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The Reaction of Re_3Br_9 with $P(CH_2OH)_3$: Diversity of Modes of Coordination of Hydroxymethylphosphine to Clusters

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Abstract—The reaction of Re_3Br_9 with $P(CH_2OH)_3$ (THP) in methanol under inert atmosphere gives a new cluster complex, $[Re_3(\mu_2\text{-}Br)_3Br_3(\mu_3\text{-}P,O,O\text{-}P(CH_2OH)(CH_2O)_2)_2H] \cdot 0.8H_2O \cdot 1.6MeOH$ (**I**). With access of air, the reaction produces a different product, $[\{Re_3(\mu_2\text{-}Br)_3Br_2(OCH_2)_2PCH_2\text{-}OP(CH_2OH)_2\}_2\text{-}\{(P(CH_2OH)(CH_2O)_2)\}_2]$ (**II**), in which two triangular clusters are linked by deprotonated THP molecules as bridging ligands. In addition, each cluster is coordinated in a tetradentate fashion by the phosphine-phosphinite ligand, resulting from the oxidative condensation of two THP molecules (CIF files CCDC 1829565 (**I**) and 1829566 (**II**)).

Keywords: rhenium, clusters, phosphine complexes, hydrophilic ligands, crystal structure

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INTRODUCTION

The preparation of stable water-soluble (hydrophilic) transition metal complexes to be used in catalysis, biology, and medicine is a relevant task of modern preparative coordination chemistry [1–6]. This is commonly done using phosphine ligands containing hydroxyl or sulfonate groups in organic substituents [1, 7]. In particular, tris(hydroxymethyl)phosphine forms stable water-soluble complexes with Pd, Pt, Rh, Re, Ru, and Ir [8–12]. These complexes could be applied as therapeutic and diagnostic agents and as green chemistry catalysts [13–17]. Tris(hydroxymethyl)phosphine (THP) and its analogues can be coordinated to molybdenum, platinum, nickel, cobalt, iron, and rhodium chalcogenide clusters [18–26]. Of particular interest is the synthesis of THP complexes of rhenium, in view of the exceptionally abundant coordination and cluster chemistry of rhenium in a wide range of oxidation states. Catalysts based on Re and Re compounds (including clusters) are active in various reactions such as glycerol hydrogenolysis, reduction of dicarboxylic acids to diols, transformations involving CH_nCO_2H moieties, thioester macrocyclization, alkane hydrogenolysis, etc. [27–35].

Of interest in rhenium chemistry are triangular $\{Re_3\}$ clusters with a rhenium–rhenium double bond, including the Re_3X_9 trihalides (X = Cl, Br, I) and their derivatives. They have played an important historical role in the formation of the views on metal– metal multiple bonds and can be involved in a variety of chemical transformations. Complexes with phosphines and arsines, $[Re_3X_9(PR_3)_3]$ (X = Cl, Br; PR_3 = PMe_3, PMe_2Ph, $PMePh_2$, PEt_2Ph, $PEtPh_2$, PPh_3, $AsPh_3$), $[Re_3Cl_9L_{1.5}]$ and $[Re_3Cl_9(\eta^1\text{-}L)_3]$ (L = bidentate diphosphines), which are readily formed from Re_3X_9 and the appropriate ligands, have been studied rather comprehensively [36–41]. It appeared reasonable to expand the range of these compounds by coordination of $P(CH_2OH)_3$.

This paper describes two products of reaction between THP and Re_3Br_9, that is, the trinuclear cluster $[Re_3(\mu_2\text{-}Br)_3Br_3(\mu_3\text{-}P,O,O\text{-}P(CH_2OH)(CH_2O)_2)_2H] \cdot 0.8H_2O \cdot 1.6CH_3OH$ (**I**) and the “dimer” composed of two triangular clusters $[\{Re_3(\mu_2\text{-}Br)_3Br_2(\mu_4\text{-}P,P,O,O\text{-}(OCH_2)_2PCH_2OP(CH_2OH)_2\}_2\{\mu_2\text{-}P,O\text{-}(P(CH_2OH)(CH_2O)_2)\}_2]$ (**II**), which contains a rare phosphine-phosphinite ligand $(HOCH_2)_2PCH_2OP(CH_2OH)_2$.

