S(2)	0.029(2)	0.028(2)	0.035(2)	−0.0053(9)	−0.0082(9)	−0.014(1)
S(3)	0.028(1)	0.031(2)	0.027(2)	−0.0064(9)	−0.0101(9)	−0.0027(9)
S(4)	0.026(1)	0.027(2)	0.036(2)	−0.0091(9)	−0.0097(9)	−0.0028(9)
S(5)	0.050(2)	0.047(2)	0.043(2)	−0.016(2)	−0.015(2)	−0.018(2)
S(6)	0.034(2)	0.034(2)	0.028(2)	−0.018(1)	−0.0056(9)	−0.0073(9)
S(7)	0.036(2)	0.032(2)	0.026(2)	−0.010(1)	−0.0143(9)	−0.0023(9)
S(8)	0.044(2)	0.046(2)	0.026(2)	−0.016(2)	−0.004(1)	−0.005(1)
S(9)	0.031(2)	0.026(2)	0.027(2)	−0.0062(9)	−0.0060(9)	−0.0062(9)
S(10)	0.044(2)	0.030(2)	0.039(2)	−0.011(1)	−0.015(2)	0.002(1)
Nb(1)	0.0305(4)	0.0284(4)	0.0280(4)	−0.0088(3)	−0.0075(3)	−0.0046(3)
Cl(1)	0.029(1)	0.032(1)	0.029(1)	−0.0125(8)	−0.0106(8)	−0.0028(8)
Cl(2)	0.036(1)	0.039(1)	0.037(1)	−0.006(1)	−0.0036(9)	−0.015(1)
Cl(3)	0.049(1)	0.047(1)	0.040(1)	−0.012(1)	−0.023(1)	−0.005(1)
Cl(4)	0.040(1)	0.034(1)	0.043(1)	−0.005(1)	−0.010(1)	−0.012(1)
Cl(5)	0.040(1)	0.046(1)	0.050(1)	−0.024(1)	−0.006(1)	−0.006(1)

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

compound (NbCl₅)Ph₃PS [11]. Therein, this apparently results from a lack of free bonding sites at phosphorus. In the case of Nb₂Cl₁₀(P₄S₁₀)₂ rather large complexes would form when niobium coordinates the terminal sulphur atoms. Certainly such complexes cannot be packed efficiently and the dimerisation of NbCl₅ is favoured.

Furthermore, it seems worth mentioning that no fragmentation of the P₄S₁₀ cages takes place. Such fragmentations are observed in several reactions of transition metal complexes with phosphorus sulphide cages, e.g. in the reaction of [RhCl(1,5-cyclooctadiene)]₂ and *triphos* (CH₃C(CH₂PPh₂)₃) with P₄S₃ [12]. A basal phosphorus atom of the P₄S₃ cage is replaced by rhodium forming [*triphos*Rh(P₃S₃)]. Such a cleavage of bonds within the phosphorus sulphide framework and the generation of adducts consisting of niobium pentachloride and smaller

Table 4a Bond distances in Nb₂Cl₁₀(P₄S₁₀)₂

Bond	Distance in Å	Bond	Distance in Å
P(1) - S(1)	1.913(3)	P(2) - S(2)	2.099(3)
- S(2)	2.102(3)	- S(5)	1.913(3)
- S(3)	2.101(3)	- S(6)	2.099(3)
- S(4)	2.098(3)	- S(7)	2.098(3)
P(3) - S(3)	2.095(3)	P(4) - S(4)	2.095(3)
- S(6)	2.103(3)	- S(7)	2.098(3)
- S(8)	1.911(3)	- S(9)	2.098(3)
- S(9)	2.094(3)	- S(10)	1.914(3)
Nb(1) - Cl(1)	2.559(2)	Nb(1) - Cl(3)	2.253(2)
- Cl(1 ⁱ)	2.566(2)	- Cl(4)	2.302(2)
- Cl(2)	2.300(2)	- Cl(5)	2.244(2)

(i): −*x*, −*y*, −*z***Table 4b** Comparison of the mean bond distances of Nb₂Cl₁₀(P₄S₁₀)₂, (NbCl₅)₂β-P₄S₄, and the binary starting materials Nb₂Cl₁₀ and P₄S₁₀

