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cis-Influence determination of ethylene and benzyl cyanide ligands in the complexes *cis*-[Pt(Me_2SO)(C_2H_4)Cl_2] and *cis*-[Pt(Me_2SO)($PhCH_2CN$)Cl_2] on the basis of X-ray structure data. IR and ^{1}H, ^{13}C and ^{195}Pt NMR characterization of the *cis*-[Pt(Me_2SO)LCl_2] series

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Abstract

Complexes of the *cis*-[Pt(Me_2SO)LCl_2] series (L = Me_2SO, Me_2S, C_2H_4, MeCN, $PhCH_2CN$, PhCN, C_5H_5N, 2Me-C_5H_4N and NH_3) were prepared by known methods and characterized by IR and ^{1}H, ^{13}C{^{1}H}, ^{195}Pt{^{1}H} NMR spectra. Structures of *cis*-[Pt(Me_2SO)(C_2H_4)Cl_2] and *cis*-[Pt(Me_2SO)($PhCH_2CN$)Cl_2] were determined by X-ray analysis. *cis*-[Pt(Me_2SO)(C_2H_4)Cl_2] crystallizes in the orthorhombic space group *Pmnb*. The unit cell parameters are $a = 8.200(1)$, $b = 12.924(3)$, $c = 8.574(1)$ Å, $V = 908.7(3)$ Å^3, $\rho_{calc} = 2.72$ g cm^{-3}, $Z = 4$. *cis*-[Pt(Me_2SO)($PhCH_2CN$)Cl_2] crystallizes in the monoclinic space group $P2_1/n$. The unit cell parameters are: $a = 12.223(4)$, $b = 16.605(4)$, $c = 6.779(2)$ Å, $\gamma = 91.10(2)$°, $V = 1375.6(7)$ Å^3, $\rho_{calc} = 2.23$ g cm^{-3}, $Z = 4$. On the basis of the X-ray structure data *cis*- and *trans*-influence of C_2H_4 and $PhCH_2CN$ ligands were determined.

Introduction

The structural *trans*-influence of ligands in complexes of transition metals has been discussed in many publications (see reviews in refs. 1–3). However, the structural *cis*-influence is a rare phenomenon and in ref. 4 it was stated that *cis*-influence is a purely dynamic effect.

Recently the authors have carried out the X-ray structure study of the platinum complex *cis*-[Pt(Me_2SO)(MeCN)Cl_2]. The comparison of the Pt–S bond length in this compound with those of *cis*-[Pt(Me_2SO)LCl_2] (L = Me_2SO, 2Me-C_5H_4N, NH_3) shows that the Pt–S distance is fairly strongly dependent on the nature of L [5]. In other words the Pt–S bond length is an indicator characteristic of the *cis*-influence of ligands. This finding has stimulated our further studies concerning the synthesis and X-ray structure analysis of a series of *cis*-[Pt(Me_2SO)LCl_2] complexes and determination of mutual ligand influence in compounds of this type.

Single crystals of the earlier known complexes *cis*-[Pt(Me_2SO)(C_2H_4)Cl_2] [6–8] and *cis*-[Pt(Me_2SO)($PhCH_2CN$)Cl_2] [9, 10] have been prepared along with their X-ray structure analysis and the *cis*-influence of ethylene and benzyl cyanide in these compounds has been determined.

Experimental

Materials and apparatus

The complexes *cis*-[Pt(Me_2SO)LCl_2] (L = Me_2SO [11], Me_2S [12], MeCN [5, 13, 14], $PhCH_2CN$ and

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PhCN [9, 10], C_5H_5N [15], 2Me-C_5H_4N [15], and NH_3 [15]) were prepared by the known methods. Elemental analysis was performed at the Chair of Analytical Chemistry at the Leningrad State University. The points of ethylene abstraction and decomposition of the complexes *cis*-$[Pt(Me_2SO)(C_2H_4)Cl_2]$ and *cis*-$[Pt(Me_2SO)(PhCH_2CN)Cl_2]$ were determined on a Kofler micro hot-stage apparatus. IR spectra were recorded using a Perkin-Elmer model 983G spectrometer in KBr pellets. ^1H, ^{13}C and ^{195}Pt NMR spectra were recorded at 200.13, 50.324 and 64.386 MHz, respectively, on Bruker model AC-200 (^1H, ^{13}C) and MSL-300 (^{195}Pt) spectrometers with DMF-d_7 internal lock using 10 mm sample tubes, at an ambient temperature 297 K. TMS and 1 M solutions of $Na_2[PtCl_6]$ in D_2O were used as external chemical shift references. Negative values denote low frequency (high field) shifts.

Table 1 shows the apparatus and conditions under which the X-ray structure analysis was run and Tables 2–5 present atomic parameters and their equivalent isotropic factors, bond lengths and bond angles.

Synthesis of cis-$[Pt(Me_2SO)(C_2H_4)Cl_2]$

cis-$[Pt(Me_2SO)(C_2H_4)Cl_2]$ was prepared by the slightly modified method described in refs. 6 and 8. To a solution of $K_2[PtCl_4]$ (1.07 g, 2.58 mmol) in 0.4 M HCl (30 ml) was added dimethyl sulfoxide (0.19 ml, 2.70 mmol) and the mixture was kept 90 °C for 15 min. After cooling it was filtered into a round-bottom flask. The *in situ* obtained solution of $K[Pt(Me_2SO)Cl_3]$ was placed in an ethylene atmosphere. After 24 h rod-like crystals began to be released from the solution. They were collected on a filter over 4 days, washed with 1% HCl (3×10 ml), ethanol (3×10 ml) and ether (3×3 ml), and dried in air at 20 °C. Yield of *cis*-$[Pt(Me_2SO)(C_2H_4)Cl_2]$: 0.43 g, 45% based on Pt. On heating in the solid phase at 120–130 °C ethylene abstraction takes place and decomposition of the resulting $[Pt(Me_2SO)(\mu\text{-}Cl)Cl]_2$ occurs at 235 °C. These points are in a good agreement with the published data [7, 14]. *Anal.* Calc. for $C_4H_{10}Cl_2OPtS$: Cl, 19.1; Pt, 52.4. Found : Cl, 19.0; Pt, 52.5%.

