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New insight into the reduction of rhenates(VII) with hydrogen chloride and into the structure of the ReOCl₅⁻ product

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ABSTRACT

Rhenate(VII) anion is reduced by gaseous HCl to yield pentachloridooxidorhenate(VI) anion. Several pentachloridooxidorhenate(VI) salts have been crystallized and the anion structure has been investigated in detail. The ReOCl₅⁻ anion structure has been compared with the ReOCl₅²⁻ structure and conclusions concerning the influence of the central atom d electrons number on the anion geometry have been drawn. © 2009 Elsevier B.V. All rights reserved.

1. Introduction

It was reported in literature that hydrogen chloride could not act as a reducing agent towards rhenate(VII) anions, contrary to the well-known reaction with manganates(VII) used already by Scheele [1] as a laboratory method of obtaining chlorine. This seems to be confirmed by the work of Jeżowska-Trzebiatowska [2]. As part of that research, gaseous HCl was bubbled through rhenates(VII) with simple inorganic cations such as K⁺, dissolved in concentrated HCl acid. The mixture underwent a colour change from yellow to red. A mechanism for this process was proposed assuming that the yellow colour results from the $\text{ReO}_2\text{Cl}_4^$ formation:

 $ReO_4{}^- + 4HCl \rightarrow ReO_2Cl_4{}^- + 2H_2O$

It was reported, that these anions could easily be reduced; however, not by HCl but by other reducing agents, such as HI. It is to note that the study of Astheimer and Schwochau [3] on the electrolytic reduction of rhenates(VII) revealed, that the first reduction step involves one-electron reduction to Re(VI). Contrary to Jeżowska-Trzebiatowska, the authors used rhenate(VII) of bulky tetrabutylammonium cation, dissolved in organic solvents. The relevant rhenate(VI) could be obtained; however the attempt to obtain the analogous potassium salt failed.

Other authors also confirmed the possibility to stabilize Re(VI) complexes obtained in the reaction of rhenates(VII) with HCl. The published results therefore seem to contradict the initial conclusions of Jeżowska-Trzebiatowska [2].

* Corresponding author. *E-mail address:* holynska@wcheto.chem.uni.wroc.pl (M. Hołyńska). Yatirayam and Singh [4] reported the preparation and properties of pentachloridooxidorhenates(VI) obtained during bubbling gaseous HCl through the suspension of potassium rhenate(VII) in acetic acid with addition of acetic anhydride. This procedure led to the rhenate(VII) dissolution and a red-coloured mixture formation. The red mixture contained pentachloridooxidorhenate(VI) anions, which could be precipitated in form of tetraphenylphosphonium and tetraphenylarsonium salts. No attempt was made to explain the formation of these compounds.

Other investigations of the products obtained in the reaction of rhenates(VII) with HCl led to crystallization of such compounds as $Cs_2[ReO_3Cl_3]$ [5,6]; bpy[ReO_3Cl] [7]; (H₂phen)[ReCl₂(H₂O)O₃]Cl [8]. Apart from that, reaction of rhenate(VII) with acetyl chloride yielded $Cs[ReO_2Cl_4]$ and $Cs[ReOCl_5]$ salts [9].

The systematic research, this work being a part of it, was begun by Lis and Jeżowska-Trzebiatowska [10]. The authors bubbled a slow stream of HCl through the suspensions of [AsPh₄]ReO₄ and [PPh₄]ReO₄ in various solvents. They observed colour changes similar to those noticed by other authors and, furthermore, reported precipitation of the relevant pentachloridooxidorhenate(VI) crystals in form of red tetragonal needles, which were stable in air when obtained from acetone or chloroform. However, when the red crystals prepared in ethanol, together with the reaction mixture, were exposed to air, rhenium(V) oxocomplexes were obtained. The authors did not offer explanation whether the rhenium (V) compounds were products of reduction or rather disproportionation.

It should be noted, that although the processes described above play an important role in inorganic syntheses (e.g. as one of first stages in the synthesis of rhenium potential radiopharmaceuticals [11]), they remain unexplained in detail.