Mean distance in Å for the bonds	Nb ₂ Cl ₁₀ (P ₄ S ₁₀) ₂	P ₄ S ₁₀ [13] and α- and β-Nb ₂ Cl ₁₀ [14, 15]	(NbCl ₅) ₂ β-P ₄ S ₄ [7]
P - S(bridging)	2.10(1)	2.10(2)	2.11(1)
P - S(terminal)	1.91(1)	1.90(2)	—
Nb - Cl(bridging)	2.56(1)	2.56(2) α, 2.57(1) β	—
Nb - Cl(terminal)	2.30(1); 2.25(1)	2.30(4) α, 2.29(1) β; 2.25(2) α, 2.25(1) β	2.32(1)

phosphorus sulphide cages or even the formation of phosphorus chlorides and niobium sulphides is not to be ruled out when applying less mild conditions to the title compound.

Raman spectroscopy

Vibrational spectroscopy is an excellent method to estimate the bonding interaction in adduct compounds. For instance, the resonances of [SbS₃^{3−}] vibrations in β-Cu₃SbS₃ range from about 280 to 330 cm^{−1} whereas the corresponding resonances for (CuI)₂Cu₃SbS₃ are found between about 330 and 370 cm^{−1} [16]. This shift is attributed to the different coordination spheres of antimony atoms with further sulphur atoms of surrounding thioantimonate units in β-Cu₃SbS₃ on the one hand and the separation of these units in (CuI)₂Cu₃SbS₃ on the other hand. Raman spectra of crystalline Nb₂Cl₁₀(P₄S₁₀)₂ were recorded in order to analyse the bonding interactions between the building units. The Raman spectrum of the title compound is shown in Figure 3. All observed bands can be attributed to vibration modes of the independent P₄S₁₀ and Nb₂Cl₁₀ molecules and no additional modes are observed. They cover a frequency range from about 100 to 720 cm^{−1}, with bands of the P₄S₁₀ cages between 110 and 720 cm^{−1} and bands of Nb₂Cl₁₀ between 100 and 420 cm^{−1}. The Raman bands of specific modes of the different molecules in the structure were assigned by comparison with reported data of the binary compounds [17], see Figure 3. The deviations of the frequencies of Nb₂Cl₁₀(P₄S₁₀)₂ and of the binaries are less than 5 cm^{−1} for all bands. Of course the environment of the

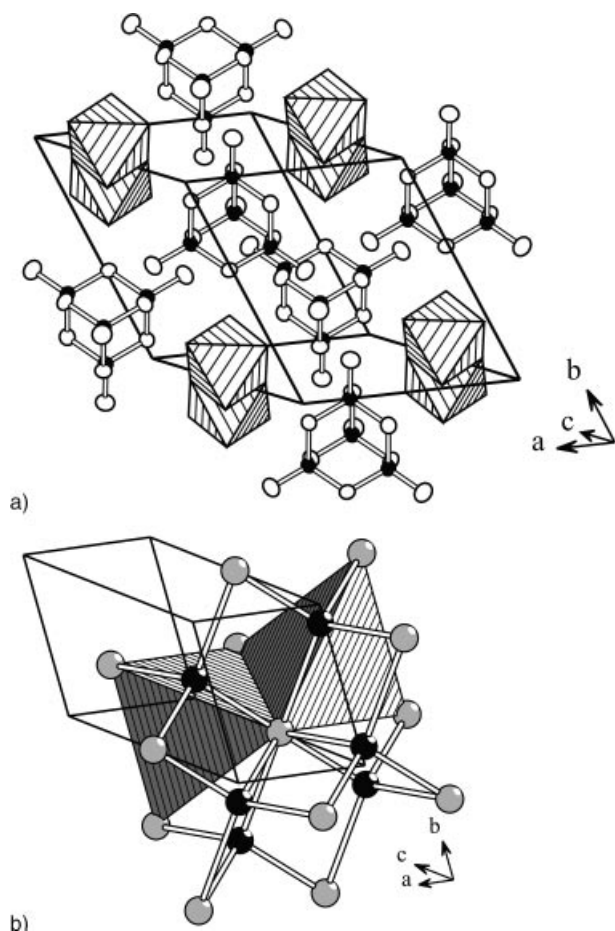


Figure 1 a) Section of the crystal structure of $\text{Nb}_2\text{Cl}_{10}(\text{P}_4\text{S}_{10})_2$. Black: phosphorus; white: sulphur; hatched double octahedra: $\text{Nb}_2\text{Cl}_{10}$. b) Arrangement of the centres of $\text{Nb}_2\text{Cl}_{10}$ (grey) and of P_4S_{10} (black) showing the relation to the CaF_2 structure type.