IR spectra (4000–200 cm^{-1}; relative intensity is given in parentheses), cm^{-1}: (i) *cis*-$[Pt(Me_2SO)(C_2H_4)Cl_2]$: 3465(w), 3014(w), 2911(w), 1634(m, broad), 1411(m), 1400(m), 1321(w), 1241(w), 1148(s), 1096(m), 1022(s), 976(m), 939(w), 918(w), 736(w), 714(w), 688(m), 444(m), 379(m), 340(m), 311(m-w), 225(w), 218(w); (ii) *cis*-$[Pt(Me_2SO)(PhCH_2CN)Cl_2]$: 3471(w), 3059(w), 3001(m), 2938(m), 2914(w), 2900(w), 2316(m), 2282(w), 1958(w), 1598(w), 1495(m), 1454(m), 1398(m), 1311(m), 1294(m), 1200(w), 1185(w), 1149(vs), 1096(s), 1031(vs), 974(m), 940(w), 923(m), 890(w), 745(s), 729(m), 698(s), 617(w), 491(w), 437(m), 379(m), 354(m), 321(m), 282(w), 246(w).

TABLE 1. Crystal data for *cis*-$[Pt(Me_2SO)(C_2H_4)Cl_2]$ and *cis*-$[Pt(Me_2SO)(PhCH_2CN)Cl_2]$

	cis-$[Pt(Me_2SO)(C_2H_4)Cl_2]$	*cis*-$[Pt(Me_2SO)(PhCH_2CN)Cl_2]$
Crystal system	orthorhombic	monoclinic
Space group	*Pmnb*	$P2_1/n$
a (Å)	8.200(1)	12.223(4)
b (Å)	12.924(3)	16.605(4)
c (Å)	8.574(1)	6.779(2)
γ (°)	90	91.10(2)
V (Å^3)	908.7(3)	1375.6(7)
Z	4	4
ρ_{calc} (g cm^{-3})	2.72	2.23
Crystal size (mm)	0.21×0.11×0.14	0.18×0.34×0.09
Absorption correction	yes	yes
μ (cm^{-1})	169.8	112.4
Diffractometer	Nicolet P3	Enraf-Nonius CAD-4
Radiation	λ(Mo Kα) = 0.71069 Å	λ(Mo Kα) = 0.71069 Å
Filter	β	no
Monochromator	no	graphite
Scan type	$\theta/2\theta$	$\theta/2\theta$
2θ scan limits (°)	50	45
Temperature (°C)	23	23
No reflections with $I \geqslant 3\sigma(I)$	721	1649
R	0.029	0.016
R_w	0.030	0.017
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.00153F^2$	$w^{-1} = \sigma^2(F) + 0.0004F^2$

TABLE 2. Atomic parameters ($\times 10^4$) and their equivalent isotropic factors ($Å^2 \times 10^3$) with e.s.d.s in parentheses for *cis*-$[Pt(Me_2SO)(C_2H_4)Cl_2]$

Atom	*x*	*y*	*z*	*U*
Pt	2500	5573(1)	5212(1)	30(1)
Cl(1)	2500	6014(2)	7828(3)	51(1)
Cl(2)	2500	3847(2)	5897(4)	51(1)
S	2500	7240(2)	4562(3)	37(1)
O	2500	7474(6)	2885(10)	55(3)
C(1)	833(15)	7880(8)	5407(13)	54(3)
C(2)	1653(11)	5123(6)	2917(10)	49(3)

TABLE 3. Atomic parameters ($\times 10^4$) and their equivalent isotropic factors ($Å^2 \times 10^3$) with e.s.d.s in parentheses for *cis*-$[Pt(Me_2SO)(PhCH_2CN)Cl_2]$

Atom	*x*	*y*	*z*	*U*
Pt	2322(1)	1733(1)	5587(1)	38(1)
Cl(1)	782(1)	2528(1)	5629(2)	56(1)
Cl(2)	1262(1)	589(1)	5627(2)	63(1)
S	3755(1)	937(1)	5538(2)	48(1)
O	3796(3)	350(2)	3944(6)	72(1)
N	3227(4)	2726(3)	5584(5)	41(1)
C(1)	3823(5)	426(3)	7809(8)	68(2)
C(2)	4998(4)	1493(3)	5541(8)	61(2)
C(3)	3766(4)	3292(3)	5617(6)	47(2)
C(4)	4479(5)	4002(3)	5626(7)	61(2)
C(5)	5681(4)	3793(3)	5507(7)	50(2)
C(6)	6240(5)	3897(4)	3795(10)	72(2)
C(7)	7327(6)	3743(5)	3673(13)	93(3)
C(8)	7869(6)	3466(5)	5305(15)	95(3)
C(9)	7321(6)	3344(4)	7039(15)	87(3)
C(10)	6233(5)	3523(3)	7137(10)	75(2)

TABLE 4. Bond lengths (Å) and bond angles (°) with e.s.d.s for *cis*-$[Pt(Me_2SO)(C_2H_4)Cl_2]$

Bond lengths			
Pt–Cl(1)	2.314(3)	Pt–Cl(2)	2.307(3)
Pt–S	2.225(3)	Pt–C(2)	2.167(8)
Pt–C(2)′	2.167(8)	S–O	1.469(9)
S–C(1)	1.755(12)	S–C(1)′	1.755(12)
C(2)–C(2)′	1.390(18)		
Bond angles			
Cl(1)–Pt–Cl(2)	89.5(1)	Cl(1)–Pt–S	90.2(1)
Cl(2)–Pt–S	179.8(3)	Cl(1)–Pt–C(2)	161.2(2)
Cl(2)–Pt–C(2)	88.4(2)	S–Pt–C(2)	91.9(2)
Cl(1)–Pt–C(2)′	161.2(2)	Cl(2)–Pt–C(2)′	88.4(2)
S–Pt–C(2)′	91.9(2)	C(2)–Pt–C(2)′	37.4(5)
Pt–S–O	116.4(4)	Pt–S–C(1)	110.7(4)
O–S–C(1)	107.9(4)	Pt–S–C(1)′	110.7(4)
O–S–C(1)′	107.9(4)	C(1)–S–C(1)′	102.4(7)
Pt–C(2)–C(2)′	71.3(2)		