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This work is intended to fill this gap, as well as to gain further insight into the structure of their products, pentachloridooxidorhenates(VI). In comparison to the analogous Re(V) oxidocomplexes, the central metal atom lacks one d electron, therefore the influence of this additional electron on the geometric parameters can be assessed. The first such analysis was published by Lis and Jeżowska-Trzebiatowska [10], who compared bond lengths and angles for ReOCl₄ and ReOCl₄⁻ (from AsPh₄[ReOCl₄] later shown by Müller [12] to be in fact AsPh₄[ReOCl₄H₂O] [13]). The relevant differences appear to be significant and affect the IR spectra parameters. The Re-Cl bond length increase in ReOCl₄⁻ was explained assuming, that one additional d electron is present on the antibonding orbital, the same as the one occupied by the unpaired electron in ReOCl₄ according to Al-Mowali and Porte [14]. Pentachloridooxidorhenates(VI) obtained by Lis and Jeżowska-Trzebiatowska [10] were affected by disorder due to the highly symmetric (tetraphenylphosphonium and tetraphenylarsonium) counterions. Accordingly. in this study it was decided to use phosphonium cations of lower symmetry (such as: methyltriphenylphosphonium, benzyltriphenylphosphonium, (4-methylbenzyl)triphenylphosphonium - see Fig. 1), that would allow to limit the crystal structure disorder. As a result, the pentachloridooxidorhenate(VI) anion geometrical parameters have been obtained, which then could be compared with the parameters reported for the analogous Re(V) compounds.

2. Experimental

2.1. General

All compounds used for syntheses and preparations were obtained commercially and not purified further.

The preparative procedure was as follows. The starting rhenate(VII) salt was placed in a flow reactor and the relevant solvent was added. Gaseous HCl obtained in reaction of concentrated H_2SO_4 with solid NaCl was bubbled through the rhenate(VII) suspension in the flow apparatus.

The relevant rhenate(VII) salts were prepared in the reaction of ammonium rhenate(VII) with phosphonium halide in aqueous solution. The obtained precipitates were filtered and washed with cold water until no halide ions were present in the filtrate [38].

The phosphonium halides were obtained commercially (ethyltriphenylphosphonium bromide, benzyltriphenylphosphonium



Fig. 1. The phosphonium cations used as counter-ions in this study. The cations from (A), (B) and (C) are provided with the corresponding letters.

chloride) or prepared in the reactions of the relevant alkyl/aryl halide with the selected phosphine in toluene¹.

In the course of this work many pentachloridooxidorhenates(VI) have been investigated by X-ray diffraction studies (Fig. 1). Very frequently problems connected with anion disorder or the presence of impurities, occured. A series of phosphonium salts structures was obtained (the methyltriphenylphosphonium salt, two polymorphs of the benzyltriphenylphosphonium salt, two polymorphs of the (4-methylbenzyl)triphenylphosphonium salt, the ethyltriphenylphosphonium salt, the 1,1,4,4-tetraphenyl-1,4-diphosphoniacyclohexane salt, (4-chloromethylbenzyl)triphenylphosphonium salt). Three structures were chosen. The criterion of choice was based on the X-ray data quality and indicators of the possible crystal structure disorder affecting the observed ReOCl₅⁻ anion geometry or impurity (e.g. the final difference Fourier map). The selected structures include the 1.1.4.4-tetraphenvl-1.4-diphosphoniacyclohexane salt (A. containing also hydrogen dichloride anions), the ethyltriphenylphosphonium salt (B) and one polymorph of the benzyltriphenylphosphonium salt (C). The three chosen data sets provide the structure of pentachloridooxidorhenate(VI) anion not affected significantly by detectable artifacts.

2.2. 1,1,4,4-Tetraphenyl-1,4-diphosphoniacyclohexane pentachloridooxidorhenate(VI) hydrogen dichloride (**A**)

Gaseous HCl was bubbled through suspension of the corresponding rhenate(VII) (0.05 g) in 0.5 ml of methanol. The solid rhenate(VII) dissolved and the reaction mixture changed from yellow through orange to red.

