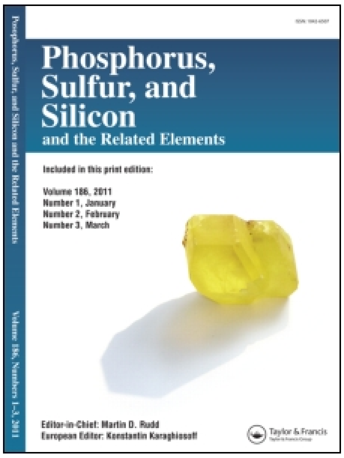

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

DEOXYGENATION OF COORDINATED SULFOXIDES AND OXIDATION OF THE METAL ION IN THE Pt(II) COMPLEXES USING HX (X = C1, Br): A CONVENIENT PROCEDURE FOR THE PREPARATION OF THIOETHER COMPOUNDS OF Pt(IV). X-RAY STRUCTURE OF POTASSIUM TRICHLORO(DIETHYL SULFOXIDE)PLATINATE(II)

Vadim Yu. Kukushkin[a]; Vitalii K. Belsky[b]; Vadim E. Konovalov[b]; Elena A. Aleksandrova[c]; Elena Yu. Pankova[c]; Anatolii I. Moiseev[c]
[a] Department of Chemistry, St. Petersburg State University, Stary Petergof, Russia [b] L. Ya. Karpov Physico-Chemical Institute, Moscow, Russia [c] Inorganic Chemistry, Lensovet Technological Institute, St. Petersburg, Russia

To cite this Article Kukushkin, Vadim Yu. , Belsky, Vitalii K. , Konovalov, Vadim E. , Aleksandrova, Elena A. , Pankova, Elena Yu. and Moiseev, Anatolii I.(1992) 'DEOXYGENATION OF COORDINATED SULFOXIDES AND OXIDATION OF THE METAL ION IN THE Pt(II) COMPLEXES USING HX (X = C1, Br): A CONVENIENT PROCEDURE FOR THE PREPARATION OF THIOETHER COMPOUNDS OF Pt(IV). X-RAY STRUCTURE OF POTASSIUM TRICHLORO(DIETHYL SULFOXIDE)PLATINATE(II)', Phosphorus, Sulfur, and Silicon and the Related Elements, 69: 1, 103 — 117

To link to this Article: DOI: 10.1080/10426509208036859
URL: http://dx.doi.org/10.1080/10426509208036859

Phosphorus, Sulfur, and Silicon, 1992, Vol. 69, pp. 103–117
Reprints available directly from the publisher
Photocopying permitted by license only

DEOXYGENATION OF COORDINATED SULFOXIDES AND OXIDATION OF THE METAL ION IN THE Pt(II) COMPLEXES USING HX (X = Cl, Br): A CONVENIENT PROCEDURE FOR THE PREPARATION OF THIOETHER COMPOUNDS OF Pt(IV). X-RAY STRUCTURE OF POTASSIUM TRICHLORO(DIETHYL SULFOXIDE)PLATINATE(II)

VADIM YU. KUKUSHKIN,*[a] VITALII K. BELSKY,[b]
VADIM E. KONOVALOV,[b] ELENA A. ALEKSANDROVA,[c]
ELENA YU. PANKOVA[c] and ANATOLII I. MOISEEV[c]

[a]*Department of Chemistry, St. Petersburg State University, Universitetsky Pr. 2, 198904 Stary Petergof, Russia;* [b]*L. Ya. Karpov Physico-Chemical Institute, Obukha St. 10, 103064 Moscow, Russia;* [c]*Inorganic Chemistry, Lensovet Technological Institute, Zagorodny Pr. 49, 198013, St. Petersburg, Russia*

(Received April 10, 1991; in final form January 9, 1992)

The complexes $Q[Pt(R_2SO)X_3]$ (Q = K, Et_4N; R = Me, Et, n-Pr, iso-C_5H_{11}, CH_2Ph; X = Cl, Br in certain combinations) were prepared following a known technique via the interaction between $K_2[PtX_4]$ and R_2SO in water and a) as a result of the reaction of $K_2[PtCl_4]$ and R_2SO in a mixture of H_2O-MeCN followed by the addition $(Et_4N)Cl$; b) splitting reaction of the bridge-type compound $(Et_4N)_2[Pt_2(\mu\text{-}Cl)_2Cl_4]$ using an adequate sulfoxide, and c) the reaction of cis-$[Pt(R_2SO)_2Cl_2]$ with $(Et_4N)Cl$ in MeCN, $MeNO_2$ or DMF media.

The complex $K[Pt(Et_2SO)Cl_3]$ was characterized by the X-ray structure analysis. This compound crystallizes in a monoclinic space group P $2_1/a$. The unit cell dimensions are: a = 8.753(8), b = 8.828(8), c = 17.412(5) Å, γ = 122.94(5)°, V = 1129(1) Å^3, ρ calc = 2.63 g cm^{-3}, Z = 4.

The reaction of $(Et_4N)[Pt(R_2SO)X_3]$ or cis-$[Pt(Me_2SO)_2Cl_2]$ with HX (X = Cl, Br) leads to sulfoxide deoxygenation and oxidation of Pt(II) into Pt(IV); the complexes of the $[Pt(R_2S)X_5]^-$ and $[Pt(R_2S)_2X_4]$ types are formed in a good yield. In the case of the complexes with (iso-$C_5H_{11})_2SO$ this reaction results in $(Et_4N)_2[PtCl_6]$ and free (iso-$C_5H_{11})_2S$. The arguments of the Pt(II) assisted deoxygenation path of coordinated sulfoxides are presented.

Key words: Deoxygenation of sulfoxides; synthesis of Pt(II) sulfoxide complexes; synthesis of Pt(IV) thioether complexes; alkyl sulfoxides; synthesis of thioethers; X-ray structure.

INTRODUCTION

Deoxygenation process of *free* sulfoxides, R_2SO, resulting in the formation of thioethers, R_2S, were reported in detail (see the book in Reference 1 and reviews in References 2–5). However, there is a few published data about deoxygenation of *coordinated* sulfoxides.[6] Earlier the reduction reactions of R_2SO molecules coordinated to the Pt(II) ion by CO,[7] $SOCl_2$,[8] and reagent systems of PCl_5/ROH type[9,10] were studied. The processes of the transformation of sulfoxides into thioethers are studied in the present paper. The deoxygenation of coordinated sulfoxides

---

*The author to whom correspondence should be addressed.

is of interest in the context of the coordinated ligands reactions. The reduction processes of the R_2SO inner-sphere molecules can be of preparative importance for the synthesis of compounds containing thioethers, R_2S. A brief account on these results has been already published.[11]

EXPERIMENTAL

Infrared spectra were recorded on a Perkin-Elmer model 983G spectrometer in KBr pellets. ^1H NMR spectra were run using Bruker model HX-270 and Tesla model BS 497 instruments. The molar conductivity was measured on a Impuls model KL2 conductometer at 20°C and complexes concentrations about 10^{-3} mol/l. R_f values on TLC were determined on a SiO_2 plates Silufol UV 254. Melting points were measured on the Kofler table and are uncorrected. The elemental analysis was made at the Analytical Chemistry, St. Petersburg State University. Tables I–IV show conditions under which the X-ray structure analysis was performed, atomic parameters and temperature factors, bond lengths and bond angles, respectively.

