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X-ray Structure Determination of *cis*-Dichloro(dimethyl sulfoxide)(acetonitrile)platinum(II) and *cis*-Dibromo(dimethyl sulfoxide)(acetonitrile)platinum(II). *cis*-Influence of Ligands in the Complexes *cis*-[Pt(Me_2SO)(ligand)Cl_2]

VITALII K. BELSKY, VADIM E. KONOVALOV

L. Ya. Karpov Physico-Chemical Institute, Obukha St. 10, 103064, Moscow (U.S.S.R.)

VADIM YU. KUKUSHKIN*

Chemical Department, Leningrad State University, Universitetsky Pr. 2, 198904, Stary Petergof (U.S.S.R.)

and ANATOLII I. MOISEEV

General and Inorganic Chemistry, Lensovet Leningrad Technological Institute, Zagorodny Pr. 49, 198013, Leningrad (U.S.S.R.)

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Abstract

The reaction of the complexes K[Pt(Me_2SO)X_3] (X = Cl, Br) with MeCN in water results in the isolation of solid *cis*-[Pt(Me_2SO)(MeCN)X_2] complexes. The latter complexes were characterized by the elemental analysis, IR and ^{1}H NMR spectra and their structure was determined by the X-ray analysis.

The complexes *cis*-[Pt(Me_2SO)(MeCN)X_2] are isostructural. *cis*-[Pt(Me_2SO)(MeCN)Cl_2] crystallizes in the triclinic space group $P\bar{1}$. The unit cell parameters are: a = 7.346(1), b = 8.865(1), c = 14.886(2) Å, α = 90.58(1), β = 96.10(1), γ = 87.44(2)°, V = 962.9(3) Å^3, ρ_{calc} = 2.65 g cm^{-3}, Z = 4; bond lengths in two crystallographically independent molecules (Å): Pt–Cl (*trans* to N) 2.278(2), 2.278(2); Pt–Cl (*trans* to S) 2.310(3), 2.322(3), Pt–N 1.977(8), 1.956(8); Pt–S 2.216(2), 2.224(3).

cis-[Pt(Me_2SO)(MeCN)Br_2] crystallizes in the triclinic space group $P\bar{1}$. The unit cell parameters are: a = 7.569(1), b = 9.053(2), c = 15.014(3) Å, α = 90.33(1), β = 95.20(1), γ = 87.12(1)°, V = 1023.3(4) Å^3, ρ_{calc} = 3.08 g cm^{-3}, Z = 4; bond lengths in two crystallographically independent molecules (Å) are: Pt–Br (*trans* to N) 2.397(2), 2.394(2), Pt–Br (*trans* to S) 2.429(2), 2.427(2), Pt–N 1.983(13), 1.986(14), Pt–S 2.228(4), 2.233(5).

Comparison of the data with those known from the literature suggests a mutual ligands influence in the *cis*-[Pt(Me_2SO)(ligand)X_2] complexes.

Introduction

The relative value of the *trans*- and *cis*-effects of dimethyl sulfoxide [1, 2] and the *trans*-effect of acetonitrile [3, 4] have been widely discussed. However, the *trans*- and *cis*-influence of Me_2SO and MeCN have been fairly poor studied. The authors have prepared single crystals of the complexes *cis*-[Pt(Me_2SO)(MeCN)X_2] (X = Cl(1), Br(2)) which provide both dimethyl sulfoxide and acetonitrile molecules. They can be used as targets for the analysis of mutual ligands influence in the complexes. The main purpose of the paper is to study the *trans*- and *cis*-influence of Me_2SO and MeCN on the basis of the X-ray structure analysis.

Experimental

Starting materials for the synthesis – the complexes K[Pt(Me_2SO)X_3] (X = Cl, Br) – were prepared by the methods described in refs. 5 and 6. Infrared spectra were recorded using a Perkin-Elmer model 983G spectrometer in pellets with KBr. ^{1}H NMR spectra were recorded using a Bruker model WP-80, in acetone-d_6 with TMS as internal standard. The points of acetonitrile abstraction and decomposition of the complexes were measured using Kofler tables. Elemental analysis was performed by the Chair of Analytical Chemistry at the Leningrad State University. 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.

Preparation of the Complexes

cis-[Pt(Me_2SO)(MeCN)Cl_2]

cis-[Pt(Me_2SO)(MeCN)Cl_2] was prepared by the method described in ref. 7 by interaction of a K[Pt(Me_2SO)Cl_3] water solution and excess MeCN. *cis*-[Pt(Me_2SO)(MeCN)Cl_2] was isolated in the solid

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*Authors to whom correspondence should be addressed.

