Inorganica Chimica Acta, *183* (1991) 57–63

Synthesis of halogen-bridged complexes $[Pt(R_2SO)(\mu\text{-}X)X]_2$ by thermolysis of *cis*-$[Pt(R_2SO)(R'CN)X_2]$. X-ray structure of di-μ-chloro-dichlorobis(diethyl sulfoxide)diplatinum(II)

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(Received April 23, 1990; revised November 16, 1990)

Abstract

The reactions of $K[Pt(R_2SO)X_3]$ with R'CN in water, substitution of acetonitrile in *cis*-$[Pt(MeCN)_2Cl_2]$ for sulfoxides and the bridge-cleavage reactions of $[Pt(R_2SO)(\mu\text{-}Cl)Cl]_2$ with R'CN lead to isolation of *cis*-$[Pt(R_2SO)(R'CN)X_2]$ (R = Me, R' = Me, X = Cl, Br; R = Et, Ph, R' = Me, X = Cl; R = Me, R' = CH_2Ph, CH_2CO_2Et, Ph, X = Cl). The reaction of $[Pd(MeCN)_2Cl_2]$ with Me_2SO in acetone followed by removal of the solvent results in isolation of the solid $[Pd(Me_2SO)(\mu\text{-}Cl)Cl]_2$. Ligands R'CN in *cis*-$[Pt(R_2SO)(R'CN)X_2]$ rapidly abstracted on heating in the solid phase or in solution producing halogen-bridged compounds $[Pt(R_2SO)(\mu\text{-}X)X]_2$. The structure of the complex $[Pt(Et_2SO)(\mu\text{-}Cl)Cl]_2$ was determined by X-ray analysis. The compound crystallizes in the $P2_1/b$ space group. The unit cell dimensions are $a = 5.925(1)$, $b = 11.175(2)$, $c = 14.195(3)$ Å, $\gamma = 98.79°$, $V = 928.8(3)$ Å^3, $Z = 2$. A comparison of Pt–Cl bond lengths in the molecule $[Pt(Et_2SO)(\mu - Cl)Cl]_2$ suggests that the *trans*-influence of diethyl sulfoxide is higher than that of the chloride ion.

Introduction

Binuclear halogen-bridged complexes $[PtL(\mu\text{-}X)X]_2$ (X = Cl, Br) are important in the chemistry of Pt(II) coordination compounds. This can be attributed to the fact that $[PtL(\mu\text{-}X)X]_2$ rapidly reacts with ligands L' with the formation of not always easily obtained compounds $[PtLL'X_2]$.

Sulfoxide-containing compounds $[Pt(R_2SO)(\mu\text{-}Cl)Cl]_2$ are rather poorly known. The complex $[Pt(Me_2SO)(\mu\text{-}Cl)Cl]_2$ was first prepared by thermal abstraction of ethylene from *cis*-$[Pt(Me_2SO)(C_2H_4)Cl_2]$ [1, 2]. Later it was synthesized by the reaction of $K[Pt(Me_2SO)Cl_3]$ and $AgNO_3$ in water [3]. The compounds $[Pt(R_2SO)(\mu\text{-}Cl)Cl]_2$ (R = Me, Et) are known to result from the reactions of *cis*-$[Pt(R_2SO)_2Cl_2]$ with $PtCl_2$ in naphthalene at 165 °C [4].

It has been reported [5] that heating the solid complex *cis*-$[Pt(Me_2SO)(MeCN)Cl_2]$ at 145 °C, results in the abstraction of acetonitrile and the formation of $[Pt(Me_2SO)(\mu\text{-}Cl)Cl]_2$ in nearly quantitative yield. Different ways of synthesis of the complexes *cis*-$[Pt(R_2SO)(R'CN)X_2]$, and their thermal conversion in the solid phase and in solution with the formation of the corresponding $[Pt(R_2SO)(\mu\text{-}X)X]_2$, are discussed along with data of the X-ray structure study of $[Pt(Et_2SO)(\mu\text{-}Cl)Cl]_2$.