Preparation of the Complexes

Synthesis of $(Et_4N)[Pt(R_2SO)Cl_3]$ (R = Me, Et, n-Pr, iso-C_5H_{11}, CH_2Ph)

To $K_2[PtCl_4]$ (1.00 g, 2.41 mmol) solution in water (20 ml) R_2SO (2.56 mmol) in acetonitrile (20 ml) was added and the obtained solution was boiled in an open

TABLE I

Crystal data for $K[Pt(Et_2SO)Cl_3]$

crystal system	monoclinic
space group	P 2_1/a
a, Å	8.753(8)
b, Å	8.828(8)
c, Å	17.412(5)
γ, deg.	122.94(5)
V, Å^3	1129(1)
Z	4
F(000)	824
ρ_{calc}, g cm^{-3}	2.63
μ, cm^{-1}	142.6
cryst. size, mm	0.30 × 0.04 × 0.14
cryst. faces	100, 010, 001
diffractometer	Nicolet P3
radiation	λ MoK_α(λ = 0.71069 Å)
filter	β
2θ max, deg.	50
temperature, K	293
number of reflections with $I \geq 3\sigma(I)$	1247
S	0.439
R	0.029
R_w	0.029
weighting scheme	$1/\sigma^2(F) + 0.008F^2$

TABLE II

Atomic parameters ($\times 10^4$) and temperature factors ($Å^2 \times 10^3$) for $K[Pt(Et_2SO)Cl_3]$

Atom	X	Y	Z	U
Pt	2584(1)	4141(1)	2117(1)	28(1)
S	1239(3)	2469(2)	1089(1)	31(1)
Cl(1)	1580(4)	1632(3)	2871(1)	41(1)
Cl(2)	3843(3)	6734(3)	1380(1)	43(1)
Cl(3)	3830(4)	5947(3)	3206(1)	41(1)
K	2595(3)	8597(3)	2656(1)	48(1)
O	23(8)	518(7)	1195(3)	39(3)
C(1)	-66(12)	3225(11)	614(5)	41(5)
C(2)	-1403(15)	1925(12)	61(5)	49(5)
C(3)	2928(13)	2878(11)	385(5)	41(5)
C(4)	4201(15)	2439(14)	699(6)	52(5)

TABLE III

Bond lengths (Å) in the $[Pt(Et_2SO)Cl_3]^-$ ion

Pt-S	2.209(2)	Pt-Cl(1)	2.299(2)
Pt-Cl(2)	2.315(2)	Pt-Cl(3)	2.331(2)
S-O	1.463(5)	S-C(1)	1.806(12)
S-C(3)	1.799(10)	C(1)-C(2)	1.467(11)
C(3)-C(4)	1.469(19)		

TABLE IV

Bond angles (°) in the $[Pt(Et_2SO)Cl_3]^-$ ion

S-Pt-Cl(1)	91.9(1)	S-Pt-Cl(2)	90.3(1)
Cl(1)-Pt-Cl(2)	175.1(1)	S-Pt-Cl(3)	175.7(1)
Cl(1)-Pt-Cl(3)	89.2(1)	Cl(2)-Pt-Cl(3)	88.9(1)
Pt-S-O	117.9(2)	Pt-S-C(1)	109.8(3)
O-S-C(1)	106.9(4)	Pt-S-C(3)	109.7(3)
O-S-C(3)	108.3(4)	C(1)-S-C(3)	103.3(5)
S-C(1)-C(2)	114.0(8)	S-C(3)-C(4)	110.6(6)

beaker within 10 min. During this time colour of the solution changed from dark-red to yellow-orange. Tetraethylammonium chloride (0.48 g, 2.90 mmol) was added to the reaction mixture and the solvent was evaporated to dryness on boiling. The complex $(Et_4N)[Pt(R_2SO)Cl_3]$ was extracted with acetone (3 × 10 ml), filtered, and the solvent was removed in vacuo. The oily residue was washed with hexane (4 × 5 ml), 2-propanol (3 × 10 ml). Then $(Et_4N)[Pt(R_2SO)Cl_3]$ was crystallized under the 2-propanol layer. The precipitate was filtered, washed on a filter with 2-propanol (3 × 5 ml) and ether (3 × 5 ml), dried in air at 20–25°C and then in a vacuum-desiccator over P_4O_{10}. Yields of $(Et_4N)[Pt(R_2SO)Cl_3]$ = 60–80% based on Pt.

Synthesis of $(Et_4N)[Pt(Me_2SO)Cl_3]$ (via substitution of dimethyl sulfoxide in cis-$[Pt(Me_2SO)_2Cl_2]$ for the chloride ion)

Acetonitrile† (30 ml) was added to the mixture of cis-$[Pt(Me_2SO)_2Cl_2]$ (1.00 g, 3.00 mmol) and $(Et_4N)Cl$ (0.57 g, 3.45 mmol) and boiled to complete homogenization (ca. 1–2 min) and then evaporated in an open beaker to one half of the starting volume. The complex $(Et_4N)[Pt(Me_2SO)Cl_3]$ was precipitated as a paste with toluene:hexane mixture (3:1 in volume), decanted the solvent and crystallized $(Et_4N)[Pt(R_2SO)Cl_3]$ under the toluene layer. The resultant precipitate was filtered, washed on a filter with hot (60°C) toluene (3 × 5 ml), hexane (3 × 5 ml), dried in air at 20–25°C. Yield of $(Et_4N)[Pt(Me_2SO)Cl_3]$ = 1.15 g, 76% based on Pt.

The complexes $(Et_4N)[Pt(Et_2SO)Cl_3]$ and $(Et_4N)[Pt((n\text{-}Pr)_2SO)Cl_3]$ were prepared in a similar way. The complex $(Et_4N)[Pt(Me_2SO)Br_3]$ was synthesized in situ affecting cis-$[Pt(Me_2SO)_2Cl_2]$ with $(Et_4N)Br$ at reagent molar ratio of 1:4.

General Procedure for the Synthesis of the Complexes $(Et_4N)[Pt(R_2S)Cl_5]$ (R = Me, Et, n-Pr, CH_2Ph)

Gaseous HCl was bubbled through the solution of $(Et_4N)[Pt(R_2SO)Cl_3]$ (2.5 mmol) in acetonitrile (30–40 ml) within 15 min, the solvent was completely removed on boiling and 2-propanol (30 ml) was added to the residue. The precipitate was filtered, washed on a filter with 2-propanol (3 × 5 ml) and ether (3 × 5 ml), dried in air at 20–25°C. Yields of $(Et_4N)[Pt(R_2S)Cl_5]$ = 70–80% based on Pt.