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TABLE 1. Crystal data for *cis*-[Pt(Me$_2$SO)(MeCN)Cl$_2$] (1) and *cis*-[Pt(Me$_2$SO)(MeCN)Br$_2$] (2)

	1	2
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	7.346(1)	7.569(1)
b (Å)	8.865(1)	9.053(2)
c (Å)	14.886(2)	15.014(3)
α (°)	90.58(1)	90.33(1)
β (°)	96.10(1)	95.20(1)
γ (°)	87.44(2)	87.12(1)
V (Å^3)	962.9(3)	1023.3(3)
Z	4	4
ρ_{calc} (g cm^{-3})	2.65	3.08
Crystal size (mm)	0.04 × 0.14 × 0.24	0.13 × 0.01 × 0.01
μ (cm^{-1})	160.3	223.0
Diffractometer	Nicolet P3	Sintex $P\bar{1}$
Radiation	Mo Kα	Mo Kα
Filter	Nb	Nb
2θ scan limits (°)	50	50
Temperature (°C)	23	23
No. of reflections with $I \geqslant 3\sigma(I)$	2402	2443
R	0.032	0.043
R_w	0.032	0.048

TABLE 2. Atom coordinates (×10^4) and equivalent isotropic temperature factors (Å^2 × 10^3) for *cis*-[Pt(Me$_2$SO)(MeCN)Cl$_2$]

Atom	x	y	z	U
Pt(1)	2326(1)	4594(1)	9247(1)	28(1)
Pt(2)	2208(1)	184(1)	4231(1)	30(1)
Cl(1)	1971(4)	3796(3)	7782(2)	55(1)
Cl(2)	1281(4)	6998(3)	8805(2)	49(1)
Cl(3)	1526(4)	224(3)	2702(2)	51(1)
Cl(4)	1833(4)	−2402(3)	4244(2)	48(1)
S(1)	3262(4)	2251(3)	9618(2)	34(1)
S(2)	2589(4)	2654(3)	4174(2)	38(1)
O(1)	4830(10)	1614(7)	9187(5)	46(2)
O(2)	4026(11)	3108(8)	3626(5)	60(3)
N(1)	2616(11)	5318(8)	10513(5)	38(3)
N(2)	2769(11)	65(9)	5543(6)	40(3)
C(1)	3699(15)	2018(12)	10814(7)	51(4)
C(2)	1351(20)	1066(14)	9364(11)	58(5)
C(3)	473(15)	3558(11)	3751(8)	55(4)
C(4)	3010(17)	3465(12)	5273(8)	54(4)
C(5)	2831(13)	5761(10)	11250(7)	37(3)
C(6)	3054(21)	6236(16)	12150(8)	69(5)
C(7)	3087(14)	−155(10)	6297(7)	39(3)
C(8)	3523(16)	−443(16)	7269(7)	61(5)

TABLE 3. Atom coordinates (×10^4) and equivalent isotropic temperature factors (Å^2 × 10^3) for *cis*-[Pt(Me$_2$SO)(MeCN)Br$_2$]

Atom	x	y	z	U
Pt(1)	2342(1)	4472(1)	9259(1)	31(1)
Pt(2)	2237(1)	222(1)	4229(1)	34(1)
Br(1)	1873(3)	3601(3)	7750(1)	67(1)
Br(2)	1184(3)	6923(2)	8789(1)	57(1)
Br(3)	1540(3)	220(2)	2642(1)	60(1)
Br(4)	1902(3)	−2429(2)	4263(1)	62(1)
S(1)	3369(5)	2197(4)	9650(3)	36(1)
S(2)	2617(6)	2648(5)	4156(3)	44(1)
O(1)	4837(15)	1571(12)	9185(7)	47(4)
O(2)	3992(16)	3116(14)	3589(9)	61(5)
N(1)	2709(16)	5247(14)	10497(9)	33(4)
N(2)	2811(18)	117(16)	5545(10)	43(5)
C(1)	3841(26)	2035(19)	10816(11)	51(7)
C(2)	1659(24)	977(19)	9473(12)	46(6)
C(3)	591(27)	3588(20)	3786(12)	55(7)
C(4)	2969(25)	3447(20)	5219(13)	54(7)
C(5)	2872(21)	5703(18)	11186(11)	37(6)
C(6)	3120(26)	6199(22)	12115(11)	54(7)
C(7)	3087(22)	−127(20)	6278(12)	43(6)
C(8)	3441(26)	−437(24)	7208(11)	57(7)

phase in the form of light yellow crystals as 'sticks'. On heating in the solid phase at 145–150 °C acetonitrile molecule abstraction takes place and decomposition of the resulting [Pt(Me$_2$SO)(μ-Cl)Cl]$_2$ occurs at 235 °C. *Anal.* Calc. for C$_4$H$_9$Cl$_2$NOPtS: Cl, 18.4; Pt, 50.7. Found: Cl, 18.3; Pt, 50.8%. IR (KBr) cm^{-1}; 2339m and 2312mw (ν(CN)), 1147vs (ν(SO)), 439m (ν(PtS)), 375m (γ(CSO)), 359s and 336s (ν(PtCl)). ^{1}H NMR, δ: 3.49 ppm (J(PtH) 22.5 Hz), 2.68 ppm (J(PtH) 14.2 Hz).