Experimental

Materials and apparatus

The complexes *cis*-$[Pt(MeCN)_2Cl_2]$ [6] and $K[Pt(R_2SO)X_3]$ (R = Me, X = Cl, Br; R = Et,

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0020-1693/91/$3.50

TABLE 1. Some physicochemical characteristics of the synthesized compounds

Compound	Elemental analysis: found (calc.) (%)		Solid phase heating behaviour (°C)	Selected peaks in IR spectrum (cm^{-1})		
	X	Pt		$\nu(SO)$	$\nu(CN)$	$\nu(PtX)$
cis-$[Pt(Me_2SO)(MeCN)Cl_2]$	18.1 (18.41)	50.8 (50.65)	145–150(–MeCN)	1147vs^{a}	2339m, 2312w^{a}	359s, 336m^{a}
$[Pt(Me_2SO)(\mu\text{-}Cl)Cl]_2$	20.5 (20.60)	56.8 (56.69)	235 (dec.)	1152vs^{a}		364s(t); 309m, 289s, 259s(μ)
cis-$[Pt(Me_2SO)(MeCN)Br_2]$	34.0 (33.71)	40.9 (41.15)	120–125(–MeCN) 210 (dec. without melt.)	1150s^{a}	2321w^{a}	215w,^{c}, 236w^{a}
$[Pt(Me_2SO)(\mu\text{-}Br)Br]_2$	37.1 (36.90)	45.4 (45.05)	220 (dec. without melt.)	1145s^{a}		244s(t), 212s(μ)^{b}
cis-$[Pt(Et_2SO)(MeCN)Cl_2]$	16.8 (17.16)	47.5 (47.21)	120–127 (melt., –MeCN), 205 (dec.)	1118vs^{c}	2313w^{c}	358s, 335s^{b}
$[Pt(Et_2SO)(\mu\text{-}Cl)Cl]_2$	18.4 (19.05)	51.7 (52.42)	164–165 (melt., dec.)	1142s^{c}		363s(t); 302s, 271m, 253w(μ)^{b}
cis-$[Pt(Ph_2SO)(MeCN)Cl_2]$	13.8 (13.92)	38.0 (38.31)	142–147(–MeCN) 155–160 (m.p.) 215 (dec.)	1148s^{c}	2324w, 2318w^{c}	349m, 347m^{c}
cis-$[Pt(Me_2SO)(EtCO_2CH_2CN)Cl_2]$	15.3 (15.51)	42.6 (42.67)	138–139 (m.p.)	1150s^{c}	2397w, 2354w, 2324w^{a}	367s, 328s^{b}
cis-$[Pt(Me_2SO)(PhCH_2CN)Cl_2]$	15.3 (15.37)	42.6 (42.40)	99–106 (m.p.)	1149s^{a}	2316w^{a}	354m, 321w^{a}
cis-$[Pt(Me_2SO)(PhCN)Cl_2]$	16.0 (15.85)	43.5 (43.62)	183–186 (m.p.)	1145vs	2292m, 2242vw	323s

IR spectra were recorded in pellets from ^{a}potassium bromide, ^{b}polyethylene, ^{c}cesium iodide.

$X = Cl$) [7] were prepared by known methods. IR spectra were recorded using a Perkin-Elmer model 983G spectrometer in KBr pellets, a Perkin-Elmer model 580 spectrometer in CsI pellets and a Fis-3-Hitachi spectrometer in polyethylene pellets. The melting points or decomposition points were measured using a Kofler table. TGA measurements were carried out by means of the Paulik, Paulik, Erdey model OD-102 derivatograph, samples being heated at 5 °/min. Elemental analysis was performed by the Chair of Analytical Chemistry at the Leningrad State University (Table 1).

Syntheses

cis-Dibromo(dimethyl sulfoxide)(acetonitrile) platinum(II)

To a solution of $K[Pt(Me_2SO)Br_3]$ (0.50 g, 0.9 mmol) in water (15 ml) was added acetonitrile (0.63 ml, 11.9 mmol) and the mixture was kept at 20 °C for 10 h. The released needles were collected on a filter, washed with water (3 × 5 ml), ethanol (3 × 5 ml), ether (3 × 5 ml), and dried in air at 20 °C. Yield of *cis*-$[Pt(Me_2SO)(MeCN)Br_2]$ = 0.24 g, 56% based on Pt.