TABLE 5. Bond lengths (Å) and bond angles (°) with e.s.d.s for *cis*-$[Pt(Me_2SO)(PhCH_2CN)Cl_2]$

Bond lengths			
Pt–Cl(1)	2.319(2)	Pt–Cl(2)	2.279(2)
Pt–S	2.215(1)	Pt–N	1.968(4)
S–O	1.457(4)	S–C(1)	1.761(6)
S–C(2)	1.764(5)	N–C(3)	1.138(7)
C(3)–C(4)	1.453(8)	C(4)–C(5)	1.519(8)
C(5)–C(6)	1.355(8)	C(5)–C(10)	1.374(8)
C(6)–C(7)	1.360(9)	C(7)–C(8)	1.374(13)
C(8)–C(9)	1.366(13)	C(9)–C(10)	1.369(9)
Bond angles			
Cl(1)–Pt–Cl(2)	91.1(1)	Cl(1)–Pt–S	178.0(1)
Cl(2)–Pt–S	86.9(1)	Cl(1)–Pt–N	88.5(1)
Cl(2)–Pt–N	179.3(1)	S–Pt–N	93.5(1)
Pt–S–O	116.6(2)	Pt–S–C(1)	108.6(2)
O–S–C(1)	108.9(2)	Pt–S–C(2)	111.7(2)
O–S–C(2)	108.2(2)	C(1)–S–C(2)	101.7(3)
Pt–N–C(3)	178.4(4)	N–C(3)–C(4)	178.3(5)
C(3)–C(4)–C(5)	112.5(5)	C(4)–C(5)–C(6)	120.3(5)
C(4)–C(5)–C(10)	120.9(5)	C(6)–C(5)–C(10)	118.8(5)
C(5)–C(6)–C(7)	121.3(6)	C(6)–C(7)–C(8)	119.6(8)
C(7)–C(8)–C(9)	120.3(7)	C(8)–C(9)–C(10)	119.0(8)
C(5)–C(10)–C(9)	121.1(7)		

Results and discussion

General description of the structures

The complexes *cis*-$[Pt(Me_2SO)(C_2H_4)Cl_2]$ and *cis*-$[Pt(Me_2SO)(PhCH_2CN)Cl_2]$ adopt a nearly square-planar geometry with Me_2SO and L ($L = C_2H_4$, $PhCH_2CN$) occupying *cis*-sites (Figs. 1 and 2). In the ethylene complex the Cl(1), Cl(2), Pt, S, O atoms and M (midpoint of C=C bond) lie in a symmetry plane. In the benzyl cyanide complex the atom deviations from the plane passing through Pt, Cl(1), Cl(2), N and S atoms are: 0.003, 0.006, −0.007, −0.008 and 0.007 Å, respectively. In both complexes the angles around the Pt atoms* are close to 90 and 180°.

In both cases the dimethyl sulfoxide molecules are coordinated to the platinum atom via sulfur in agreement with results obtained by analysis of the IR and NMR spectra (see below). The sulfur atoms of Me_2SO ligands in the complexes studied are in an approximate tetrahedral environment. The O–S–C angles (107.9(4), 107.9(4) for the C_2H_4 complex and 108.9(2), 108.2(2)° for the $PhCH_2CN$ complex) and C–S–C angles (102.4(7) for the C_2H_4 complex and 101.7(3)° for the $PhCH_2CN$ complex) are in agreement with those in the free Me_2SO molecule ~107 and 97.4°, respectively [17]. The S=O bond distances (1.469(9) for the C_2H_4 complex and 1.457(4) Å for the

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*In *cis*-$[Pt(Me_2SO)(C_2H_4)Cl_2]$ the S–Pt–M, Cl(1)–Pt–M and Cl(2)–Pt–M angles equal 92.0, 177.8 an 88.3°, respectively.

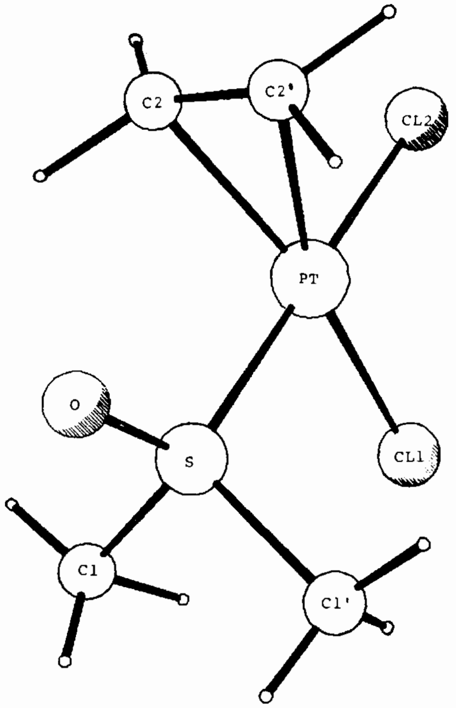

Fig. 1. View of the structure and atom-labelling scheme for *cis*-[Pt(Me$_2$SO)(C$_2$H$_4$)Cl$_2$].

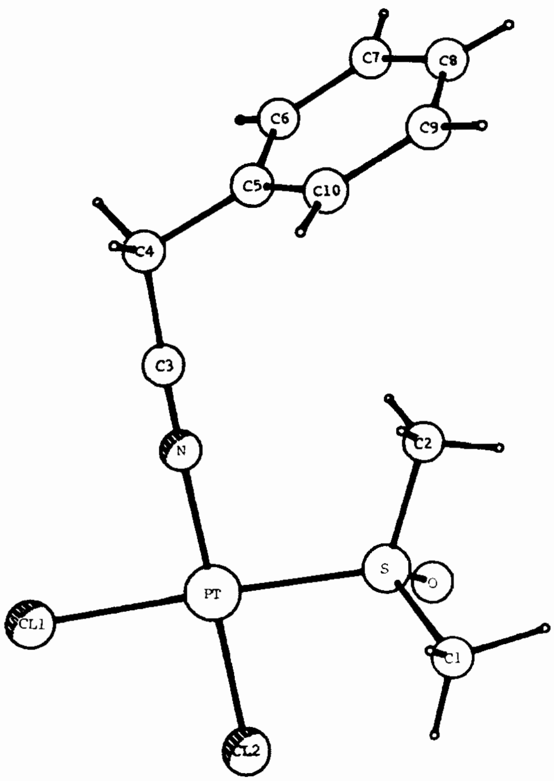

Fig. 2. View of the structure and atom-labelling scheme for *cis*-[Pt(Me$_2$SO)(PhCH$_2$CN)Cl$_2$].