EXPERIMENTAL

The compound Re_3Br_9 was synthesized by a published procedure [42]. The other reagents were commercial chemicals used as received. Methanol was purified by distillation over magnesium. Elemental analysis was performed using a Toshiba TM2000 microscope and a vario MICRO cube CHNS analyzer. $^{31}P\{^1H\}$ NMR spectra were recorded on a BrukerAvance 500 spectrometer at room temperature relative to 85% H_3PO_4 as an external standard. Electrospray ionization mass spectra were run on a Quattro LC (Micromass, Manchester, UK). Nitrogen was used as a drying and working gas at flow rates of 400 and 80 mL/h, respectively. The sample solutions were injected through a syringe pump at a rate of 6 μL/min. The capillary voltage was 3.5 kV and the voltage in the chamber was varied from –10 to –60 V. The composition of each peak was determined by comparing the calculated and experimental isotopic distributions using the MassLynx 3.5 software.

Synthesis of I. A weighed portion of Re_3Br_9 (0.67 g, 0.52 mmol) was placed into a Schlenk flask and dissolved in methanol (10 mL). The flask was degassed and filled with argon. Solid THP (0.40 g, 3.23 mmol) was added to the resulting solution, which was then magnetically stirred under argon for 2 weeks. The solution color gradually changed to dark green. The solution was concentrated under vacuum and left for crystallization. After 2 weeks, the precipitated brown crystals were decanted from the mother liquor and washed with cold diethyl ether. The yield was 0.17 g (25%).

For $C_{7.6}H_{23}O_{8.4}P_2Br_6Re_3$

Anal. calcd., %	C. 6.78	H, 1.72	Br, 35.54	Re, 41.41
Found, %	C, 6.21	H, 1.57	Br, 36.08	Re, 42.06

Electrospray mass spectrum (*m/z*): 1281.1 (M^+). $^{31}P\{^1H\}$ NMR (CD_3OD; δ, ppm): 36.8.

Synthesis of II. A weighed portion of Re_3Br_9 (0.10 g, 78.3 μmol) was placed into a Schlenk flask and dissolved in methanol (5 mL) The flask was degassed and filled with argon. Solid THP (0.06 g, 4.70 mmol) was added to the resulting solution, which was then magnetically stirred under argon for 2 weeks. The solution color gradually changed to dark green. The solution was concentrated under vacuum and transferred in air into an NMR tube (4 mm inner diameter). The tube was closed with a lid and left for crystallization. After 4 weeks, the precipitated green crystals were separated from the mother liquor and washed with diethyl ether. The yield was 0.01 g (11%).

For $C_{16}H_{40}O_{16}P_6Br_{10}Re_6$

Anal. calcd., %	C, 7.41	H, 1.56	Br, 30.84	Re, 43.12
Found, %	C, 7.49	H, 1.53	Br, 30.42	Re, 42.74

X-ray diffraction. The sets of reflections were obtained on New Xcalibur (Agilent Technologies) (**I**, 130 K) and Bruker X8 Apex (**II**, 100 K) instruments (MoK_α radiation, λ = 0.71073 Å, φ- and ω-scan mode, 0.5° for narrow frames. The absorption corrections were applied empirically by the SADABS [43] and SCALE3 ABSPACK programs (CrysAlisPro, Agilent Technologies, Version 1.171.37.35 (issued on August 13, 2014, CrysAlis 171.NET)). The structures were solved by the direct method and refined by the full-matrix least-squares method on $|F|^2$ in the anisotropic approximation (SHELX 2014/7, ShelXle) [44, 45]. The CH_2 and OH hydrogen atoms in **I** were fixed in the calculated positions. The hydroxyl H atoms of **II** were added to the composition of compounds calculated from X-ray diffraction data. Crystallographic data and refinement details for **I** and **II** are summarized in Table 1 and selected bond lengths for **I** and **II** are given in Table 2.