cis-Dichloro(dimethyl sulfoxide)(organonitrile) platinum(II) (organonitrile = $PhCH_2CN$, $EtCO_2CH_2CN$, PhCN)

R′CN (9.3 mmol) was added to a suspension of $[Pt(Me_2SO)(\mu\text{-}Cl)Cl]_2$ (2.13 g, 3.1 mmol) in acetone (25–40 ml) and boiled to complete homogenization within 5–10 min. The solution was filtered and the solvent was removed on boiling to the formation of an oily mass. After cooling the resulting product was isolated by addition of ether (20–30 ml), filtered, washed on a filter with ether (2 × 5 ml), and dried in air at 20 °C. Yield of the complexes 60–70% based on Pt.

cis-Dichloro(diphenyl sulfoxide)(acetonitrile) platinum(II)

A suspension of *cis*-$[Pt(MeCN)_2Cl_2]$ (2.67 g, 7.7 mmol) and diphenyl sulfoxide (2.3 g, 11.5 mmol) in nitromethane (75 ml) was boiled and stirred for 15 min. The mixture was cooled, filtered and the filtrate was evaporated in an open vessel on boiling of the mixture to 15 ml. After cooling, the precipitate was filtered, washed on a filter with hot toluene (2 × 5 ml), ether (3 × 5 ml), and dried in air at 20 °C. Yield of *cis*-$[Pt(Ph_2SO)(MeCN)Cl_2]$ = 1.72 g, 52% based on Pt.

Di-μ-chloro-dichlorobis(diethyl sulfoxide) diplatinum(II)

Diethyl sulfoxide (0.3 ml, 3.1 mmol) was added to a solution of *cis*-$[Pt(MeCN)_2Cl_2]$ (0.99 g, 2.8 mmol) in hot (100 °C) nitromethane (30 ml), and the mixture was diluted with *p*-xylene (45 ml). The resultant mixture was boiled in an open vessel for 5 min. The precipitate was filtered off and the filtrate was boiled and stirred for another 20 min. After cooling, the precipitate was filtered, washed on a filter with ether (3 × 5 ml), and dried in air at 20 °C. Yield of $[Pt(Et_2SO)(\mu\text{-}Cl)Cl]_2$ = 0.52 g, 49% based on Pt.

Preparation of $[Pt(R_2SO)(\mu\text{-}X)X]_2$ by thermolysis of corresponding cis-$[Pt(R_2SO)(MeCN)X_2]$ ($R = Me$, Et, Ph, $X = Cl$; $R = Me$, $X = Br$)

The complexes *cis*-$[Pt(R_2SO)(MeCN)X_2]$ were powdered with a pestle in agate mortar, spread in a thin layer and kept in a thermostat. Thermosynthesis temperatures are given in 'Results and discussion'. The reaction was controlled by change of the sample mass. Yields of $[Pt(R_2SO)(\mu\text{-}X)X]_2$ are almost quantitative.

Di-μ-chloro-dichlorobis(dimethyl sulfoxide) dipalladium(II)

Dimethyl sulfoxide (0.11 ml, 1.61 mmol) was added to a suspension of $[Pd(MeCN)_2Cl_2]$ (0.4 g, 1.54 mmol) in acetone (20 ml) with stirring. After 5 min, the solution was filtered from the small amount of precipitated *trans*-$[Pd(Me_2SO)_2Cl_2]$ and the solvent was removed by natural evaporation at 20 °C. Yield of $[Pd(Me_2SO)(\mu\text{-}Cl)Cl]_2$ = 0.27 g, 69% based on Pd.

Structure determination

Diffraction data were collected on a Syntex P$\bar{1}$ diffractometer, using Mo Kα radiation, β-filter; cell parameters from refined angles of 12 centered reflections with 2θ between 21 and 27°; 1412 independent reflections of which 1322 with $I \geqslant 3\sigma(I)$ measured up to $2\theta \leqslant 50°$ by $\theta/2\theta$ scan technique. Scan speed 3.0–12.0° min^{-1}. Standard reflections 300, 040, 008 measured every 100 reflections showed no change with time. Diffractometer data were processed by the program PROFIT [8] with profile analysis of reflections. Structure was solved by means of Fourier syntheses based upon the Pt atom coordinates obtained from the Patterson synthesis and was refined by full-matrix least-squares based on F with weights $w = 1/\sigma(F) + 0.0080F^2$. All non-hydrogen atoms were treated isotropically. H atoms were not refined. $R = 0.059$, $R_w = 0.055$, $S = 0.862$. Lorentz, polarization and absorption correction were made (crystal size: 0.10 × 0.05 × 0.09 × 0.09, crystal faces (100), (001), (011), (0$\bar{1}$1)). Calculations were carried out with SHELXTL [9] on a Nova-3 computer. Table 2 shows the crystallographic data for $[Pt(Et_2SO)(\mu\text{-}Cl)Cl]_2$, and Table 3 presents atomic parameters and their equivalent isotropic factors.