At this stage (red homogenous mixture) the bubbling of the HCl gas through the reaction mixture was stopped and 0.05 g of rhenate(VII) was added under HCl atmosphere to the mixture. The vessel with the mixture was sealed and stored in a freezer at about -10 °C. After a few days crystals in form of red needles began to appear. The crystals, which were very unstable, were quickly filtered off and covered with polyfluoroalkylether. One monocrystal was chosen for X-ray data collection.

2.3. Ethyltriphenylphosphonium pentachloridooxidorhenate(VI) (B)

Ethyltriphenylphosphonium rhenate(VII) (0.05 g) was suspended in 0.5 ml of ethanol. Gaseous hydrogen chloride was bubbled through the suspension. Similar colour changes as in case of (**A**) were observed. At this stage (red homogenous mixture) the bubbling of HCl gas through the reaction mixture was stopped and 0.01 g of rhenate(VII) was added under HCl atmosphere to the mixture. The vessel with the mixture was sealed and stored in a freezer at about -10 °C. As a result, red crystals in the form of plates were obtained after a few days. The crystals were filtered

¹ Beilstein's Handbook of Organic Chemistry, 16, 759. The 1,1,4,4-tetraphenyl-1,4diphosphoniacyclohexane bromide used in the preparation of the starting rhenate(VII) for A was obtained in the reaction of ethane-1,2-bis(triphenylphosphine) with the excess of 1,2-dibromoethane in toluene. The compound is known [23]; however, the present authors could not retrieve the synthesis description, which was published in Ph. D. thesis cited in the paper on the crystal structure [23]. Therefore the here applied procedure is described. 1 g of PPh₂CH₂CH₂PPh₂ was placed in a 50 ml flask. 25 cm³ of toluene and 3 cm³ of ethylene bromide were added. The mixture was heated under reflux over 2 h. A white precipitate was obtained, comprising 1,1,4,4tetraphenyl-1,4-diphosphoniacyclohexane bromide (yield: 70%). Elemental Anal. Calc. 10.6% P; obs.: 10.2% P. IR (KBr pellet): 443.2 (w), 500 (vs), 657.0 (w), 688.6 (m), 728.2 (vs), 761.5 (m), 780.1 (w), 844.4 (m), 928.2 (vw), 995.6 (w), 1026.3 (vw), 1112.4 (m), 1133.0 (s), 1198.7 (vw), 1340.9 (vw), 1403.7 (w), 1415.8 (w), 1439.1 (s), 1487.6 (vw), 1584.4 (w), 1623.7 (w), 2088.5 (vw), 2241.5 (vw), 2582.2 (vw), 2788.0 (m), 2851.4 (s), 2913.7 (w), 3007.7 (m), 3036.8 (m), 3069.4 (w), 3431.9 (s). MS spectrum obtained for solution in methanol – m/z (I, a. u.) – positive ions: (M–2) 213.1 (3.6-104), 213.6 (8.103), 214.1 (103); 314.1 (103), 399.1 (9.102), 453.1 (103).

off, covered with polyfluoroalkylether and next one monocrystal was chosen for X-ray data collection.

2.4. Benzyltriphenylphosphonium pentachloridooxidorhenate(VI), one of the monoclinic modifications (C)

Reaction of gaseous HCl was performed using as starting material 0.1 g of benzyltriphenylphosphonium rhenate(VII) suspended in 3 ml of isopropyl alcohol. Similar reaction as in case of (**A**) led to precipitation of red crystals. However, the quality of the crystals was very bad, therefore the mixture was sealed in the reaction vessel and left for recrystallization. After a few days the crystals were filtered and their examination showed them to be a mixture of two polymorphs: in form of needles (majority, compound (**C**)) and blocks. Both polymorphs were unstable and on exposure to air underwent decomposition to yellow polycrystalline products.