Synthesis of $(Et_4N)[Pt(Me_2S)Cl_5]$ (Interaction between HCl and the Complex $(Et_4N)[Pt(Me_2SO)Cl_3]$ Generated in Situ)

The suspension of the complex cis-$[Pt(Me_2SO)_2Cl_2]$ (1.06 g, 2.5 mmol) and tetraethylammonium chloride (0.50 g, 3.0 mmol) in acetonitrile (10 ml) was boiled (ca. 3 min) to the formation of a transparent yellow solution. The mixture was cooled, filtered from minor admixtures, and HCl (2 ml; ρ 1.18 g cm^{-3}) was added to filtrate and boiled within 3 min. After cooling ethanol (40 ml) was added, precipitate was filtered. The filtrate was evaporated by 2/3, cooled and the second batch of the product was filtered together with the first one. The precipitate was

---

†Nitromethane or DMF can be used as a solvent for the synthesis.

washed on a filter with ethanol (3 × 0.5 ml) and hexane (3 × 5 ml). Dried in air at 90°C. Yield of $(Et_4N)[Pt(Me_2S)Cl_5]$ = 1.07 g, 76% based on Pt.

One Pot Synthesis of the Complex $(Et_4N)[Pt((PhCH_2)_2S)Cl_5]$

Dibenzyl sulfoxide (0.74 g, 3.21 mmol) in acetonitrile (30 ml) was added to the solution of $K_2[PtCl_4]$ (1.27 g, 3.06 mmol) in water (20 ml), boiled within 10 min and $(Et_4N)Cl$ (0.61 g, 3.68 mmol) in acetonitrile (15 ml) was added. The mixture was boiled for another 5 min, cooled, filtered from microcontaminants. The filtrate was evaporated to dryness and $(Et_4N)[Pt((PhCH_2)_2SO)Cl_3]$ was extracted with acetone (2 × 10 ml) and the solution was filtered. HCl (3 ml; ρ 1.18 g cm^{-3}) was added to the filtrate and boiled to evaporation of the main mass of the solvent. 50 ml of 2-propanol/acetonitrile mixture (1:1 by volume) was added to the residue and filtered from the undissolved part. The filtrate was evaporated by 4/5 and desired product was precipitated by adding hexane (50 ml). After decantation of the solvent the precipitate was washed in a beaker with hot (60°C) toluene (10 × 3 ml), filtered and washed on a filter with hot toluene (2 × 3 ml) and hexane (3 × 3 ml). Dried in air at 20–25°C. Yield of $(Et_4N)[Pt((PhCH_2)_2S)Cl_5]$ = 0.83 g, 38% based on Pt.

Synthesis of Trans-$[Pt(Me_2S)_2Br_4]$ (Deoxygenation of Me_2SO, Oxidation of Pt(II) and Substitution of Cl^- for Br^-)

Hydrobromic acid (10 ml; ρ 1.36 g cm^{-3}) was added to the complex cis-$[Pt(Me_2SO)_2Cl_2]$ (0.97 g, 2.30 mmol). After homogenization the reaction mixture was boiled on stirring within 10 min and cooled. The precipitate was filtered, washed on a filter with water (3 × 5 ml), ethanol (3 × 5 ml) and ether (3 × 5 ml). Dried in air at 20–25°C. Yield of trans-$[Pt(Me_2S)_2Br_4]$ = 0.84 g, 57% based on Pt.

Synthesis of $(Et_4N)[Pt(Me_2S)Br_5]$ Proceeding from $(Et_4N)[Pt(Me_2SO)Br_3]$ Prepared in Situ

Suspension of the complex cis-$[Pt(Me_2SO)_2Cl_2]$ (1.99 g, 4.7 mmol) and tetraethylammonium bromide (3.97 g, 18.9 mmol) in acetonitrile (10 ml) was heated to boiling (when the mixture homogenized and acquired bright-orange colour) and evaporated the solvent to dryness. The prepared complex $(Et_4N)[Pt(Me_2SO)Br_3]$ was extracted with boiling acetone (2 × 10 ml), filtered and HBr (2 ml; ρ 1.36 g cm^{-3}) was added to the filtrate cooled to 20–25°C. The precipitation of the desired product crystals terminated in 30 min. Ethanol (30 ml) was added to the mixture and precipitate was filtered. The filtrate was evaporated on boiling of the solvent to the beginning of crystallization, cooled and the second batch of the product was filtered together with the first one. The residue was washed on a filter with hot (60°C) toluene (3 × 5 ml), hexane (3 × 5 ml). Dried in air at 20–25°C. Yield of $(Et_4N)[Pt(Me_2S)Br_5]$ = 2.46 g, 66% based on Pt.

Synthesis of $(Et_4N)[Pt(Me_2S)Cl_5]$ via substitution of Me_2S in trans-$[Pt(Me_2S)_2Cl_4]$

The complex trans-$[Pt(Me_2S)_2Cl_4]$ (0.46 g, 1.0 mmol) was suspended in 10–15 ml of nitromethane (acetonitrile or acetone can be used as a solvent for the synthesis), $(Et_4N)Cl$ (0.20 g, 1.2 mmol) was added, and a mixture was heated at 80–90°C on stirring to complete conversion of trans-$[Pt(Me_2S)_2Cl_4]$ (progress of the reaction was monitored using TLC technique). After completion of the reaction the solvent was removed in vacuo and residue was recrystallized from acetonitrile-ethanol mixture. Yield of $(Et_4N)[Pt(Me_2S)Cl_5]$ = 0.50 g, 89% based on Pt. The complex $(Me_4N)[Pt(Me_2S)Cl_5]$ was prepared in a similar way (yield 93% based on Pt).

RESULTS AND DISCUSSION

Synthesis of the Starting Sulfoxide Compounds

A series of complexes $(Et_4N)[Pt(R_2SO)X_3]$ (R = Me, Et, n-Pr, iso-C_5H_{11}, CH_2Ph, X = Cl; R = Me, X = Br) as a well known compound cis-$[Pt(Me_2SO)_2Cl_2]$[12–15] were chosen for the study. The fact that most complexes are soluble both in water and in aprotic polar solvents is a peculiar feature of $(Et_4N)[Pt(R_2SO)X_3]$ complexes. Therefore, they are convenient when reactions are studied both in water and nonaqueous homogeneous liquid media.

The first monosulfoxide complexes $K[Pt(Me_2SO)X_3]$ were prepared via the interaction of $K_2[PtX_4]$ and dimethyl sulfoxide in water at a reagent molar ratio of 1:1.[12,16,17] Then, using a slightly modified technique the other dialkyl sulfoxide complexes $K[Pt(R_2SO)Cl_3]$ (R = Et,[18] n-Pr,[19] iso-Pr,[19] C_2H_4Cl,[20] 1/2 C_3H_6,[21] 1/2 C_4H_8[22]) were synthesized. The complexes Pt(II) with aryl-containing sulfoxides have not been prepared in such a way. Apparently, it can be attributed to a low solubility of these ligands in water.