TABLE 2 Crystallographic data for $[Pt(Et_2SO)(\mu\text{-}Cl)Cl]_2$

Crystal system	monoclinic
Space group	$P2_1/b$
a (Å)	5 925(1)
b (Å)	11 175(2)
c (Å)	14 195(3)
γ (°)	98 79(2)
V (Å^3)	928 8(3)
Z	2
ρ_{calc} (g cm^{-3})	2 66
μ (cm^{-1})	166

TABLE 3 Atomic parameters ($\times 10^4$) and their equivalent isotropic factors (Å^2 $\times 10^3$) with e s d s in parentheses

Atom	x	y	z	U
Pt	6291(1)	3896(1)	5553(1)	42(1)
Cl(1)	6507(7)	6022(3)	5585(2)	56(1)
Cl(2)	9061(7)	4008(3)	6667(4)	88(2)
S	6012(6)	1924(3)	5466(2)	42(1)
O	4028(12)	1327(6)	4897(7)	48(3)
C(1)	8609(17)	1522(10)	5000(11)	47(4)
C(2)	8864(20)	1819(13)	3927(12)	66(5)
C(3)	5805(21)	1243(11)	6626(10)	57(5)
C(4)	3675(26)	1407(17)	7092(14)	96(8)

Results and discussion

Synthesis of $[Pt(R_2SO)(R'CN)X_2]$

The simplest method of preparation of $[Pt(R_2SO)(R'CN)X_2]$ is a halogenide ion replacement with the R'CN molecule in $K[Pt(R_2SO)X_3]$ The reaction proceeds in water at 20 °C and results in release of the complexes required into the solid phase

$$K[Pt(R_2SO)X_3] + R'CN \xrightarrow{H_2O} cis\text{-}[Pt(R_2SO)(R'CN)X_2] + KX \quad (1)$$

R = Me, R' = Me, Ph, X = Cl

R = Me, R' = Me, X = Br

Reaction (1) does not always give the required result Therefore, we could not prepare the complex *cis*-$[Pt(Et_2SO)(MeCN)Cl_2]$, and the compounds *cis*-$[Pt(Me_2SO)(R'CN)Cl_2]$ (R' = CH_2Ph, CH_2CO_2Et) were obtained in very small yields

It was recognized that organonitrile in the obtained complexes *cis*-$[Pt(R_2SO)(R'CN)X_2]$ is easily replaced with an X^- ion in solutions of dichloromethane, 1,1,2,2-tetrachloroethane, nitromethane, dimethylformamide and even in the medium of corresponding R'CN

$$cis\text{-}[Pt(R_2SO)(R'CN)X_2] + Q^+X^- \longrightarrow Q[Pt(R_2SO)X_3] + R'CN \quad (2)$$

Q = Et_4N, Ph_4As, Ph_3PCH_2Ph,$[(Ph_3P)_2N]$

Hence, the replacement reactions in water and in non-aqueous solvents proceed in different ways A low solubility of $[Pt(R_2SO)(R'CN)X_2]$ and a relatively high energy of hydration of the formed KX is apparently one of the possible driving forces of reaction (1)

The other possible way of synthesis of the title complexes is the organonitrile replacement in $[Pt(R'CN)_2X_2]$ with the sulfoxide molecule The process was implemented to prepare the acetonitrile complex

$$cis\text{-}[Pt(MeCN)_2Cl_2] + Ph_2SO \xrightarrow{MeNO_2} cis\text{-}[Pt(Ph_2SO)(MeCN)Cl_2] + MeCN \quad (3)$$