2.5. X-ray data collection

Selected crystallographic data for compounds (**A**), (**B**) and (**C**) are given in Table 1. Data were collected on KM4CCD diffractometer [39] with graphite-monochromatised Mo K α radiation. All structures were solved by Patterson method using SHELXS97 and refined using SHELXL software [40]. All cation H atoms positions were calculated from geometry and their displacement parameters were constrained as $1.2U_{eq}$ (parent atom). In (**A**) the H6 atom in the [HCl₂]⁻ anion (containing Cl5 and Cl6 atoms) was found on the difference Fourier map closer to the Cl6 atom. All parameters of H6 were first refined and then constrained. The difference Fourier peak near the Cl5 atom was interpreted as sign of slight disorder. As a result, Cl5 atom was modelled as disordered between two positions (with occupancies of 0.972(8) and 0.028(8), respectively).

3. Results and discussion

3.1. The reduction of rhenates(VII) with hydrogen chloride

Based on the experimental data collected in this study, the role of HCl in its reaction with rhenates(VII) could be defined, apart

Table	1		
C	1	1	

Crystal and refinement	data	for	(A),	(B)	and	(C))
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from that of a complexing agent, also as the reducing agent. In all the syntheses involving various phosphonium rhenates(VII) suspended in different solvents as starting materials the precipitated red crystals contained pentachloridooxidorhenates(VI). HCI was at the same time oxidised to chlorine what would be demonstrated when bubbling the gas coming out from the flow reaction vessel through KI aqueous solution, which would turn brown as a result of free iodine formation. Therefore, the process could be summarized as follows. In the first stage in accordance to Jeżowska-Trzebiatowska [2] the yellow complex [ReO₃Cl₃]^{2–} and subsequently [ReO₂Cl₄]⁻ ions are formed according to the following scheme:

 $\text{ReO}_{4}^{-} \overset{\text{HCl}-\text{H}_{2}\text{O}}{\rightarrow} \text{ReO}_{3}\text{Cl}_{3}^{2-} \overset{\text{HCl}-\text{H}_{2}\text{O}}{\rightarrow} \text{ReO}_{2}\text{Cl}_{4}^{-}$

Subsequently, the colour changes to red as a result of reduction process:

 $2[ReO_2Cl_4]^- + 4HCl = 2ReOCl_5^- + Cl_2 + 2H_2O$

It is possible to isolate the relevant Re(VI) oxidocomplexes as bulky phosphonium cations present in the reaction environment facilitate their precipitation [15].

3.2. The pentachloridooxidorhenate(VI) anion structure. $\text{Re}^{VI}\text{OCl}_5^{-}$ versus $\text{Re}^{V}\text{OCl}_5^{2-}$

In the pentachloridooxidorhenate(VI) anion the central Re atom is surrounded by five chloride ligands and one oxide ligand, placed in vertices of a distorted octahedron (Fig. 2). The Re–O bond may be regarded as a triple bond [16] and should be expected to influence the Re–Cl_{trans} bond length (see Scheme 1), which is longer than the Re–Cl_{cis} bonds. The overall anion distortion with the O– Re–Cl_{cis} bond angles greater than 90° should also be expected. All these features occur in the ReOCl₅^{2–} anion [17] (in the potassium salt).

The Re–O and Re–Cl distances are collected in Table 2 ((**A**), (**B**) and (**C**) as well as K₂ReOCl₅). In (**B**) and (**C**) the anions occupy general positions. In the crystal structure of K₂ReOCl₅ [17] the ReOCl₅^{2–} anion lies in special position of *m* site symmetry. A similar situation is observed in case of the ReOCl₅[–] anion in (**A**). There-