PhCH$_2$CN complex) are consistent with those in other dimethyl sulfoxide Pt(II) complexes (see Table 7 in ref. 5).

Based on the series of *cis*-[Pt(Me$_2$SO)LCl$_2$] complexes (L = C$_2$H$_4$, MeCN [5, 18], PhCH$_2$CN, C$_5$H$_5$N [19], 2Me-C$_5$H$_4$N [20] and NH$_3$ [21], it is possible to conclude that there is no regular trend in rotations of Me$_2$SO ligands relative to the coordination plane or relative to the L ligands. However, in the bis-sulfoxide complexes of the *cis*-[Pt(R^{1}R^{2}SO)$_2$L$_2$] type (in particular, *cis*-[Pt(R$_2$SO)$_2$Cl$_2$]) sulfoxide ligands are in a way oriented with respect to each other (Fig. 3). Table 6 shows that their relative position is such that the oxygen atom of a sulfoxide ligand is directed towards the sulfur atom of the other ligand in the complex. This suggests a weak intramolecular contact S(1)...O(2) or S(2)...O(1)*. Apparently, the inequivalent character of sulfoxide ligands in solid *cis*-[Pt(R^{1}R^{2}SO)$_2$L$_2$] complexes may be attributed to such an interaction. The following relationship holds true for most complexes of the series (Table 6): when the S(1)...O(2) distance is less than the S(2)...O(1) distance

(i) Pt–S(1) bond length is larger than Pt–S(2);

(ii)Pt–S(1)–O(1) bond angle is less than the Pt–S(2)–O(2) one;

(iii) O(1) atom shows larger displacement from the coordination plane than that of the O(2) atom.

When describing *cis*-[Pt(Me$_2$SO)LCl$_2$] (L = C$_2$H$_4$, PhCH$_2$CN) structures it should also be noted that the Pt–Cl bond lengths (*trans* to S) (2.307(3) Å for L = C$_2$H$_4$ and 2.319(2) Å for L = PhCH$_2$CN) and Pt–Cl bond lengths (*trans* to S) in other *cis*-[Pt(Me$_2$SO)LCl$_2$] complexes (L = Me$_2$SO av. 2.309(4) [22] and 2.316(3) Å [23]; MeCN av. 2.316(8) [5] and 2.324(2) Å [18]; C$_5$H$_5$N 2.316(4) Å [19]; 2Me-C$_5$H$_4$N 2.307(4) Å [20]; NH$_3$ 2.321(5) Å [21]) do not strongly

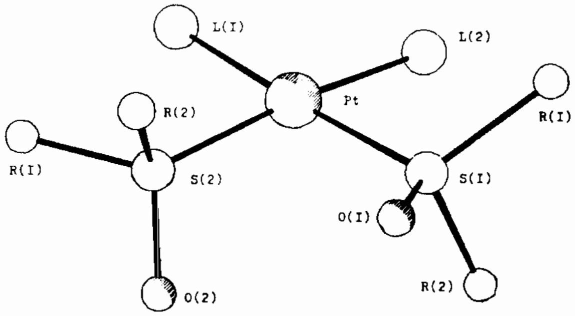

Fig. 3. Schematic representation of the structure for complexes of the *cis*-[Pt(R^{1}R^{2}SO)$_2$L$_2$] type.

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*It is noteworthy that all contacts S(1)...O(2) or S(2)....O(1) in complexes of the *cis*-[Pt(R^{1}R^{2}SO)$_2$L$_2$] type exceed the average value of normal S...O interatomic contact of 3.08 Å [34].

TABLE 6. Some structural data for the complexes with '*cis*-$Pt(R_2SO)_2$' units

Complex	Reference	Interatomic distances (Å)				Angles (°)		Deviation of O(1)(O(2)) atoms from coordination plane (Å)
		Pt–S(1) Pt–S(2)	S(2)–O(1) S(1)–O(2)	S(1)–O(1) S(2)–O(2)	Pt–L(1) Pt–L(2)	Pt–S(1)–O(1) Pt–S(2)–O(2)	Dihedral angle[a]	
$[Pt(Me_2SO)_2Cl_2]^b$	22	2.244	3.444	1.459	2.307	112.75	119.64	1.250
		2.228	3.112	1.452	2.312	117.49	10.88	−0.273
	23	2.251	3.457	1.473	2.314	112.62	119.87	−1.250
		2.238	3.115	1.456	2.318	117.01	10.87	0.268
$[Pt(Me_2SO)_2Br_2]$	24	2.260	3.426	1.463	2.442	111.8	120.9	−1.283
		2.244	3.125	1.486	2.447	117.1	12.3	0.347
$[Pt(Me_2SO)_2Ph_2]^b$	25	2.325	3.335	1.480	2.043	113.47	45.57	1.090
		2.315	3.313	1.474	2.049	115.49	38.55	−0.921
$[Pt(Me_2SO)_2(O_2C_6Cl_4)]^b$	26, 27	2.224	3.345	1.451	1.995	118.82	5.09	−0.095
		2.238	4.724	1.468	2.017	114.68	3.35	−0.049
$[Pt(Me_2SO)_2(\mu\text{–}OH)]_2\text{-}(ClO_4)_2^b$	28	2.224	3.722	1.478	2.028	113.93	74.47	1.280
		2.203	3.267	1.466	2.064	119.52	172.12	−0.068
$[Pt(Me_2\underline{S}O)_2(Me_2S\underline{O})_2]\text{-}(CF_3SO_3)_2^{d,\,c}$	29	2.208	3.233	1.453	2.051	118.5	2.0	0.061
		2.205	2.838	1.454	2.040	112.2	3.4	−0.059
$[Pt(Me_2SO)_2En]\text{-}(PF_6)_2 \cdot Me_2SO^c$	30	2.248	4.633	1.467	2.068	110.2	9.4	−0.257
		2.248	3.237	1.452	2.064	116.4	161.4	0.443
$[Pt(MeEtSO)_2Cl_2]^c$	31	2.257	3.299	1.470	2.312	118.9	3.5	−0.009
		2.272	4.703	1.460	2.317	116.6	5.3	−0.183
$[Pt(C_4H_8SO)_2Cl_2]^b$	32	2.247	3.701	1.460	2.310	114.53	74.21	−1.301
		2.227	3.089	1.456	2.313	115.93	3.32	−0.066
$[Pt\{(n\text{-}Pr)_2SO\}_2Cl_2]^c$	31	2.263	4.742	1.459	2.302	117.4	0.9	0.002
		2.248	3.272	1.471	2.288	116.4	2.1	0.055
$[Pt(Me^ptolSO)_2Cl_2]^c$	33	2.249	3.402	1.482	2.303	112.1	57.2	−1.235
		2.239	3.147	1.473	2.299	116.6	24.3	0.613