Atomic coordinates and other structure parameters are deposited with the Cambridge Crystallographic Data Centre (CCDC 1829565 (**I**) and 1829566 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

On treatment of Re_3Br_9 with $P(CH_2OH)_3$ in methanol away from air, slow reaction takes place (for 2 weeks), with the solution color changing from dark orange to dark green. This is accompanied by a decrease in the intensity of the initial THP signal (δ = –24.3 ppm) in the ^{31}P NMR spectrum and simultaneous appearance of a signal at +36.8 ppm corresponding to coordinated THP. Crystallization gives brown single crystals of compound **I** with the composition $[Re_3(\mu_2\text{-}Br)_3Br_3(\mu_3\text{-}P,O,O\text{-}P(CH_2OH)(CH_2O)_2)_2H] \cdot 0.8H_2O \cdot 1.6MeOH$ (X-ray diffraction and elemental analysis data). Methanol solutions of **I** produce the same NMR signal as the reaction mixture, that is, a single peak at 36.8 ppm. Thus, even at a high molar excess of THP (cluster to ligand ratio of 1 : 6), the reaction gives product **I** in which only two THP ligands are coordinated to the cluster core. The structure of **I** is composed of neutral triangular clusters $[Re_3(\mu_2\text{-}Br)_3Br_3(\mu_3\text{-}P(CH_2OH)(CH_2O)_2)_2H]$ (Fig. 1a) containing the $\{Re_3(\mu_2\text{-}Br)_3\}^{6+}$ core with rhenium atoms forming three equivalent Re=Re double bonds (2.45–2.48 Å). Each rhenium atom forms a pentagonal (with inclusion of metal–metal bonds) or trigonal (without these bonds) bipyramid as the coordination polyhedron. Apart from two rhenium atoms, the metal coordination sphere contains two bridging and one terminal bromine atom as equatorial ligands and either two oxygen atoms (Re(2)) or one oxygen and one phosphorus atom (Re(1) pair) as apical ligands. The Re(1) atoms in the cluster are connected by a twofold rotation axis that passes through the Br(4), Re(2), and Br(2) atoms. The Re–(μ_2-Br), Re–Br, Re–P, and Re–O bond lengths (2.53, 2.58–2.67, 2.36, and 1.99–2.13 Å, respectively) are close to those observed for other phosphine complexes [36–41]. The product stoichiometry (the absence of an anion) requires charge neutralization by means of deprotonation of three coordination hydroxyl groups of the THP ligands. In all probability, the proton is located at one of the oxygen atoms corresponding to longer bonds (Re(1)–O(2), 2.128(11) Å). Shorter distances (Re(2)–

Table 1. Key crystallographic data and refinement parameters for compounds **I** and **II***

Parameter	Value	
	I	**II**
M	1348.86	2590.60
System; space group	Tetragonal; $I4_1/acd$	Monoclinic; $C2/c$
a, Å	17.7135(5)	10.1233(4)
b, Å	17.7135(5)	16.0065(7)
c, Å	33.5816(12)	28.0801(14)
β, deg	90	98.072(2)
V, Å^3	10536.8(7)	4505.0(3)
Z	16	4
μ, mm^{-1}	23.00	25.20
Crystal size, mm	0.22 × 0.06 × 0.06	0.15 × 0.10 × 0.06
Absorption correction	Multiscan CrysAlisPRO 1.171.38.41 (Rigaku Oxford Diffraction, 2015). Empirical, using spherical harmonics, according to the SCALE3 ABSPACK algorithm	Multiscan SADABS (Bruker-AXS, 2004)
$T_{\min}$, $T_{\max}$	0.232, 1.000	0.544, 0.723
Number of measured/unique/observed reflections with $I > 2\sigma(I)$	14231/3346/1750	18023/5159/4163
R_{int}	0.086	0.050
Ranges of θ, deg	3.8–29.7	2.4–27.5
$(\sin\theta/\lambda)_{\max}$, Å^{-1}	0.697	0.649
Limits of h, k, l	$-17 \le h \le 22$, $-24 \le k \le 16$, $-44 \le l \le 46$	$-10 \le h \le 13$, $-20 \le k \le 20$, $-36 \le l \le 36$
$R(F^2 > 2\sigma(F^2))$, $wR(F^2)$; S	0.060, 0.139; 1.01	0.039, 0.088; 1.02
Number of reflections/refined parameters/constraints	3346/122/6	5159/244/0
Weighing scheme	$w = 1/[\sigma^2(F_o^2) + (0.053P)^2 + 211.8261P]$, $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0288P)^2 + 154.836P]$, $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{\max}/\Delta\rho_{\min}$, e Å^{-3}	5.22/–3.37	2.32/–1.35