	(A)	(B)	(C)
Formula	[PPh ₂ (CH ₂ CH ₂) ₂ PPh ₂] [ReOCl ₅][HCl ₂]	[PPh ₃ CH ₂ CH ₃] [ReOCl ₅]	[PPh3CH2Ph][ReOCl5]
Formula weight	877.80	670.79	732.85
T (K)	100(2)	100(2)	100(2)
λ (Å)	0.71073	0.71073	0.71073
Crystal system	orthorhombic	orthorhombic	monoclinic
Space group	Pnma	Pbca	P2 ₁ /c
a (Å)	8.504(3)	16.500(5)	10.984(3)
b (Å)	16.666(5)	16.240(5)	17.906(5)
<i>c</i> (Å)	22.976(7)	17.414(5)	14.069(4)
β (Å)			108.60(3)
V (Å ³)	3256(2)	4666(2)	2623(2)
Z, ρ_{calc} (g cm ⁻³)	4, 1.791	8, 1.910	4, 1.856
$\mu (\mathrm{mm}^{-1})$	4.43	5.86	5.22
F(000)	1716	2584	1420
Crystal size (mm)	$0.29 \times 0.05 \times 0.017$	$0.20\times0.08\times0.04$	$0.15 \times 0.12 \times 0.09$
θ Range (°)	2.8-36.9	2.8-35.0	3.0-38.5
Reflections total/unique	55633/8259	65037/10054	45819/13560
R _{int}	0.0829	0.0725	0.0943
Absorption correction	analytical	analytical	analytical
Minimum, maximum transmission factors	0.417, 0.822	0.387, 0.829	0.553, 0.639
Data/restraints/parameters	8259/0/191	10054/0/253	13560/0/298
Goodness-of-fit on F^2	1.018	1.016	0.928
$R_1 \left[I > 2\sigma(I) \right]^{\rm a}$	0.036	0.032	0.052
wR ₂ (all data)	0.039	0.035	0.055
Maximum, minimum $\Delta ho_{ m elect}$ (e Å $^{-3}$)	1.48/-1.42	1.76/-1.68	1.55/-1.55

^a $R = \sum ||F_0| - |F_c|| / \sum |F_0|.$



Fig. 2. Pentachloridooxidorhenate(VI) anion in (**A**) and (**B**), (**C**) (on example of (**B**)) with atom labelling scheme (for the sake of comparison the anion labelling scheme in **A** corresponds to the labelling scheme used for the ReOCl_5^{2-} anion by Głowiak et al. [17], see article text). The thermal ellipsoids have been drawn at 30% probability level. Symmetry code: [i] x, 0.5 – y, z.

fore a comparison of the two data sets gives a good opportunity to compare the influence of the additional d electron on the overall ReOCl_5^{n-} (n = 1 or 2) anion geometry. Table 2 shows, that in both cases the Re–O bond length is comparable within the experimental error. This bond length is similar to the triple Re–O bond length reported for other Re(VI) oxidocomplexes [18], as well as the value fitted by Pyykkö et al. [16] as the sum of the O and Re covalent radii in a triple bond.



Scheme 1. Labelling in the ReOCl_5^{n-} anion (where n = 1 or 2) often used in the general considerations concerning the bond lengths in this paper.

The most striking difference between the ReOCl₅⁻ anion in A and the ReOCl₅²⁻ anion in K₂ReOCl₅ is connected with the Re-Cl bond lengths, in particular the Re-Cl_{cis} bond lengths. All these bonds are longer in case of the ReOCl_5^{2-} anion. The Re-Cl_{trans} bond length is longer by 0.034(2) Å and the average Re-Cl_{cis} bond lengths differ by 0.054(5) Å. This may be explained based on the available theoretical studies on Re(V) and Re(VI) oxidocomplexes. A general molecular orbital diagram for the X–M–L moiety in complex molecules (where M - metal, X - ligand imposing trans influence on the ligand L) was provided by Shustorovich et al. [19]. Natkaniec and Jeżowska-Trzebiatowska [20] reported the molecular orbital diagram for the ReOCl₅²⁻ anion based on theoretical calculations, as well as spectroscopic, magnetic and EPR measurements. The authors carried out theoretical calculations assuming $C_{4\nu}$ symmetry of the ReOCl₅^{2–} anion. However, still their results are helpful in the analysis of the here reported data. The authors explain the *trans*-effect in the ReOCl₅^{2–} anion (elongation of the Re-Cl bond placed in the trans position with respect to the oxide ligand) as a result of decrease in the total π overlap population in the affected bond. This decrease corresponds to the fact, that the bonding and antibonding $b_2(\pi)$ orbitals are filled with

Table 2

The pentachloridooxidorhenate(VI) anion (in (A), (B) and (C)) versus the pentachloridooxidorhenate(V) anion [17] geometrical parameters