Monosulfoxide complexes (including dibenzyl sulfoxide) were found to be easily formed by the interaction between $K_2[PtX_4]$ and R_2SO in water-acetonitrile mixture. The addition of MeCN becomes necessary to make R_2SO soluble. The complexes $K[Pt(R_2SO)X_3]$ resulted from the substitution can be isolated into the solid phase and identified (see as an example the complexes $K[Pt(R_2SO)X_3]$ where R = Me, Et, n-Pr, X = Cl and R = Me, X = Br; the complex $K[Pt(Et_2SO)Cl_3]$ was determined using the X-ray structure analysis).

In those cases when tetraethylammonium salts are to be prepared it is not necessary to separately isolate $K[Pt(R_2SO)X_3]$. In all the cases studied $(Et_4N)Cl$ was added to the mixture containing $K[Pt(R_2SO)X_3]$ and KX, the solvent was removed completely on boiling and the resultant complex $(Et_4N)[Pt(R_2SO)X_3]$ extracted in acetone and upon removal of Me_2CO the final products were obtained in a solid state.

The synthesis of some compounds from the series $(Et_4N)[Pt(R_2SO)Cl_3]$ was performed in a different way. For example, the complexes with Me_2SO, Et_2SO and $(n\text{-}Pr)_2SO$ were prepared from cis-$[Pt(R_2SO)_2Cl_2]$ and tetraethylammonium chloride at the reagent molar ratio of 1:1 in $MeNO_2$ or in MeCN:

$$\text{cis-}[Pt(R_2SO)_2Cl_2] + (Et_4N)Cl \rightarrow (Et_4N)[Pt(R_2SO)Cl_3] + R_2SO$$

These reactions proceed fast and in a good yield. However, the application of the method is limited due to the fact that bis-sulfoxide complexes with bulky hydrophobic ligands (for example, with $(PhCH_2)_2SO$) are fairly difficult to synthesize.

The complex $(Et_4N)[Pt((PhCH_2)_2SO)Cl_3]$ was prepared according to the following scheme:

$$\mathrm{K_2[PtCl_4]} \xrightarrow[\mathrm{(H_2O)}]{\mathrm{2\ MeCN}} \mathrm{cis\text{-}[Pt(MeCN)_2Cl_2]}$$

$$\xrightarrow[\mathrm{(MeNO_2)}]{\mathrm{(Et_4N)Cl^{23,24}}} \mathrm{(Et_4N)[Pt(MeCN)Cl_3]} \xrightarrow[\text{solid phase}]{\Delta^{25,26}}$$

$$\mathrm{1/2\ (Et_4N)_2[Pt_2(\mu\text{-}Cl)_2Cl_4]} \xrightarrow{\mathrm{(PhCH_2)_2SO}} \mathrm{(Et_4N)[Pt((PhCH_2)_2SO)Cl_3]}$$

This path is efficient for the synthesis of monosulfoxide complexes with bulky hydrophobic ligands. However, the procedure consists of four stages and is time-consuming.

Structure of $K[Pt(Et_2SO)Cl_3]$

The complex $K[Pt(Et_2SO)Cl_3]$ consists of the discrete potassium and $[Pt(Et_2SO)Cl_3]^-$ ions between which a rather strong interionic interaction is observed. Figure 1

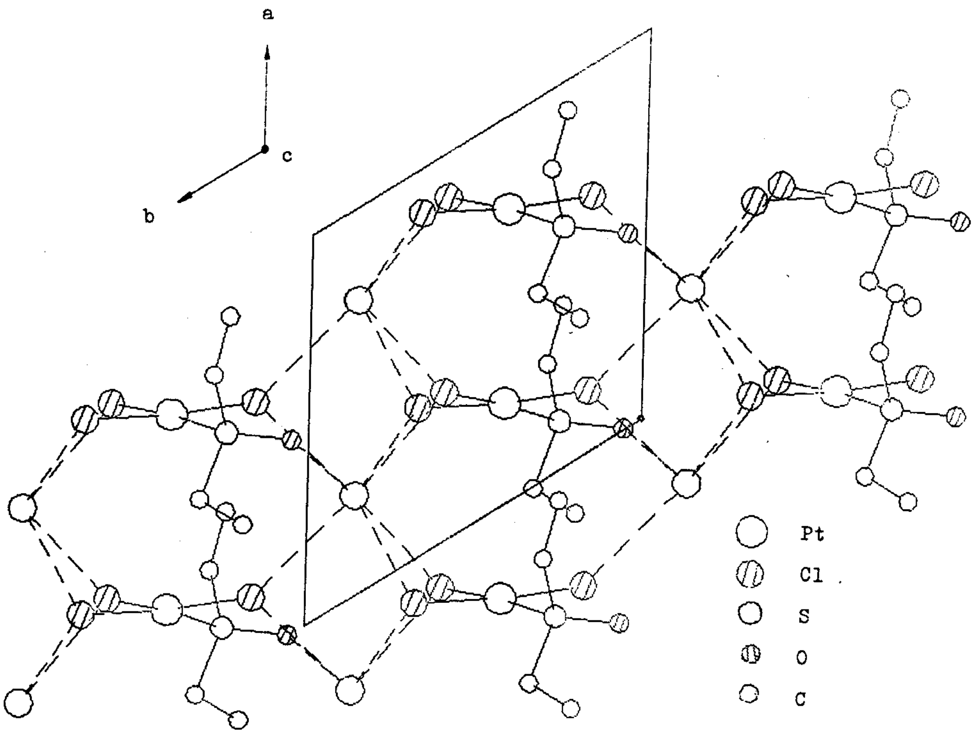

FIGURE 1 Packing diagram of $K[Pt(Et_2SO)Cl_3]$ viewed down the c axis. H atoms are omitted for clarity. Dotted lines indicate the interionic bonds.

illustrates the crystal structure of the complex and Table V shows K-Cl and K—O distances and corresponding angles.