[a] Dihedral angle between the coordination plane and that passing through Pt, S(1), O(1) and Pt, S(2), O(2) atoms. [b] Estimated by the authors from the data published in the Cambridge Structural Databank. [c] Estimated by the authors from the data published in original papers. [d] Distance O(2)–S(3) shown instead of O(2)–S(1) because it is much shorter.

depend on the pattern of the L ligand. Apparently, Pt–Cl bond lengths (*trans* to S) are mainly determined by the *trans*-influence of dimethyl sulfoxide.

In the molecule of *cis*-$[Pt(Me_2SO)(C_2H_4)Cl_2]$ ethylene is perpendicular to the coordination plane which is known from other ethylene Pt(II) complexes characterized by X-ray structure analysis (Table 7). C=C distance is 1.39(2) Å and Pt–M is 2.052(7) Å. These bond lengths are consistent with those of other C_2H_4–$[Pt^{II}]$ complexes. Pt–Cl bond length (*trans* to C_2H_4) equals 2.314(3) Å which is slightly shorter than the Pt–Cl bond lengths (*trans* to C_2H_4) in $K[Pt(C_2H_4)Cl_3]\cdot H_2O$, *cis*-$[Pt(C_2H_4)_2Cl_2]$ and *cis*-$[Pt(C_2H_4)(C_7H_{13})Cl_2]$ (Table 7).

In the complex *cis*-$[Pt(Me_2SO)(PhCH_2CN)Cl_2]$ as in other Pt(II) organonitrile compounds [5, 45–53] the fragment Pt–N≡C–C is linear. Pt–N–C and N–C–C angles are 178.4(4) and 178.3(5)°, respectively. Pt–N and N≡C bond lengths equal 1.968(4) and 1.138(7) Å which is in agreement with av. 1.967(15) and av. 1.149(15) Å [5] and also with 1.976(7) and 1.153(11) Å [18] in *cis*-$[Pt(Me_2SO)(MeCN)Cl_2]$. The Pt–Cl (*trans* to N) distance (2.279(2) Å) also in fact does not differ from that in *cis*-$[Pt(Me_2SO)(MeCN)Cl_2]$ (av. 2.278(2) [5] and 2.282(2) Å [18]).

cis-Influence of ethylene and benzyl cyanide in complexes of the cis-$[Pt(Me_2SO)LCl_2]$ *type*

As mentioned above, the Pt–S bond lengths in complexes of the *cis*-$[Pt(Me_2SO)LCl_2]$ type can be used as indicators of the L ligand *cis*-influence. Structural studies enabled us to construct a *cis*-influence series which according to decreasing Pt–S bond lengths (Å) is as follows: Me_2SO (2.240(9)) > C_2H_4 (2.225(3)) ≥ MeCN (av. 2.222(5)), $PhCH_2CN$ (2.215(1)) > C_5H_5N (2.209(4)) ≥ 2Me-C_5H_4N (2.200(3)) > NH_3 (2.186(4)). The ligands having pronounced π-acceptor properties and fairly strong σ-donors are arranged in the left and right part of the series respectively. The relative position of N-donor ligands (MeCN, C_5H_5N, NH_3) in the *cis*-influence series is consistent with that of the Chatt constants series [54] also reflecting the π-acceptor and σ-donor ability of ligands.

IR spectra of complexes of the cis-$[Pt(Me_2SO)LCl_2]$ *series*

ν(SO) and γ^{as}(CSO) bands

The bands assigned as ν(SO) of coordinated sulfoxides exhibit high intensity and occur in a relatively narrow spectral range of 1200–900 cm^{-1} for different platinum complexes and different S- and O-coordinated R_2SO (Table 8). By the S-coordination the ν(SO) band is considered to displace into the high frequency range and by the O-coordination, to the low frequency range as compared to the ν(SO) band in the R_2SO free molecule. As a rule the ν(SO) band in complexes of the $[Pt^{II}]$–$S(O)R_2$ type fall within the range of 1000–1160 cm^{-1} [61]; in complexes of the $[Pt^{IV}]$–$S(O)R_2$ type, in the range of 1180–1150 cm^{-1} (Table 8) and in complexes of the $[Pt^{II}]$–OSR_2 type, in the range of 900–1000 cm^{-1} [61]. The position of the ν(SO) band often being used for the determination of a coordination mode of the R_2SO molecules, two possibilities of errors occurring are to be taken into account.

First, the ν(SO) band in the free R_2SO molecules is highly sensitive to spectrum measurement conditions. For example, the frequency of ν(SO) decreases by about 50 cm^{-1} as Me_2SO passes from the gaseous phase into the liquid phase [61]; the position of the band is also strongly dependent on solvent properties [62]. Naturally, in those cases when R_2SO coordination to metal ions leads to slight changes in $\Delta\nu$(SO) (see ref 63) a question arises as what the values of ν(SO) of the R_2SO free molecule can be compared with.

Second, the determination of the R_2SO coordination mode based on the change in $\Delta\nu$(SO) is incorrect in the case when a corresponding spectral range is overlapped by other bands.