-					
Salt		А		В	С
Anion	ReOCl ₅ ²⁻	ReOCl ₅ ⁻		ReOCl ₅ ⁻	ReOCl ₅ -
Re–O	1.655(6)	1.675(2)	Re–O	1.686(2)	1.668(3)
Re-Cl1	2.379(2)	2.322(1)	Re-Cl1	2.314(1)	2.325(2)
			Re-Cl4	2.351(1)	2.330(1)
Re-Cl2	2.371(2)	2.314(2)	Re-Cl2	2.316(1)	2.327(2)
Re-Cl3	2.502(2)	2.468(2)	Re-Cl3	2.408(1)	2.405(1)
Re-Cl4	2.382(2)	2.336(2)	Re-Cl5	2.341(1)	2.344(2)
O-Re-Cl1	94.7(2)	95.6(1)	O-Re-Cl1	94.7(1)	93.2(1)
			O-Re-Cl4	91.8(1)	94.7(1)
O-Re-Cl2	97.2(2)	96.0(1)	O-Re-Cl2	95.8(1)	93.7(1)
O-Re-Cl3	179.4(2)	175.5(1)	O-Re-Cl3	176.7(1)	179.2(1)
O-Re-Cl4	95.1(2)	92.2(1)	O-Re-Cl5	92.9(1)	93.8(1)
Cl1-Re-Cl1 ^a	170.6(1)	168.8(1)	Cl1-Re-Cl4	173.4(1)	171.9(1)
Cl1-Re-Cl2	89.3(1)	89.0(1)	Cl1-Re-Cl2	89.9(1)	91.4(1)
Cl1-Re-Cl3	85.3(1)	84.4(1)	Cl1-Re-Cl3	87.6(1)	86.0(1)
Cl1-Re-Cl4	89.7(1)	90.2(1)	Cl1-Re-Cl5	90.1(1)	88.8(1)
Cl2-Re-Cl3	83.4(1)	88.5(1)	Cl2-Re-Cl3	86.6(1)	85.9(1)
Cl2-Re-Cl4	167.7(1)	171.8(1)	Cl2-Re-Cl5	171.3(1)	172.4(1)
Cl3-Re-Cl4	84.3(1)	83.3(1)	Cl3-Re-Cl5	84.8(1)	86.5(1)

^a Symmetry code: [i] *x*, 0.5 – *y*, *z*.

electrons. The authors imply, that if the magnitudes of the *trans* effect for d^2 and d^1 electron central ion are different, this provides an indirect evidence, that the second d electron of the central ion is also in the antibonding $2b_2$ (d_{xy}) orbital. The here reported data are probably an experimental proof for this conclusion. Also, e.g. Neuhaus et al. [21] reported as a result of a theoretical study that the Re–Cl bonds should involve the *d* orbitals of Re.

The symmetries of the ReOCl_5^- anions in (**A**) and (**B**), (**C**) are different. The difference is connected with a slight change at bond angles values, e.g. in (**C**) the O–Re–Cl_{trans} bond angle is closer to 180°, as in the ReOCl_5^{2-} anion [17] (Table 2). However, the main difference concerns the Re–Cl_{trans} bond length, which in (**B**) and (**C**) is shorter than in (**A**) (the values for (**B**) and (**C**) are essentially equal). This leads to the conclusion, that the main effect of the Re–Cl_{trans} bond length may to a higher extent be an effect of the crystal structure packing.

In case of the anions in (**A**)–(**C**) and K_2ReOCl_5 [17] the equatorial Cl ligands lie in one plane and the Re atom is shifted from this plane towards the O ligand. It is to be noted, that these shifts are different: in case of K_2ReOCl_5 the value calculated based on the available atom coordinates [17] is 0.255(1) Å, whereas in case of (**A**) it is 0.196(1) Å, in case of (**B**): 0.155(1) Å and for (**C**): 0.158(1) Å.

3.3. The crystal structure packing in (A), (B) and (C)

It would be justified to take a closer look on the crystal structure packing, that allowed to capture the ReOCl_5^- anions selectively and to stabilize their positions. For all crystal structures (**A**)–(**C**) the crystal packing is cation-dominated with numerous phenyl rings embrace interactions [22,38], with weak C–H…Cl or C–H…O hydrogen bonds and without any phenyl rings stacking interactions.