Coordination polyhedron of the platinum atom is a distorted square-planar (Figure 2). The deviations of the Pt, S, Cl(1), Cl(2) and Cl(3) atoms from a plane passed through these atoms are −0.002, −0.086, 0.086, −0.087, −0.084 Å, respectively. The diethyl sulfoxide molecule is coordinated to Pt through the sulfur atom like in other dialkyl sulfoxide platinum complexes.[27–29] Bond lengths and bond angles in Et$_2$SO are of normal values.[27,30]

The bond Pt—Cl(3) [2.331(2) Å] is longer than the other two Pt—Cl(1) [2.299(2) Å] and Pt—Cl(2) [2.315(2) Å]. This implies that trans-influence of Et$_2$SO is higher than that in Cl$^-$ ion. Noteworthy that in a series of structurally characterized dialkyl

TABLE V
The K—Cl and K—O distances (Å) and related angles (°)

Symmetry code

Superscript			
None	x	y	z
(i)	x	1.0 + y	z
(ii)	0.5 + x	1.0 + y	0.5 − z
(iii)	−0.5 + x	y	0.5 − z

K-Cl(1)^{ii}	3.166(3)	K-Cl(3)	3.211(4)
K-Cl(1)^{i}	3.271(4)	K-Cl(3)^{iii}	3.193(3)
K-Cl(2)	3.285(4)	K-O^{ii}	2.735(5)
K-Cl(2)^{iii}	3.231(3)		

Cl(2)-K-Cl(1)^{i}	143.2(1)	Cl(2)-K-Cl(3)	60.1(1)
Cl(2)-K-Cl(1)^{ii}	73.4(1)	Cl(3)-K-Cl(1)^{i}	155.7(1)
Cl(1)^{i}-K-Cl(1)^{ii}	90.3(1)	Cl(3)-K-Cl(1)^{ii}	92.9(1)
Cl(3)-K-Cl(2)^{iii}	97.2(1)	Cl(2)-K-Cl(2)^{iii}	128.3(1)
		Cl(1)^{i}-K-Cl(2)^{iii}	72.8(1)
Cl(1)^{ii}-K--Cl(2)^{iii}	158.2(1)	Cl(2)-K-Cl(3)^{iii}	78.9(1)
Cl(3)-K-Cl(3)^{iii}	103.2(1)	Cl(1)^{i}-K-Cl(3)^{iii}	91.3(1)
Cl(1)^{ii}-K--Cl(3)^{iii}	135.0(1)	Cl(2)^{iii}-K-Cl(3)^{iii}	60.8(1)
Cl(3)-K-O^{ii}	77.1(2)	Cl(2)-K-O^{ii}	116.6(2)
Cl(1)^{ii}-K-O^{ii}	63.9(1)	Cl(1)^{i}-K-O^{ii}	82.7(2)
Cl(3)^{iii}-K-O^{ii}	160.4(2)	Cl(2)^{iii}-K-O^{ii}	99.6(1)

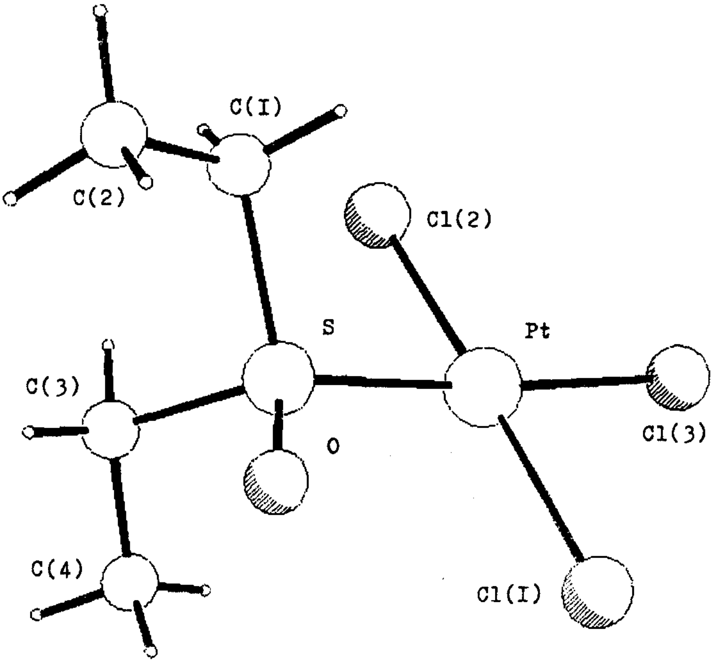

FIGURE 2 View of the $[Pt(Et_2SO)Cl_3]^-$ ion, showing the atomic numbering.

sulfoxide complexes $Q[Pt(R_2SO)Cl_3]$ (R = Me, Q = K^+,[31], $(Ph_3PCH_2Ph)^+$,[28] $[Pt(NH_3)_4]^{2+}$,[32] $[Pt(C_3H_{10}N_2)_2]^{2+}$ [33]; R = Et, Q = K) a linear relationship between Pt—S and Pt—Cl_{trans} distances as a direct correlation is observed (Figure 3).

Deoxygenation of Sulfoxides in the Pt(II) Complexes

Deoxygenation reactions of free sulfoxides are known to fairly easily proceed with participation of HX (X = Cl, Br, I) acids and in a general form these processes are described by the following equation[3]:

$$R-\overset{\overset{\displaystyle O}{\|}}{S}-R + 2\,HX \longrightarrow R-S-R + X_2 + H_2O$$

There are also examples showing that reduction with participation of HCl is valid also for coordinated molecules of R_2SO. Reference 12 shows that when suspension of $[Pt(Me_2SO)_2Cl_2]$ is kept in the aqueous HCl, $[Pt(Me_2S)_2Cl_4]$ is formed in a small amount. The reaction was mentioned to be accompanied by other reactions and the final complex of Pt(IV) becomes contaminated by by-products of transformations.

The behavior of the complexes $[Pt(amine)_2(Me_2SO)Cl]Cl$ and cis-$[Pt(Me_2SO)(C_2H_4)Cl_2]$ in $HClO_4$ and HCl aqueous solutions, respectively, is discussed in References 34 and 35. The authors of both publications stated that when pH of solutions decreases the process of dimethyl sulfoxide reduction is observed

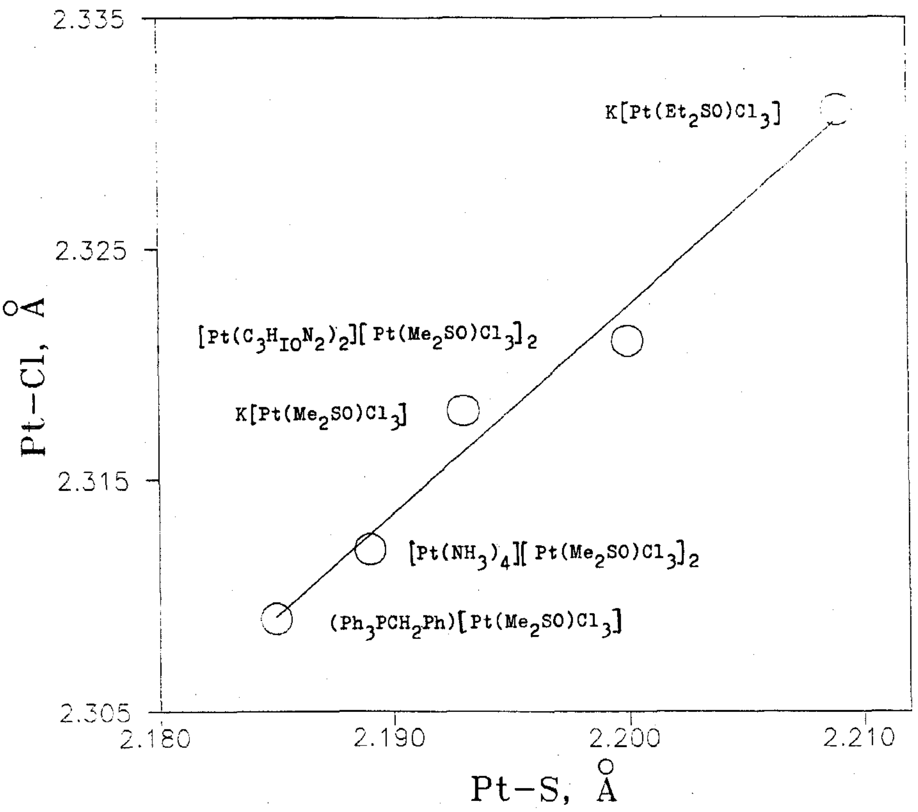

FIGURE 3 Plot of Pt-Cl_{trans} vs. Pt-S for the series $Q[Pt(R_2SO)Cl_3]$.