To reliably identify the sulfoxide coordination mode some additional criterion should be used apart from the $\Delta\nu$(SO) criterion. In particular, in ref. 64 it is the presence or absence of the γ^{as}(CSO) band in the case of the Me_2SO-containing complexes. The band is present in spectra of the S-coordinated molecules and absent in those of the O-coordinated complexes. The γ^{as}(CSO) falls in the fairly narrow spectral range (370–390 cm^{-1}) and is not strongly dependent on metal ions [64], intermolecular interactions [65] and the type, structure, and charge of the complex (Tables 8, 9). Unfortunately, the vibrations of γ^{as}(CSO) are spectrally more complexly manifested in complexes of the $[M]$–$S(O)R_2$ ($R \neq Me$) type and hence cannot be used for determination of a coordination mode.

ν(Pt–S) bands

Medium intensity bands in the 400–500 cm^{-1} range in spectra of platinum complexes with S-coordinated sulfoxides usually belong to ν(Pt–S) vibrations (see refs. 61, 63 and loc. cit.). Such high frequencies of ν(Pt–S) bands in complexes of the $[Pt]$–$S(O)R_2$ type as compared to complexes of the $[Pt]$–SR_2 type (320 ± 20 cm^{-1} [66]) may be attributed to a shorter Pt–S bond in sulfoxide compounds (Table 9) as compared to thioether ones (2.26–2.27 Å [66–70]).

TABLE 7. Some structural parameters for C_2H_4–[Pt(II)] complexes

Complex	Dihedral angle[a] (°)	Angle[b] (°)	Pt–M[c]	C=C′	Pt–C	Pt–C′	Pt–Cl (*trans* to C_2H_4)	Pt–Cl (*cis* to C_2H_4)	Pt–Cl′ (*cis* to C_2H_4)	Reference
K[Pt(C_2H_4)Cl_3]·H_2O	88.95	3.07	2.016	1.375	2.127	2.134	2.340	2.301	2.302	35
	90.00	3.05	2.040	1.375	2.140	2.165	2.335	2.297	2.297	36
cis-[Pt(C_2H_4)$_2$$Cl_2$]	84.50	5.66	2.082	1.434	2.205	2.198	2.304	3.303		37, 38
	88.51	2.12	2.075	1.445	2.230	2.164	2.303	2.304		
cis-[Pt(C_2H_4)(Me_2SO)Cl_2]	90.00	0.00	2.052	1.390	2.167	2.167	2.314	2.307		this work
cis-[Pt(C_2H_4)($C_7H_{13}N$)Cl_2][d]	90.00	0.00	2.044	1.354	2.154	2.154	2.337	2.284		39
trans-[Pt(C_2H_4)(C_6H_7N)Cl_2][e]	85.79	4.58	2.040	1.320	2.154	2.134		2.290	2.293	40
	89.35	3.59	2.067	1.389	2.210	2.150		2.294	2.292	41
trans-[Pt(C_2H_4)($C_8H_{11}N$)Cl_2][f]	89.97	0.84	2.055	1.363	2.141	2.189		2.296	2.295	41
trans-[Pt(C_2H_4)(C_7H_9N)Cl_2][g]	72.23	17.77	2.045	1.495	2.177	2.177		2.291	2.291	42
trans-[Pt(C_2H_4)(Me_2NH)Cl_2]	90.00	0.00	2.088	1.474	2.215	2.215		2.300	2.333	43
trans-[Pt(C_2H_4)($C_3H_4N_2$)][h]	88.66	3.42	2.041	1.361	2.123	2.179		2.282	2.279	44

[a] Dihedral angle between PtCC′ plane and coordination plane. [b] Angle between the vector drawn across C and C′ atoms and the normal to the coordination plane. [c] M is the midpoint of the coordinated C=C bond. [d] $C_7H_{13}N$ = 2,6-dimethylpiperidine. [e] C_6H_7N = 4-methylpyridine. [f] $C_8H_{11}N$ = 2,4,6-trimethylpyridine. [g] C_7H_9N = 2,6-dimethylpyridine. [h] $C_3H_4N_2$ = pyrazole.

TABLE 8. Some IR data[a] for the different type dimethyl sulfoxide Pt(II) and Pt(IV) complexes

Complex	ν(SO) (cm^{-1})	γ^{as}(CSO) (cm^{-1})	ν(PtS)[b] (cm^{-1})	ν(PtCl) ,(cm^{-1})	Reference	
					IR	X-ray
K[Pt(Me_2SO)Cl_3]	1100	384	440	350 and 313	this work	55
(Ph_3PCH_2Ph)[Pt(Me_2SO)Cl_3]	1125 and 1110	379	440	343 and 304	this work	56
cis-[Pt(Me_2SO)$_2$$Cl_2$]	1155 and 1131	379	430	334 and 310	this work	22, 23
trans-[Pt(Me_2SO)$_2$$Cl_2$]	1130	376	415	350	57 and this work	
[Pt(Me_2SO)(μ-Cl)Cl]$_2$	1152	376	445	365, 290 and 260	this work	
cis-[Pt($Me_2\underline{S}O$)$_2$($Me_2S\underline{O}$)$_2$]X_2	1154, 1143 and 897, 879	[c]	455 and 438		58[d]	29[e]
[PtEn(Me_2SO)Cl]Cl	1145	[c]	434	344	59	
cis-[Pt(Me_2SO)PyCl_4]	1162	375	427	347, 329 and 316	this work	
trans-[Pt(Me_2SO)PyCl_4]	1179	376	452 and 431	350 and318(sh)	this work	
(Et_4N)[Pt(Me_2SO)Cl_5]	1172	374	429	340 and 320(sh)	this work	60
[Pt(Me_2SO)$_2$$Cl_4$]	1161	375	424	350	this work	

[a] All spectra were recorded in KBr pellets. [b] Such an assignment seems debatable. [c] This band is not discussed in a corresponding publication. [d] X = ClO_4. [e] X = CF_3SO_3.

TABLE 9. Some bands in IR spectra of the *cis*-[Pt(Me_2SO)(ligand)Cl_2] series

Ligand	Pt-S (Å)	ν(SO) (cm^{-1})	γ^{as}(CSO) (cm^{-1})	ν(PtS)[a] (cm^{-1})	ν(PtCl) (cm^{-1})	
					ν^{as}	ν^{S}
Me_2SO	av. 2.240[b]	1155 and 1131	379	430	334	310
Me_2S		1143	378	444	333	309
C_2H_4	2.225	1148	380	444	342 and 330	311
MeCN	av. 2.222[b]	1147	375	439	358	320
$PhCH_2CN$	2.215	1149	379	437	354	321
PhCN		1145	376	439	356	322
C_5H_5N	2.209	1150 and 1141	378	443	345	318
2Me-C_5H_4N	2.200	1138	376	452 and 438	348	323
NH_3	2.186	1128	383	443	342	309

[a] Such an assignment seems debatable. [b] Average value for two independent measurements.