* The following software was used: CrysAlisPro 1.171.38.41 (Rigaku OD, 2015), APEX2 (Bruker-AXS, 2004), SAINT (Bruker-AXS, 2004), SHELXS2014 (Sheldrick, 2014), SHELXL2014 (Sheldrick, 2014), ShelXle (Hübschle, 2011), CIFTAB-2014 (Sheldrick, 2014).

O(1), 1.984(10) Å) are found in the case of deprotonated hydroxymethyl group. The full crystal structure of **I** is determined by packing of the cluster and water and methanol of crystallization molecules, which are hydrogen-bonded. The solvate molecules occupy channels stretched along the [001] crystallographic direction (Fig. 2).

A different product was isolated upon the reaction in air. On slow crystallization (1 month) of an aerated solution containing the initially formed complex **I**, green-colored single crystals of **II** were formed. According to X-ray diffraction data, the structure of this product is described as $[\{Re_3(\mu_2\text{-}Br)_3Br_2(\mu_4\text{-}P,P,O,O\text{-}(OCH_2)_2PCH_2OP(CH_2OH)_2)_2\}_2\{\mu_2\text{-}P,O\text{-}$

$(P(CH_2OH)(CH_2O)_2)\}_2]$ (Fig. 1b). The hexanuclear molecular complex **II** is composed of two $\{Re_3(\mu_2\text{-}Br)_3(P,P\text{-}PCH_2OP)\}$ cluster cores ($(P,P\text{-}PCH_2OP)^{2-}$ = $((OCH_2)_2PCH_2OP(CH_2OH)_2)^{2-}$), which are linked by two deprotonated THP ligands to form dimers. Each rhenium atom in the $\{Re_3(\mu_2\text{-}Br)_3\}$ triangular cluster core is linked to the other two Re atoms by short Re=Re double bonds (2.48–2.53 Å) and by bridging bromine atoms located in the metal core plane ($Re–(\mu_2\text{-}Br)$ = 2.53–2.56 Å). The remaining three coordination sites are occupied by terminal bromine atoms and also phosphorus and oxygen atoms. Two triangular $\{Re_3(\mu_2\text{-}Br)_3\}^{6+}$ clusters are connected by a pair of deprotonated THP ligands via the Re(3) atoms, thus forming the $\{(O)_2Re–(\mu_2\text{-}O)_2–Re(O)_2\}$ structural motif ($Re–(\mu_2\text{-}O)$, 2.05–2.20 Å). The Re(3) coordination polyhedron can be described as $\{ReO_3Br_2\}$. The Re(2) atom is coordinated to bromine (Re–Br 2.55 Å) and to both phosphorus atoms (phosphinite and phosphine ones) by the deprotonated bidentate ligand $((OCH_2)_2PCH_2OP(CH_2OH)_2)^{2-}$. The Re–P distance is markedly longer for the phosphinite atom than for the phosphine atom (2.48 and 2.34 Å, respectively), which is attributable to weaker donor properties of the phosphinite type phosphorus. Thus, the Re(2) coordination polyhedron is described as $ReBr_3P_2$. The Re(1) atom is coordinated by the THP phosphorus atom and the alkoxide oxygen atom of the deprotonated OCH_2 group (in the axial positions) (Re(1)–P, 2.41; Re(1)–O, 2.03 Å) and by the bromine atom in the equatorial position (Re(1)–Br 2.61 Å). All these distances are typical of Re_3Br_9 complexes [36–41]. The molecule of hexanuclear complex **II** is electrically neutral, with the charge of two cluster cores being counterbalanced by deprotonation of the $–CH_2OH$ hydroxyl groups. Note that deprotonation of the $(HOCH_2)_2PCH_2OP(CH_2OH)_2$ ligand was observed for the first time, although reversible deprotonation of structurally similar $(HOCH_2)_2PCH_2CH_2P(CH_2OH)_2$ ligand have been reported [19]. In the crystal structure, the cluster molecules form wriggling chains via weak H···Br hydrogen bonds (Fig. 3).