but transformation products have not been isolated and identified. Not long ago it has been established that standing $[PtEn(Me_2SO)Cl]Cl$ in concentrated HCl leads to the formation of a mixture of complexes containing $[Pt(HEn)(Me_2S)Cl_4]Cl$ and $[Pt(HEn)Cl_5]$.[36] Finally, the splitting reaction of the bridge-type complex $H_2[Pt(Me_2SO)(\mu\text{-}O)Cl]_2$ by HCl in water as a by-product results in the formation of trans-$[Pt(Me_2S)_2Cl_4]$ characterized by the X-ray structure analysis.[37] Thus, the literature data imply that R_2SO molecules can be reduced by HCl not only in the free state but in a coordinated state as well. However, the processes studied at present time have not been at least of preparative importance.

The present authors established that reactions of sulfoxide deoxygenation in the Pt(II) complexes may have a synthetic value and may be used to prepare thioether Pt(IV) compounds. In this case the syntheses should be performed not in aqueous suspension but in non-aqueous solution. For example, the interaction between solutions of the monosulfoxide complexes $(Et_4N)[Pt(R_2SO)Cl_3]$ (R = Me, Et, n-Pr, CH_2Ph) in MeCN and HCl proceeds easily and results in thioether complexes of Pt(IV) in the yields of 70–80%:

$$(Et_4N)[Pt^{II}(R_2SO)Cl_3] + 2\,HCl \rightarrow (Et_4N)[Pt^{IV}(R_2S)Cl_5] + H_2O$$

Compounds prepared in such a way have satisfactory elemental analysis (Tables

VI and VII). Absorption bands of $\nu(SO)$ and $\gamma(CSO)$ characteristic of coordinated sulfoxides (Table VIII) in Pt(II) complexes disappear in the IR spectra of the Pt(IV) compounds; Me_2SO- and Me_2S-containing complexes provide examples of considerable differences in ^1H NMR spectra of starting and final complexes (Table IX). The complex $(Et_4N)[Pt(Me_2S)Cl_5]$ was prepared also by independent synthesis:

$$K_2[PtCl_4] \xrightarrow[/HCl^{38,39}]{Me_2SO/SnCl_2/} trans\text{-}[Pt(Me_2S)_2Cl_4] \longrightarrow$$

$$\xrightarrow[-Me_2S]{(Et_4N)Cl} (Et_4N)[Pt(Me_2S)Cl_5]$$

The comparison of melting points, R_f values and parameters of IR and ^1H NMR spectra shows the authenticity of samples synthesized as a result of deoxygenation and substitution.

The process of the interaction between HCl and the complex $(Et_4N)[Pt((iso\text{-}C_5H_{11})_2SO)Cl_3]$ follows a different way. In this case, not only the transformation of sulfoxide into thioether but substitution of a neutral ligand takes place as well. After completion of HCl bubbling $(iso\text{-}C_5H_{11})_2S$ was detected chromatographically in a reaction mixture and $(Et_4N)_2[PtCl_6]$ isolated into a solid phase. The latter was identified using the elemental analysis and based on a specific IR spectrum.[40]

Noteworthy, that the synthesis of $(Et_4N)[Pt(R_2S)Cl_5]$ can be performed proceeding from $(Et_4N)[Pt(R_2SO)Cl_3]$ which may be prepared in situ by: (i) the reaction between cis-$[Pt(R_2SO)_2Cl_2]$ and $(Et_4N)Cl$ in acetonitrile or (ii) the reaction between $K_2[PtCl_4]$ and equimolar amount of R_2SO in H_2O/MeCN mixture followed by addition of $(Et_4N)Cl$.

TABLE VI

Some parameters for the identified complexes

Complex (no.)	M.P. with dec., °C	Colour	Λ Ohm^{-1} cm^2 mol^{-1} (in DMF)	R_f on TLC (Me_2CO: $CHCl_3$ in volume)
(1) $(Et_4N)[Pt(Me_2SO)Cl_3]$	93	light yellow	125[a]	0.37(4:1)
(2) $(Et_4N)[Pt(Et_2SO)Cl_3]$	97	yellow	58	0.41(6:1)
(3) $(Et_4N)[Pt((n\text{-}Pr)_2SO)Cl_3]$	b	yellow	67	0.50(4:1)
(4) $(Et_4N)[Pt((iso\text{-}C_5H_{11})_2SO)Cl_3]$	70–72	yellow	61	0.42(3:2)
(5) $(Et_4N)[Pt((PhCH_2)_2SO)Cl_3]$	143–146	beige	56	0.51[c]
(6) $(Et_4N)[Pt(Me_2S)Cl_5]$	171–173	orange	137[a]	0.47(7:3)
(7) $(Et_4N)[Pt(Me_2S)Br_5]$	190–203	red	59	0.56(7:3)
(8) $(Me_4N)[Pt(Me_2S)Cl_5]$	180[d]	orange	62	0.57(4:1)
(9) $(Et_4N)[Pt(Et_2S)Cl_5]$	220[d]	orange	67	0.71(6:1)
(10) $(Et_4N)[Pt((n—Pr)_2S)Cl_5]$	269[d]	orange	85	0.60(4:1)
(11) $(Et_4N)[Pt((PhCH_2)_2S)Cl_5]$	215	yellow	64	0.54[c]
(12) trans-$[Pt(Me_2S)_2Cl_4]$	b	yellow		0.45(1:1)
(13) trans-$[Pt(Me_2S)_2Br_4]$	b	deep orange		0.73[e]

[a] Measured in MeCN.

[b] This complex has no pronounced melting point.

[c] Acetone: toluene 7:3 in volume.

[d] Decomposition without melting.

[e] Chloroform: toluene 3:2 in volume.