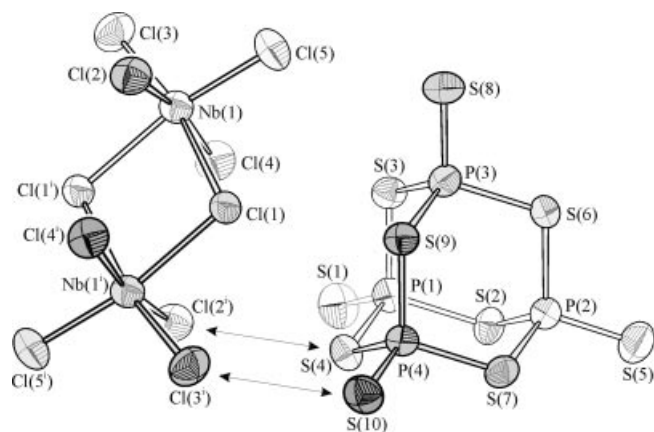


Figure 2 Adjacent molecules $\text{Nb}_2\text{Cl}_{10}$ (left side; i : $-x$, $-y$, $-z$) and P_4S_{10} (right side). Ellipsoids enclose 70% probability for atomic displacement. Arrows indicate shortest distances between the molecules (3.66 Å), being slightly longer than the van der Waals distance (3.6 Å) for the considered atoms.

molecules in the binary phases differs from the environment of those in the title compound. The minimum intermolecu-

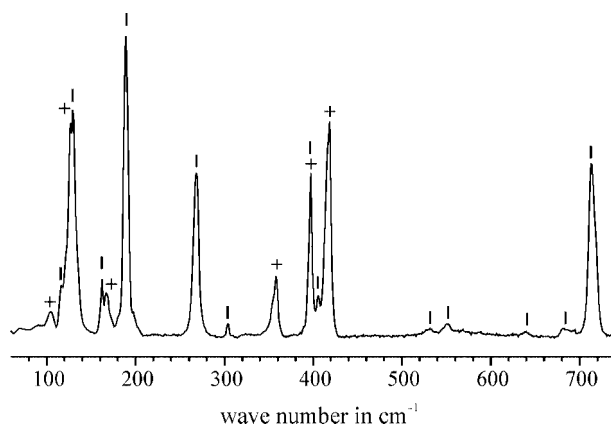


Figure 3 Raman spectrum of $\text{Nb}_2\text{Cl}_{10}(\text{P}_4\text{S}_{10})_2$ (excitation wavelength 633 nm). P_4S_{10} bands are marked with “|” and $\text{Nb}_2\text{Cl}_{10}$ bands with “+”.

lar (non-bonding) distance of sulphur atoms in P_4S_{10} is 3.56 Å and the minimum intermolecular (non-bonding) distance of chlorine atoms in α - and β - $\text{Nb}_2\text{Cl}_{10}$ is 3.63 Å. In the co-crystal $\text{Nb}_2\text{Cl}_{10}(\text{P}_4\text{S}_{10})_2$ we observe a minimum intermolecular (non-bonding) distance between sulphur and chlorine atoms of 3.66 Å. It is quite obvious that this fact does not influence molecular vibration frequencies. This emphasises the “independence” of both kinds of molecules once more.

Conclusion

There are exclusively van der Waals interactions present between the constituting molecules in $\text{Nb}_2\text{Cl}_{10}(\text{P}_4\text{S}_{10})_2$. A similar situation is to be found in WCl_6S_8 [18], a co-crystal consisting of single sulphur rings S_8 and WCl_6 octahedra. A coordination of sulphur atoms of the phosphorus sulphide species to niobium pentachloride does not occur here. This is contrary to chemically related compounds [7] and numerous other compounds of phosphorus chalcogenide cages and transition metal complexes that are described in the literature, where different coordination types including several fragmentation possibilities of the cages are found. E.g., in $\text{Ag}^+ \cdot \text{P}_4\text{S}_3$ complexes with weakly coordinating counterions [19] the coordination of the cage to the metal is realised via the apical or basal phosphorus atoms as well as via bridging sulphur atoms.

It is still an open question under which conditions these coordination compounds form – with or without fragmentation or bond cleavage –, and – in case of their formation – which atoms interact and why. Detailed investigations to the discussed problems will follow.

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