Table 2. Selected interatomic distances (Å) for **I** and **II***

Bond	*d*, Å	Bond	*d*, Å
		I	
Br(1)–Re(1)	2.5802(16)	Br(4)–Re(2)	2.665(2)
Br(2)–Re(1)	2.5265(19)	O(1)–Re(2)	1.984(10)
$Br(2)–Re(1)^{i}$	2.5265(19)	O(2)–Re(1)	2.128(11)
$Br(3)–Re(1)^{i}$	2.5302(16)	$P(1)–Re(1)^{i}$	2.365(4)
Br(3)–Re(2)	2.5086(14)		
Angle	ω, deg	Angle	ω, deg
		II	
Re(1)–Br(4)	2.5392(10)	Re(1)–O(1)	2.035(7)
Re(1)–Br(5)	2.5289(11)	Re(3)–O(2)	1.956(6)
Re(1)–Br(7)	2.6135(12)	Re(3)–O(4)	2.053(6)
Re(2)–Br(5)	2.5300(11)	$Re(3)–O(4)^{ii}$	2.205(7)
Re(2)–Br(6)	2.5547(11)	Re(1)–P(3)	2.409(3)
Re(2)–Br(8)	2.5496(11)	Re(2)–P(1)	2.339(3)
Re(3)–Br(4)	2.5385(10)	Re(2)–P(2)	2.477(3)
Re(3)–Br(6)	2.5325(10)		

* The coordinates of dependent atoms were obtained using symmetry codes: ^{i} $y - 1/4, x + 1/4, -z + 5/4$ (**I**); ^{ii} $-x + 2, -y + 2, -z + 1$ (**II**).

The bidentate phosphine-phosphinite $(HOCH_2)_2PCH_2OP(CH_2OH)_2$ ligand could have resulted from condensation of two $P(CH_2OH)_3$ molecules. Unfortunately, low solubility of **II** in common solvents precludes the use of ^{31}P NMR spectroscopy and mass spectrometry for detailed investigation of the formation of this ligand. We can only assume a mechanism of its formation by analogy with the mechanisms we described previously for $[Ni_3S_2((HOCH_2)_2PCH_2OP(CH_2OH)_2)_3]$ [25]. Oxygen is required for one of the key steps, in particular, (2):

$$HOCH_2P(CH_2OH)_2 = HP(CH_2OH)_2 + CH_2O, \quad (1)$$

$$2HP(CH_2OH)_2 + O_2 = 2HOP(CH_2OH)_2, \quad (2)$$

$$\begin{aligned} &HOP(CH_2OH)_2 + HOCH_2P(CH_2OH)_2 \\ &= (HOCH_2)_2PCH_2OP(CH_2OH)_2 + H_2O. \end{aligned} \quad (3)$$

It is also known that the reaction of $MCl_2(P(CH_2OH)_3)_2]$ (M = Pd, Pt) with excess THP affords $[M\{(CH_2OH)_2PCH_2OP(CH_2OH)_2\}_2]^{2+}$, but attempts to isolate the free ligand from these complexes induce its decomposition into $P(CH_2OH)_3$ and $HP(O)(CH_2OH)_2$ [46]. Other examples of THP condensation are also known [47].