TABLE VII

Elemental analyses

Complex	Found, %		Formula	Calculated, %	
(no.)	X	Pt		X	Pt
(1)	38.30	21.08	$C_{10}H_{26}Cl_3NOPtS$	38.27	20.86
(2)	35.94	19.94	$C_{12}H_{40}Cl_3NOPtS$	36.27	19.77
(3)	34.66	18.27	$C_{14}H_{34}Cl_3NOPtS$	34.47	18.79
(4)	31.76	17.28	$C_{18}H_{42}Cl_3NOPtS$	31.37	17.10
(5)	29.17	15.77	$C_{22}H_{34}Cl_3NOPtS$	29.47	16.06
(6)	31.25	17.73	$C_{20}H_{30}Cl_3NOPtS$	31.57	17.21
(7)	34.34	31.30	$C_{10}H_{26}Cl_5NPtS$	34.55	31.39
(8)	25.17	50.76	$C_{10}H_{26}Br_5NPtS$	24.79	50.77
(9)	37.52	33.85	$C_6H_{18}Cl_5NPtS{\cdot}0.5H_2O$	37.70	34.26
(10)	29.60	32.30	$C_{12}H_{40}Cl_5NPtS$	29.42	32.38
(11)	30.61	28.28	$C_{14}H_{34}Cl_5NPtS$	31.43	28.55
(12)	24.39	27.21	$C_{22}H_{34}Cl_5NPtS$	24.72	27.21
(13)	30.57	42.11	$C_4H_{12}Cl_4PtS$	30.75	42.31
(14)	30.47	50.07	$C_4H_{12}Br_4PtS$	30.53	50.02

Not only substitution of dimethyl sulfoxide but exchange of Cl^- for Br^- is observed by the interaction between cis-$[Pt(Me_2SO)_2Cl_2]$ and $(Et_4N)Br$ at the reagent molar ratio of 1:4. The reaction of the prepared complex $(Et_4N)[Pt(Me_2SO)Br_3]$ with HBr in acetonitrile leads to $(Et_4N)[Pt(R_2S)Br_5]$. Boiling of cis-$[Pt(Me_2SO)_2Cl_2]$ with HBr in aqueous solution results in the formation and precipitation of trans-$[Pt(Me_2S)_2Br_4]$.

The interaction between cis-$[Pt(Me_2SO)_2Cl_2]$ and HCl in acetonitrile, nitromethane, and in acetone-d_6 was studied using TLC technique on SiO_2 and ^1H NMR spectroscopy.‡ We found that cis-$[Pt(Me_2S)(Me_2SO)Cl_4]$ and cis-$[Pt(Me_2S)_2Cl_4]$ are the first to appear. In time, the two compounds in solution are subject to cis → trans geometrical isomerization which agrees with the statement made in Reference 41. A gradual disappearance of cis- and trans-$[Pt(Me_2S)(Me_2SO)Cl_4]$ occurs concurrently with the process of ligand rearrangement; concentration of trans-$[Pt(Me_2S)_2Cl_4]$ increasing in solution. The latter is the final product in a series of transformations. By running the reaction of cis-$[Pt(R_2SO)_2Cl_2]$ with HCl in acetonitrile, apart from the products mentioned above, the formation of cis-$[Pt(Me_2SO)(MeCN)Cl_4]$[40] was recorded as well.

Therefore, the interaction between Pt(II) sulfoxide complexes in solutions and

---

‡At least part of possible products of oxidation and deoxygenation of the complex cis-$[Pt(Me_2SO)_2Cl_2]$[8,28] has been earlier synthesized, isolated, and characterized (including R_f values on TLC and parameters of ^1H NMR spectra).

TABLE VIII
Infrared spectra

Complex (no.)	Some bands in the IR spectrum (cm^{-1})
(1)	1182 s and 1125 vs (ν_{SO}), 438 m (ν_{PtS}), 375 m (γ_{CSO}), 334 m and 320 m (ν_{PtCl})
(2)	1140 s (ν_{SO}), 430 m (ν_{PtS}), 340 m (ν_{PtCl})
(3)	1125 s (ν_{SO}), 450 m (ν_{PtS}), 336 m (ν_{PtCl})
(4)	1150 s (ν_{SO}), 435 m (ν_{PtS}), 340 m (ν_{PtCl})
(5)	1120 vs (ν_{SO}), 415 m (ν_{PtS}), 334 m and 324 sh (ν_{PtCl})
(6)	1031 m, 998 m and 980 m (ρ_{Me}), 337 s and 320 s (ν_{PtCl})
(7)	1036 m, 997 s-m and 977 m (ρ_{Me}), 317 s (ν_{PtS}), 234 m (ν_{PtBr})
(8)	1033 m and 977 s-m (ρ_{Me}), 345 m and 327 s (ν_{PtCl})
(9)	340 s and 320 sh (ν_{PtCl})
(10)	337 s and 320 sh (ν_{PtCl})
(11)	335 s and 316 m (ν_{PtCl})
(12)	1032 m and 976 s (ρ_{Me}), 347 s, 335 s and 316 s (ν_{PtCl})
(13)	1036 m, 1027 m and 975 s (ρ_{Me}), 318 s (ν_{PtS}), 239 m and 222 m (ν_{PtBr})

HX (X = Cl, Br) acids leads to the complexes of R_2S-Pt(IV) type. These processes are of synthetic importance for the preparation of thioether compounds of platinum and also can be used in the organic chemistry of sulfur to synthesize R_2S. In the latter case, thioethers may be isolated in a free state from the Pt(IV) complexes via substitution for thiocyanate ligands in water§ or by the reduction of Pt(II) ion in complexes to metal via N_2H_4 in aqueous-alkali medium. The isolated R_2S are extracted in $CHCl_3$ or in CH_2Cl_2 and hence become separated from other products of syntheses.

In conclusion it should be noted that the reaction of HCl with *free* and *coordinated*

---

§By interaction of the complex $(Et_4N)[Pt((PhCH_2)_2S)Cl_5]$ with KSCN in water and subsequent extraction of products in $CHCl_3$ apart from $(PhCH_2)_2S$ $PhCH_2NCS$ was found as well. Noteworthy that under comparable conditions the authors have not observed the interaction between free $(PhCH_2)_2S$ and SCN^-. Apparently, benzylation of the thiocyanate ion takes place owing to coordinated $(PhCH_2)_2S$.

TABLE IX

^1H NMR parameters for the complexes with "$Me_2(O)S$—Pt" and "Me_2S—Pt" units

Complex (no.)	δ, ppm	$^3J(Pt, H)$, Hz	Solvent
1	3.31	21.06	acetone-d_6
7	2.35	31.08	dmso-d_6
8	2.75	34.50	DMF-d_7
9	2.35	31.08	dmso-d_6
12	2.48	31.03	DMF-d_7
13	2.76	33.50	acetone-d_6

dibenzyl sulfoxide proceeds in a different way. For example, the interaction of $(PhCH_2)_2SO$ with HCl gives five products: $(PhCH_2)_2S$ was isolated from this mixture in 9% yield.[42] The reaction of the coordinated dibenzyl sulfoxide in the complex $(Et_4N)[Pt((PhCH_2)_2SO)Cl_3]$ with HCl was established to lead to $(Et_4N)[Pt((PhCH_2)_2S)Cl_5]$ in about 70% yield.|| A different course of reactions with HCl of the free and coordinated $(PhCH_2)_2SO$ suggests an process path assisted by Pt(II). The oxidation state of platinum changes with deoxygenation of the coordinated sulfoxide which argues for the statement.