TABLE 10. Selected ^1H, ^{13}C and ^{195}Pt NMR parameters for *cis*-[Pt(Me_2SO)LCl_2] series (DMF-d_7 solutions) along Pt–S bond lengths

Ligand	Pt-S (Å)	^1H NMR: δ (ppm) ($^3J(^{195}Pt-^1H)$) for Me_2SO ligands	^{13}C NMR: δ (ppm) ($^2J(^{195}Pt-^{13}C)$) for Me_2SO ligands	^{195}Pt NMR: δ (ppm) ($^1J(^{195}Pt-^{14}N)$)
Me_2SO	av. 2.240	3.56(23) 3.62(23), acetone-d_6 [56]	44.29(52)	−3463 −3459, Me_2SO [74]
Me_2S		3.45(23) 3.60(23), acetone-d_6 [12]	4.69(56)	−3528
C_2H_4	2.225	3.55(20) 3.55(20), $CDCl_3$ [8]	43.85(44)	−3515
MeCN	av. 2.222	3.37(23) 3.49(23), acetone-d_6 [5]	44.34(59)	−3007(356 ± 10)
$PhCH_2CN$	2.215	3.37(24)	44.39(56)	−3007(350 ± 20)
PhCN		3.37(26)	44.39(59)	−2994(350 ± 20)
C_5H_5N	2.209	3.25(26)	44.10(59)	−2867(260 ± 20) −2856, Me_2SO-d_6 [75]
2Me-C_5H_4N	2.200	3.39(24)	44.43(61)	−2879(275 ± 10) −2871, Me_2SO-d_6 [75]
NH_3	2.186	3.34(26)	44.19(59)	−3044(210 ± 10) −3046, Me_2SO-d_6 [76]

To a first approximation and disregarded kinematic factors it is natural to look for the ν(Pt–S) bands in the platinum sulfoxide compounds in a more high frequency spectral range as compared to that of thioether compounds.

There is also some doubt as to correct assignment of the ν(Pt–S) frequency due to the fact that frequencies of absorption bands of about 440 cm^{-1} in IR spectra of complexes in the *cis*-[Pt(Me_2SO)LCl_2] series do not actually change despite changes in the Pt–S bond lengths (Table 9). Table 8 shows that frequencies of absorption bands commonly assigned to ν(Pt–S) vary slightly as the type of Pt(II) complex changes, even on oxidation of Pt(II) complexes into corresponding Pt(IV) complexes. The latter seems even more strange because the Pt–S bond becomes longer by more than 0.1 Å on oxidation of [Pt^{II}]–S(O)R_2 into [Pt^{IV}]–S(O)R_2 [60]. Apparently, the identification of the ν(Pt–S) absorption bands in IR spectra of sulfoxide complexes needs to be studied in more detail.

ν(Pt–Cl) bands

The ν(Pt–Cl) bands exhibit a fairly high intensity and fall in the 350–280 cm^{-1} range [71, 72]. As a rule it is not difficult to identify these bands. As one would expect for *cis*-[Pt(Me$_2$SO)LCl$_2$] compounds there are two bands ν^{as}(Pt–Cl) and ν^{s}(Pt–Cl) in the above spectral range (Table 9). It has been shown in ref. 73 that asymmetry of the PtCl$_2$ fragment along the bond lengths in the main factor responsible for the splitting of $\Delta\nu(\text{Pt–Cl}) = \nu^{as} - \nu^{s} \geqslant 20$ cm^{-1}. The asymmetry in turn is determined by the mutual influence of ligands and especially by the *trans*-influence of ligands. The calculation of the interatomic Pt–Cl distances in the series of *cis*-[Pt(Me$_2$SO)LCl$_2$] complexes based on the ν(Pt–Cl) frequency analysis [72] gives Pt–Cl interatomic distances close to those obtained using X-ray structure analysis.

NMR spectra of complexes of the cis-[Pt(Me$_2$SO)LCl$_2$] series

Table 10 shows parameters for ^{1}H, ^{13}C and ^{195}Pt NMR spectra of the series of *cis*-[Pt(Me$_2$SO)LCl$_2$] complexes in DMF-d$_7$. In ^{1}H NMR spectra the signal from methyl groups of the coordinated dimethyl sulfoxide has a satellite structure from ^{195}Pt–^{1}H coupling; it falls about 1 ppm in the low field as compared to that from free Me$_2$SO. The range of chemical shifts and $^3J(^{195}\text{Pt}–^1\text{H})$ values imply [63] the S-coordination of the dimethyl sulfoxide molecules in all the complexes studied.

In the ^{13}C{^{1}H} NMR spectra of the *cis*-[Pt(Me$_2$SO)LCl$_2$] compounds the signal of the methyl