The authors also made an attempt to prepare $[Pd(Me_2SO)(MeCN)Cl_2]$ from the interaction of $[Pd(MeCN)_2Cl_2]$ with dimethyl sulfoxide However, when these reagents are mixed in a 1 1 molar ratio in acetone followed by removal of the solvent a chloro-bridged complex $[Pd(Me_2SO)(\mu\text{-}Cl)Cl]_2$ is formed, which has already been reported [10]

It is noteworthy that a possible method for the formation of *cis*-$[Pt(R_2SO)(R'CN)X_2]$ is the replacement of one of the sulfoxides in *cis*-$[Pt(R_2SO)_2X_2]$ It was shown earlier [11] that on heating *cis*-$[Pt(Me_2SO)_2Cl_2]$ in acetonitrile solution an equilibrium is attained

$$cis\text{-}[Pt(Me_2SO)_2Cl_2] + MeCN \rightleftarrows cis\text{-}[Pt(Me_2SO)(MeCN)Cl_2] + Me_2SO \quad (4)$$

The reaction can be completely shifted towards the formation of *cis*-$[Pt(Me_2SO)(MeCN)Cl_2]$ through alkylation of a dimethyl sulfoxide free molecule resulted from eqn (4)

Probably, the universal method for the synthesis of the complexes $[Pt(R_2SO)(R'CN)X_2]$ is the interaction of the halogen-bridged compounds $[Pt(R_2SO)(\mu\text{-}X)X]_2$ with the corresponding R'CN

$$[Pt(R_2SO)(\mu\text{-}X)X]_2 + 2R'CN \xrightarrow{Me_2CO} 2\ cis\text{-}[Pt(R_2SO)(R'CN)X_2] \quad (5)$$

R = Me, R' = CH_2Ph, CH_2CO_2Et,Ph, X = Cl

R = Me, R' = Me, X = Br

R = Et, R' = Me, X = Cl

Using reaction (5) we were able to synthesize complexes containing weak donor organonitriles (e g *cis*-$[Pt(Me_2SO)(EtCO_2CH_2CN)Cl_2]$) However, the use of reaction (5) is limited by the fairly poor preparation of the above sulfoxide complexes of the bridge-type. Therefore, the authors have worked out simple techniques for the synthesis of some of these compounds.

Thermolysis of cis-$[Pt(R_2SO)(MeCN)X_2]$ *in the solid phase and in solution*

TGA studies of the complexes *cis*-$[Pt(R_2SO)(MeCN)X_2]$ show a mass loss on TG curves corresponding to the abstraction of the acetonitrile molecule. On heating of *cis*-$[Pt(R_2SO)(MeCN)X_2]$ using a Kofler table at the mass loss temperatures a drastic colour change from pale yellow to bright orange was observed. The IR spectra of samples after heating show the disappearance of the $\nu(CN)$ absorption bands and the appearance of the $\nu(PtCl\text{-}\mu)$ bands. The elemental analyses of the products of thermosynthesis fit the halogen-bridged sulfoxide complexes (Table 1). Therefore, thermolysis of the complexes *cis*-$[Pt(Me_2SO)(MeCN)X_2]$ ($X = Cl$, Br) and *cis*-$[Pt(Et_2SO)(MeCN)Cl_2]$ in the solid phase at 145, 130 and 120 °C, respectively, results in dimer products.

$$2\ cis\text{-}[Pt(R_2SO)(MeCN)X_2] \xrightarrow[-2MeCN]{\Delta} [Pt(R_2SO)(\mu\text{-}X)X]_2$$

Complexes synthesized in this way contain no by-products and can be used in further reactions without additional purification.

Thermolysis can run in a solution as well. In this case, the complex *cis*-$[Pt(MeCN)_2Cl_2]$ was heated in an open vessel containing equimolar amount of an appropriate sulfoxide with a mixture of nitromethane with *p*-xylene (see 'Experimental'). However, by this method a pure product was only synthesized for Et_2SO. In all other cases, the halogen-bridged complexes need further purification.