REFERENCES

1. J. S. Grossert in "Chemistry of Sulphones and Sulphoxides," Eds. S. Patai, Z. Rappoport and C. J. M. Stirling, Chichester: Wiley, 1988, p. 925.
2. W. W. Epstein and F. W. Sweat, *Chem. Rev.*, **67**, 247 (1967).
3. J. Drabowicz, T. Numata and S. Oae, *Org. Prep. Proc. Int.*, **9**, 63 (1977).
4. J. Drabowicz, H. Togo, M. Mikolajczyk and S. Oae, *Org. Prep. Proc. Int.*, **16**, 171 (1984).
5. A. J. Mancuso and D. Swern, *Synthesis*, 165 (1981).
6. V. Yu. Kukushkin, *Uspekhi Khimii (Russ. Chem. Rev.)*, **59**, 1453 (1990).
7. V. Yu. Kukushkin and A.I. Moiseev, *Zh. Obsch. Khim.*, **60**, 692 (1990).
8. V. Yu. Kukushkin and E. Yu. Pankova, *Koord. Khim.*, **15**, 531 (1989).
9. V. Yu. Kukushkin and E. Yu. Pankova, *Zh. Obsch. Khim.*, **57**, 2391 (1987).
10. V. Yu. Kukushkin, E. Yu. Pankova, S. A. Simanova, S. S. Sotman, V. S. Fundamensky, I. G. Zenkevich and I. A. Polyakova, *Zh. Obsch. Khim.*, **60**, 587 (1990).
11. V. Yu. Kukushkin, E. A. Aleksandrova and B. V. Zhadanov, *Phosphorus, Sulfur, and Silicon*, **53**, 433 (1990).
12. Yu. N. Kukushkin, Yu. E.Vyazmensky, L. I. Zorina and Yu. L. Pazukhina, *Zh. Neorgan. Khim.*, **13**, 1595 (1968).
13. Yu. N. Kukushkin, V. N. Spevak and V. P. Kotelnikov, *Zh. Neorgan. Khim.*, **18**, 1128 (1973).
14. R. Melanson and F. D. Rochon, *Can. J. Chem.*, **53**, 2371 (1975).
15. R. P. Shibaeva, *Koord. Khim.*, **11**, 129 (1985).
16. Yu. N. Kukushkin, Yu. E. Vyazmensky and L. I. Zorina, *Zh. Neorgan. Khim.*, **13**, 3052 (1968).
17. Yu. N. Kukushkin and Yu. E. Vyazmensky, *Zh. Neorgan. Khim.*, **15**, 480 (1970).
18. Yu. N. Kukushkin and V. N. Spevak, *Zh. Neorgan. Khim.*, **17**, 1686 (1972).
19. Yu. N. Kukushkin, M. A. Kuzmina and V. N. Spevak, *Radiokhimia*, **15**, 716 (1973).
20. Yu. N. Kukushkin, I. V. Pakhomova and A. N. Shanko, *Zh. Obsch. Khim.*, **45**, 1582 (1975).
21. Yu. N. Kukushkin, E. A. Andronov, G. P. Guryanova and V. P. Yustratov, *Zh. Neorgan. Khim.*, **19**, 146 (1974).
22. Yu. N. Kukushkin and Tz. Naidenova-Todorova, *Zh. Neorgan. Khim.*, **17**, 1078 (1972).
23. I. A. Krol, V. Yu. Kukushkin, Z. A. Starikova, V. M. Tkachuk and B. V. Zhadanov, *Zh. Obsch. Khim.*, **58**, 2625 (1988).

||Strictly speaking the deoxygenation conditions for free and coordinated dibenzyl sulfoxide cannot be directly correlated.

24. V. Yu. Kukushkin, I. A. Krol, Z. A. Starikova and V. M. Tkachuk, *Koord. Khim.*, **14**, 1406 (1990).
25. V. Yu. Kukushkin and A. I. Moiseev, *Koord. Khim.*, **15**, 419 (1989).
26. V. Yu. Kukushkin, V. M. Tkachuk, I. A. Krol, Z. A. Starikova, B. V. Zhadanov and N. P. Kiseleva, *Zh. Obsch. Khim.*, **61**, 51 (1991).
27. V. K. Belsky, V. E. Konovalov, V. Yu. Kukushkin and A. I. Moiseev, *Inorg. Chim. Acta*, **169**, 101 (1990).
28. S. S. Sotman, V. S. Fundamensky, V. Yu. Kukushkin and E. Yu. Pankova, *Zh. Obsch. Khim.*, **58**, 2297 (1988).
29. J. A. Davies, *Adv. Inorg. Chem. Radiochem.*, **24**, 115 (1981).
30. V. Yu. Kukushkin, V. K. Belsky, V. E. Konovalov, R. R. Shifrina, A. I. Moiseev and R. A. Vlasova, *Inorg. Chim. Acta*, **183**, 57 (1991).
31. R. Melanson, J. Hubert and F. D. Rochon, *Acta Crystallogr., Sect. B*, **32**, 1914 (1976).
32. P. Khodadad and N. Rodier, *Acta Crystallogr., Sect. C.*, **43**, 1690 (1987).
33. B. Viossat, P. Toffoli, P. Khodadad and N. Rodier, *Acta Crystallogr., Sect. C*, **44**, 92 (1988).
34. P. D. Braddock, R. Romeo and M. L. Tobe, *Inorg. Chem.*, **13**, 1170 (1974).
35. H. Boucher and B. Bosnich, *Inorg. Chem.*, **16**, 717 (1977).
36. F. P. Fanizzi, G. Natile, L. Maresca, A. M. Manotti-Lanfredi and A. Tiripicchio, *J. Chem. Soc., Dalton Trans.*, 1467 (1984).
37. I. V. Pakhomova, L. V. Konovalov, N. T. Komyagin, A. I. Yanovsky, Yu. T. Struchkov and Yu. N. Lukin, *Zh. Obsch. Khim.*, **58**, 733 (1988).
38. Yu. N. Kukushkin, P. G. Antonov, T. M. Lukicheva and L. N. Mitronina, *Zh. Obsch. Khim.*, **47**, 964 (1977).
39. Yu. N. Kukushkin, P. G. Antonov and K. I. Dubonos, *Zh. Obsch. Khim.*, **45**, 854 (1975).
40. V. Yu. Kukushkin, I. G. Zenkevich, V. K. Belsky, V. E. Konovalov and E. O. Sidorov, *Inorg. Chim. Acta*, **166**, 79 (1989).
41. V. Yu. Kukushkin, *Zh. Neorgan. Khim.*, **33**, 1905 (1988).
42. J. A. Smythe, *J. Chem. Soc.*, **95**, 349 (1909).