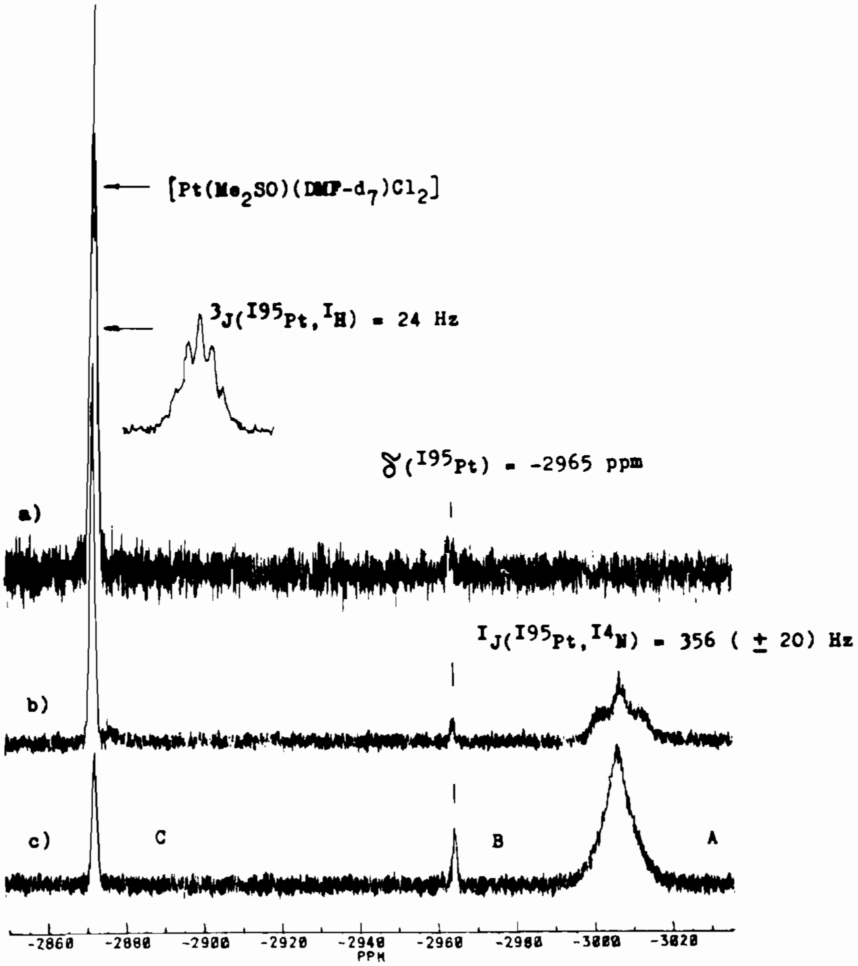

Fig. 4. ^{195}Pt NMR spectra at a frequency of 64.386 (b, c) and 43.022 (a) MHz for solutions in DMF-d$_7$: a) *trans*-[Pt(Me$_2$SO)(μ-Cl)Cl]$_2$ kept at 70 °C for 1 h; b) *cis*-[Pt(Me$_2$SO)(PhCH$_2$CN)Cl$_2$] for 1 h after dissolution at the ambient temperature; c) *cis*-[Pt(Me$_2$SO)(PhCH$_2$CN)Cl$_2$] kept in about 20 min after dissolution at the ambient temperature (~25 °C).

group carbon of the inner-sphere Me_2SO was recorded in a low field as compared to that of the free ligand; besides ^{13}C–^{195}Pt coupling occurs on the spectra which is characteristic of the S-bound dimethyl sulfoxide molecules [77]. Therefore, in solutions of the *cis*-[Pt(Me_2SO)LCl_2] complexes in DMF-d_7 the S-coordination of Me_2SO molecules takes place as in the solid phase.

Signals in the $^{195}Pt\{^1H\}$ NMR spectra of the *cis*-[Pt(Me_2SO)LCl_2] complexes appear within the range of chemical shifts from −2867 to 3528 ppm. In the complexes with N-donor ligands the ^{195}Pt signals exhibit broadening and have a triplet structure (with triplet component intensities ratio 1:1:1) due to the ^{195}Pt–^{14}N coupling. The values of $^1J(^{195}Pt–^{14}N)$ decrease when hybridization of the N-donor atom of the coordinated ligand changes form sp- to sp^2- and then to sp^3-type.

It is noteworthy that the *cis*-[Pt(Me_2SO)(RCN)Cl_2] complexes in solutions of dimethyl formamide are subject to solvolysis. For example, in ^{195}Pt NMR spectra apart from the signal from *cis*-[Pt(Me_2SO)($PhCH_2CN$)Cl_2] (A) signals are registered with chemical shifts −2965 (B) and −2872 (C) (Fig. 4). The intensity of line C increases with exposition of the solution and concurrently the intensity of signal A decreases; the resonance line B has a low intensity under all conditions. Figure 4 shows that signal C is identical to that from the complex [Pt(Me_2SO)(DMF-d_7)Cl_2] ($\delta(^{195}Pt)$ −2871 ppm, septet, $^3J(^{195}Pt–^1H)$ 24 Hz; $\delta(^{13}C)$ 45.55 ppm, $^2J(^{195}Pt–^{13}C)$ 64 Hz]. The latter results from the dimer-splitting reaction

$$[Pt(Me_2SO)(\mu\text{-}Cl)Cl]_2 + 2DMF\text{-}d_7 \longrightarrow 2[Pt(Me_2SO)(DMF\text{-}d_7)Cl_2]$$

Apparently, signals C and B belong to different geometric isomers of the complex [Pt(Me_2SO)(DMF-d_7)Cl_2].

The data listed in Table 10 show that the change of substituents in the ligands of the same type does not strongly affect the ^{195}Pt chemical shifts. The absence of such spectral changes has been reported earlier for complexes of the $[Pt(PR_3)Cl_3]^-$ type having different PR_3 phosphines [78]. In the ^{195}Pt NMR spectra of the complexes *cis*-[Pt(Me_2SO)LCl_2] the ^{195}Pt chemical shift depends on the type of donor atom; there is no evident correlation between Pt–S(O)Me_2 bond distances and values of ^{195}Pt chemical shifts. Based on the data obtained by the authors and those by Kerrison and Sadler [74] it is possible to construct a magnetochemical series of the ligands: OH^- < Py, 2Me-Py < Cl < MeCN, PhCN, PhCH_2CN < NH_3; Br^- < Me_2SO < C_2H_4, Me_2S.

This series is mainly consistent with that for the Pt(IV) complexes [79].

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Note added in proof

After reading this paper, Professor M. A. Porai-Koshits noted that all bis-sulfoxide complexes which are listed in Table 6 may be divided into two types. In complexes of the first type the oxygen atom of one of the sulfoxide ligands occupies a non-equatorial position and contacts with an equatorial oxygen atom of another R_2SO ligand. In the second type of complex oxygen atoms of both the sulfoxide ligands have an equatorial position. Differences in Pt—S distances and Pt—S—O angles are manifested clearly in the first type of complex. Apparently, equatorial orientation of the S=O bond makes π-conjugation of the Pt d_{π} orbitals on the line Pt—S—O easy. This leads to strengthening of the S=O π-interaction. The latter results in a shortening of the Pt—S and S=O bond lengths and an increase of the Pt—S—O angle due to repulsion of electrons of the Pt—S and S=O bonds. We thank Professor M. A. Porai-Koshits for helpful discussions.