Structure of $[Pt(Et_2SO)(\mu\text{-}Cl)Cl]_2$ (Fig. 1)

It was established that the molecule of the complex is in the center of symmetry. Both platinum atoms, chlorine and sulfur atoms are sited practically on the same plane. The deviations of Pt, Cl(1), Cl(2) and S atoms from this plane are −0.008, +0.005, −0.001 and +0.005 Å, respectively. Bond angles between platinum and ligands are comparable with those in other compounds of the $[PtL(\mu\text{-}Cl)Cl]_2$ type (Tables 4 and 5).

The bond between the platinum(II) ion and diethyl sulfoxide is accomplished through the sulfur atom as in most other platinum complexes with dialkyl sulfoxides [19, 20]. At present only two structures with O-coordinated Me_2SO molecules are known [21, 22]. The Pt–S bond length is 2.188(3) Å (Table 4) which is in good agreement with bond lengths in the complexes with the anion $[Pt(Me_2SO)Cl_3]^-$ [19, 23–25] but slightly lower than in compounds $[Pt(R_2SO)LCl_2]$ ($L = R_2SO$ [26–30], MeCN [31]).

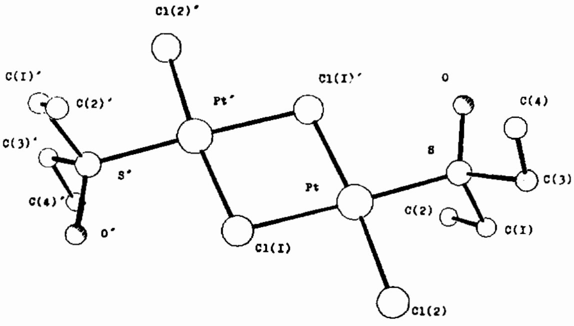


Fig. 1. View of the molecular structure of the $[Pt(Et_2SO)(\mu\text{-}Cl)Cl]_2$ complex with the atomic numbering scheme. Positions of the hydrogen atoms are not shown.

TABLE 4. Bond lengths (Å) and bond angles (°) for $[Pt(Et_2SO)(\mu - Cl)Cl]_2$ with e.s.d.s in parentheses

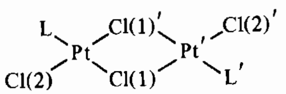
Bond lengths			
Pt–Cl(1)	2.360(4)	Pt–Cl(2)	2.268(5)
Pt–S	2.188(3)	Pt–Cl(1)′	2.327(4)
Cl(1)–Pt′	2.327(4)	S–O	1.496(9)
S–C(1)	1.794(12)	S–C(3)	1.811(15)
C(1)–C(2)	1.561(22)	C(3)–C(4)	1.461(22)
Bond angles			
Cl(1)–Pt–Cl(2)	90.2(1)	Cl(1)–Pt–S	177.5(1)
Cl(2)–Pt–S	92.2(1)	Cl(1)–Pt–Cl(1)′	84.4(1)
Cl(2)–Pt–Cl(1)′	174.6(1)	S–Pt–Cl(1)′	93.2(1)
Pt–Cl(1)–Pt′	95.6(1)	Pt–S–O	114.4(3)
Pt–S–C(1)	109.7(4)	O–S–C(1)	109.6(6)
Pt–S–C(3)	111.2(4)	O–S–C(3)	107.8(5)
C(1)–S–C(3)	103.6(6)	S–C(1)–C(2)	111.4(9)
S–C(3)–C(4)	111.3(11)		

The sulfur atom in diethyl sulfoxide exhibits a tetrahedral configuration. The bond angles of C–S–C and O–S–C fall in the range 104–110°. Ethyl groups in the sulfur atom exhibit a W-configuration. The dihedral angle between a plane passed through Pt, O, S atoms and the main plane of the complex is 9.8°.

The interatomic distances of Pt–Cl(2) and Pt–Cl(1)′ differ by about 0.06 Å. Such a difference between bond lengths of the platinum with terminal and bridge chlorine atoms is also characteristic of other complexes of the $[PtL(\mu\text{-}Cl)Cl]_2$ type (Table 5). Bond lengths of Pt–Cl(2) and Pt–Cl(1)′ in the complex $[Pt(Et_2SO)(\mu\text{-}Cl)Cl]_2$ are in fact identical to those of Pt–Cl(t) and Pt–Cl(μ) in the complex $(C_3R_3)_2[Pt_2(\mu\text{-}Cl)_2Cl_4]$ [32].