Thus, we demonstrated that the reaction of Re_3Br_9 with tris(hydromethyl)phosphine, unlike the reaction with nonfunctionalized phosphines, does not afford the expected $[Re_3Br_9(THP)_3]$ complex. The differences are caused, first, by the involvement of the THP

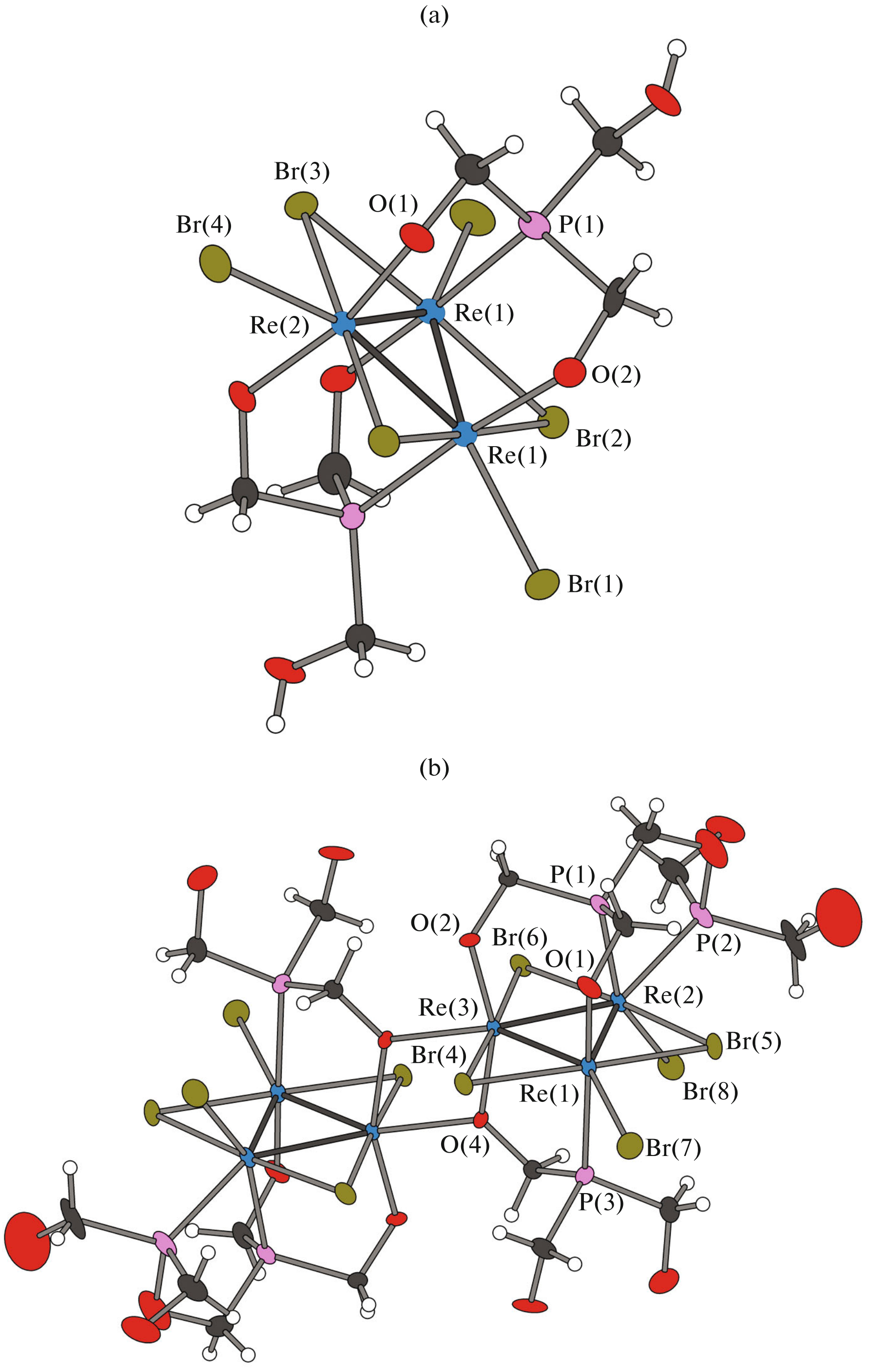

Fig. 1. Structures of (a) $[\mathrm{Re_3(\mu_2\text{-}Br)_3((P(CH_2O)_2(CH_2OH))_2H]}$ in **I** and (b) $[\{\mathrm{Re_3(\mu_2\text{-}Br)_3Br_2(\mu_4\text{-}P,P,O,O\text{-}(OCH_2)_2PCH_2OP\text{-}(CH_2OH)_2)_2}\}_2\{\mathrm{\mu_2\text{-}P,O\text{-}(P(CH_2OH)(CH_2O)_2)}\}_2]$ in **II**.