(**A**) is the second determined crystal structure with the 1,1,4,4-tetraphenyl-1,4-diphosphoniacyclohexane cation. In the bromide structure published by Brown and Trefonas [23] the core 1,4-diphosphoniacyclohexane ring adopts a chair conformation, a similar conformation is observed in (**A**). Another uncommon feature of

the crystal (**A**) is the presence of $[HCl_2]^-$ anions. Such anions have been subject to spectroscopic [24,25], as well as theoretical [26], neutron [27] and X-ray diffraction studies [28–36]. It was shown, based on IR spectra analysis [24,25], that the $[HCl_2]^-$ anion should be linear. Two spectroscopically distinguishable cases were described: (1) non-centrosymmetric case (asymmetric stretching mode at 1540–1700 cm⁻¹), (2) centrosymmetric case (broad band at 690–810 cm⁻¹). The H atom of the $[HCl_2]^-$ anion in (**A**) was localized on the difference Fourier map nearer to one of the CI atoms. Moreover, preliminary IR spectra indicate the presence of a broad band at 1500–1800 cm⁻¹, what suggests the former possibility [25,26].

For the ethyltriphenylphosphonium cation both in (**B**) and in the corresponding rhenate(VII) [37] the P atom of nearly tetrahedral environment deviates from the phenyl rings planes (the maximum deviation values: 0.261(4) and 0.138(4) Å for (**B**) and the corresponding rhenate(VII), respectively). The methyl group deviation from the phenyl group in *trans* position in (**B**) (-0.153(7) Å) is not as significant as in case of the rhenate(VII) (-0.879(6) Å). Thus the cation in (**A**) adopts the other possible ethyltriphenylphosphonium cation geometry [37].

The phosphonium cation conformation is not strictly the same in case of (**C**) in comparison to the corresponding rhenate(VII) [38]. The differences concerning the interplanar angles for phenyl rings from the $-PPh_3$ moiety as well as C-P-C-C torsion angles with respect to the benzyltriphenylphosphonium cation in the corresponding rhenate(VII) [38] could be found. The P atom with nearly tetrahedral environment in each case deviates from the phenyl rings planes (0.064(5) and either 0.203(4) or 0.201(4) Å in two symmetry-independent cations in (**C**) and for the corresponding rhenate(VII) [38], respectively).

In (**A**), the cations are arranged in layers perpendicular to [010]. Between the layers the pentachloridooxidorhenate(VI) and hydrogen dichloride anions are located, forming columns (one set of columns consisting of pentachloridooxidorhenate(VI) anions and the other set of columns comprising hydrogen dichloride anions) along [100] (Fig. 3). The crystals (**B**) and (**C**) are built from cation and an-



ion columns extending along the [010] and [001] direction, respectively (Fig. 3).

4. Conclusion

The results obtained in this study verify the state-of-the-art view on the reduction of rhenates(VII) with gaseous hydrogen chloride. It has been proved that the reaction is possible and that hydrogen chloride may act there not only as the complexing agent. but also as the reducing agent. One of the products formed is pentachloridooxidorhenate(VI) anion. A series of phosphonium salts with this anion was obtained and investigated using X-ray diffraction. The obtained data sets were analyzed. Three crystals were chosen to obtain pentachloridooxidorhenate(VI) anions geometrical parameters not affected by such phenomena as disorder or co-crystallization of other rhenium complexes. A comparison of the obtained data with the analogous data reported previously [17] for the pentachloridooxidorhenate(V) anion allowed to draw the following conclusion. Upon going over from the ReOCl_5^- (d¹ system) to the ReOCl_5^{2-} (d² system) the additional d electron does not affect significantly the Re-O bond length, but mainly the Re-Cl bond lengths, above all in the Re-Cl_{cis} bonds (the Re-Cl_{trans} bond length may depend on the crystal structure packing). These results provide new insight into the Re(VI) chemistry, which is still underinvestigated due to the Re(VI) compounds instability.

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Appendix A. Supplementary material

CCDC 706455, 706456 and 706457 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. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2009.01.035.

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