Complexes of the $[PtL(\mu\text{-}Cl)Cl]_2$ type are useful for determining the *trans*-influence of ligands L as compared to the chloride ion. In this case the bond lengths of Pt–Cl(μ) on the coordinates

TABLE 5. Some structural parameters for the complexes



Ligand	Bond length (Å)			Bond angle (°)				Reference
	Pt–Cl(1)	Pt–Cl(1)'	Pt–Cl(2)	Cl(2)–Pt–Cl(1)	Cl(1)–Pt–Cl(1)'	L–Pt–Cl(1)'	L–Pt–Cl(2)	
PPr_3	2.425(8)	2.315(8)	2.279(9)	91.5(3)	83.6(2)	96.5(3)	88.4(4)	12
$C(CH_2CMe_3)$ $(OCHMe_2)$[a]	2.40(1)	2.32(1)	2.28(1)	92.3(5)	82.7(5)	95(2)	90(2)	13
$AsMe_3$	2.394(6)	2.312(5)	2.268(6)	94.2(2)	84.6(2)	94.7(2)	88.5(2)	14
$Me_2C{=}C{=}CMe_2$[a]	2.382(5)	2.342(5)	2.273(5)	89.5(2)	82.8(2)	95.2(5)	93.5(5)	15
Et_2SO	2.360(4)	2.327(4)	2.268(5)	90.2(1)	84.4(1)	93.2(1)	92.2(1)	this work
C_5H_8[b,c]	2.349(5)	2.320(5)	2.264(6)	90.8(2)	82.5[e]	99.0	87.7	16
C_7H_{12}[b,d]	2.362(6)	2.328(6)	2.257(6)	88.9(2)	83.9[e]	96.4	90.8	16
C_7H_9N[f]	2.320(3)	2.321(3)	2.272(3)	93.3(1)	84.7(1)	93.3(3)	88.8(3)	17
$(MeO)_2\overset{+}{C}-\overset{-}{C}H_2$[a]	[e]	2.324(7)	2.264(8)	91.6(18)	84.2(15)	96.8(4)	87.3(4)	18

[a] Coordination of σ-C type. [b] Coordination of η^2-C=C type. [c] Cyclopentene. [d] Cycloheptene. [e] The data were not given in the original paper; data from the Cambridge Structural Database, released 1987. [f] 2,6-Lutidine.

L–Pt–Cl(μ) are compared with the bond length Pt–Cl(μ) on the coordinates Cl(t)–Pt–Cl(μ). The analysis of structure data for different complexes of $[PtL(\mu\text{-}Cl)Cl]_2$ (Table 5) shows that the *trans*-influence of diethyl sulfoxide is higher than that of the chloride ion. The *trans*-influence of ligands in the complexes of the $[PtL(\mu\text{-}Cl)Cl]_2$ type decreases in the order: $PPr_3 > C(CH_2CMe_3)(OCHMe_2) > AsMe_3 > Me_2C{=}C{=}CMe_2 > Et_2SO > C_7H_{12} > C_5H_8 > C_7H_9N$.