hydroxy groups in coordination and, second, by the oxidative condensation of two THP molecules. A typical feature of the coordination of both hydromethylphosphine ligands (THP and the product of its condensation) is the tendency to form five-membered rings via the (P,O)-bridging function of the ligand towards the rhenium–rhenium bond.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

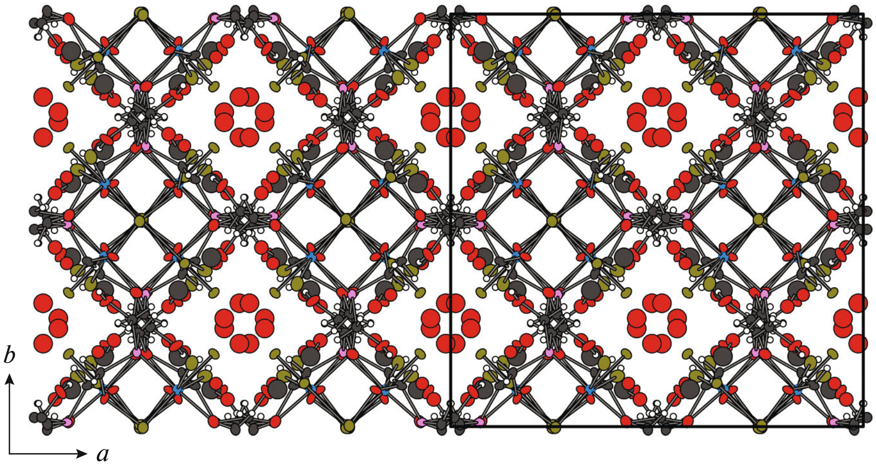

Fig. 2. Channels along the [001] crystallographic direction in structure **I**.

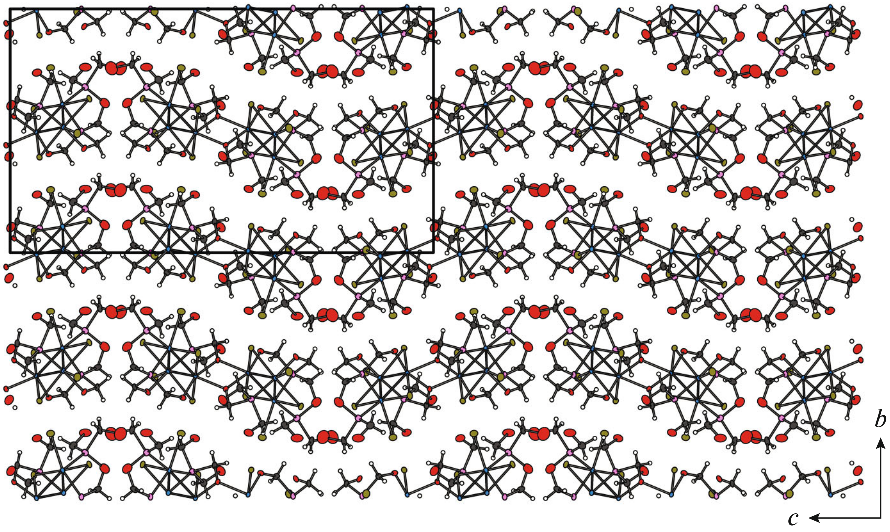

Fig. 3. Packing of molecules in the crystal structure of **II**.

AUTHOR CONTRIBUTIONS

M.N. Sokolov (Head of the Project) put forward the idea and discussed the results; A.V. Anyushin (principal investigator) conducted experiments. P.A. Abramov performed X-ray diffraction analysis. M.N. Sokolov and A.V. Anyushin co-wrote the paper.

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