References

1 Yu. N. Kukushkin and I. V. Pakhomova, *Zh. Neorg. Khim.*, *15* (1970) 1882.

2 I. V. Pakhomova, Yu. N. Kukushkin, L. V. Konovalov and V. V. Strukov, *Zh. Neorg. Khim.*, *29* (1984) 1000.

3 P.-Ch. Kong and F. D. Rochon, *Inorg. Chim. Acta*, *37* (1979) L457.

4 G. Annibale, M. Bonivento, L. Canovese, L. Cattalini, G. Michelon and M. L. Tobe, *Inorg. Chem.*, *24* (1985) 797.

5 V. Yu. Kukushkin and A. I. Moiseev, *Koord. Khim.*, *15* (1989) 419.

6 K. A. Hoffmann and G. Bugge, *Bcr.*, *40* (1907) 1772.

7 V. Yu. Kukushkin, V. K. Belsky, V. E. Konovalov, E. A. Aleksandrova, E. Yu. Pankova and A. I. Moiseev, in press.

8 V. A. Strcl'tsov and V. E. Zavodnik, *Kristallografia*, *34* (1989) 1369.

9 G. M. Sheldrick, *SHELXTL Program Library*, Revision 4.1, Nicolet Instrument Corporation, Madison, WI, 1983.

10 Yu. N. Kukushkin, R. A. Vlasova and Yu. L. Pazukhina, *Zh. Prikl. Khim.*, *41* (1968) 2381.

11 V. Yu. Kukushkin, E. Yu. Pankova, T. N. Fomina and N. P. Kiseleva, *Koord. Khim.*, *14* (1988) 1110.

12 M. Black, R. H. B. Mais and P. G. Owston, *Acta Crystallogr.*, *Sect. B*, *25* (1969) 1760.

13 V. B. Pukhnarevich, Yu. T. Struchkov, G. G. Aleksandrov, S. P. Sushchinskaya, E. O. Tsetlina and M. G. Voronkov, *Koord. Khim.*, *5* (1979) 1535.

14 S. F. Watkins, *J. Chem. Soc. A*, (1970) 168.

15 T. G. Hewitt and J. J. De Boer, *J. Chim. Soc. A*, (1971) 817.

16 J. Bordner and D. W. Wertz, *Inorg. Chem.*, *13* (1974) 1639.

17 F. D. Rochon and R. Melanson, *Acta Crystallogr.*, *Sect. B*, *37* (1981) 690.

18 A. De Renzi, B. Di Blasio, G. Paiaro, A. Panuzi and C. Pedone, *Gazz. Chim. Ital.*, *106* (1976) 765.

19 S. S. Sotman, V. S. Fundamensky, V. Yu. Kukushkin and E. Yu. Pankova, *Zh. Obshch. Khim.*, *58* (1988) 2297.

20 J. A. Davies, *Adv. Inorg. Chem. Radiochem.*, *24* (1981) 115.

21 L. I. Elding and A. Oskarsson, *Inorg. Chim. Acta*, *130* (1987) 209.

22 F. A. Cotton, L. R. Falvello and S. Han, *Inorg. Chem.*, *21* (1982) 2889.

23 R. Melanson, J. Hubert and F. D. Rochon, *Acta Crystallogr.*, *Sect. B*, *32* (1976) 1914.

24 P. Khodadad and N. Rodier, *Acta Crystallogr.*, *Sect. C*, *43* (1987) 1690.

25 B. Viossat, P. Toffoli, P. Khodadad and N. Rodier, *Acta Crystallogr.*, *Sect. C*, *44* (1988) 92.

26 R. P. Shibaeva, *Koord. Khim.*, *11* (1985) 129.

27 R. Melanson and F. D. Rochon, *Can. J. Chem.*, *53* (1975) 2371.

28 R. Melanson, C. de la Chevrotiere and F. D. Rochon, *Acta Crystallogr.*, *Sect. C*, *41* (1985) 1482.

29 R. Melanson and F. D. Rochon, *Acta Crystallogr.*, *Sect. C*, *43* (1987) 1869.

30 R. Melanson and F. D. Rochon, *Acta Crystallogr.*, *Sect. C*, *44* (1988) 1893.

31 A. I. Moiseev, V. Yu. Kukushkin, S. A. Simanova, V. K. Belsky and V. E. Konovalov, *XIV Chernyaev Conf. Novosibirsk*, *U.S.S.R.*, *June 26–28, 1989*, Vol. 1, IONKh, Novosibirsk, 1989, p. 55.

32 C. D. Cowman, J. C. Thibeault, R. F. Ziolo and H. B. Gray, *J. Am. Chem. Soc.*, *98* (1976) 3209.

Note added in proof

Addition of Et_2SO to a solution of *cis*-$[Pt(MeCN)_2Cl_2]$ followed by boiling of the mixture leads to the formation of the precipitate (see 'Experimental'). We have established that this precipitate is *trans*-$[Pt(MeCN)_2Cl_2]$. The latter has recently been obtained by the thermal isomerization of *cis*-$[Pt(MeCN)_2Cl_2]$ in the solid phase (V. Yu. Kukushkin and V. M. Tkachuk, unpublished results) and in aqueous suspension (F. P. Fanizzi, F. P. Intini, L. Maresca and G. Natile, *J. Chem. Soc.*, *Dalton Trans.*, (1990) 199).