cis-[Pt(Me$_2$SO)(MeCN)Br$_2$]

To a solution of K[Pt(Me$_2$SO)Br$_3$] (0.50 g, 0.9 mmol) in water (15 ml) was added acetonitrile (0.62

TABLE 4. Bond lengths (Å) and bond angles (°) for *cis*-[Pt(Me$_2$SO)(MeCN)Cl$_2$]

Bond lengths			
Pt(1)–Cl(1)	2.278(2)	Pt(1)–Cl(2)	2.310(3)
Pt(1)–S(1)	2.216(2)	Pt(1)–N(1)	1.977(8)
Pt(2)–Cl(3)	2.278(2)	Pt(2)–Cl(4)	2.322(3)
Pt(2)–S(2)	2.224(3)	Pt(2)–N(2)	1.956(8)
S(1)–O(1)	1.465(8)	S(1)–C(1)	1.788(10)
S(1)–C(2)	1.796(15)	S(2)–O(2)	1.472(9)
S(2)–C(3)	1.774(11)	S(2)–C(4)	1.782(12)
N(1)–C(5)	1.160(13)	N(2)–C(7)	1.138(14)
C(5)–C(6)	1.395(16)	C(7)–C(8)	1.471(15)
Bond angles			
Cl(1)–Pt(1)–Cl(2)	90.3(1)	Cl(1)–Pt(1)–S(1)	87.5(1)
Cl(2)–Pt(1)–S(1)	177.5(1)	Cl(1)–Pt(1)–N(1)	179.1(2)
Cl(2)–Pt(1)–N(1)	88.8(2)	S(1)–Pt(1)–N(1)	93.4(2)
Cl(3)–Pt(2)–Cl(4)	90.6(1)	Cl(3)–Pt(2)–S(2)	87.8(1)
Cl(4)–Pt(2)–S(2)	178.2(1)	Cl(3)–Pt(2)–N(2)	177.7(3)
Cl(4)–Pt(2)–N(2)	87.2(2)	S(2)–Pt(2)–N(2)	94.5(2)
Pt(1)–S(1)–O(1)	116.7(3)	Pt(1)–S(1)–C(1)	112.0(4)
O(1)–S(1)–C(1)	109.2(5)	Pt(1)–S(1)–C(2)	107.7(4)
O(1)–S(1)–C(2)	109.0(6)	C(1)–S(1)–C(2)	101.0(7)
Pt(2)–S(2)–O(2)	115.4(3)	Pt(2)–S(2)–C(3)	108.5(3)
O(2)–S(2)–C(3)	109.0(5)	Pt(2)–S(2)–C(4)	111.9(4)
O(2)–S(2)–C(4)	108.6(5)	C(3)–S(2)–C(4)	102.6(6)
Pt(1)–N(1)–C(5)	178.1(8)	Pt(2)–N(2)–C(7)	173.2(8)
N(1)–C(5)–C(6)	177.5(11)	N(2)–C(7)–C(8)	179.3(12)

TABLE 5. Bond lengths (Å) and bond angles (°) for *cis*-[Pt(Me$_2$SO)(MeCN)Br$_2$]

Bond lengths			
Pt(1)–Br(1)	2.397(2)	Pt(1)–Br(2)	2.429(2)
Pt(1)–S(1)	2.228(4)	Pt(1)–N(1)	1.983(13)
Pt(2)–Br(3)	2.394(2)	Pt(2)–Br(4)	2.427(2)
Pt(2)–S(2)	2.233(5)	Pt(2)–N(2)	1.986(14)
S(1)–O(1)	1.454(12)	S(1)–C(1)	1.760(18)
S(1)–C(2)	1.745(19)	S(2)–O(2)	1.482(14)
S(2)–C(3)	1.763(19)	S(2)–C(4)	1.753(20)
N(1)–C(5)	1.111(21)	N(2)–C(7)	1.123(22)
C(5)–C(6)	1.462(24)	C(7)–C(8)	1.424(24)
Bond angles			
Br(1)–Pt(1)–Br(2)	90.2(1)	Br(1)–Pt(1)–S(1)	88.1(1)
Br(2)–Pt(1)–S(1)	178.2(1)	Br(1)–Pt(1)–N(1)	178.5(4)
Br(2)–Pt(1)–N(1)	88.3(4)	S(1)–Pt(1)–N(1)	93.5(4)
Br(3)–Pt(2)–Br(4)	90.0(1)	Br(3)–Pt(2)–S(2)	88.6(1)
Br(4)–Pt(2)–S(2)	177.8(1)	Br(3)–Pt(2)–N(2)	177.2(4)
Br(4)–Pt(2)–N(2)	87.1(4)	S(2)–Pt(2)–N(2)	94.2(4)
Pt(1)–S(1)–O(1)	116.9(5)	Pt(1)–S(1)–C(1)	111.6(6)
O(1)–S(1)–C(1)	110.8(8)	Pt(1)–S(1)–C(2)	109.4(6)
O(1)–S(1)–C(2)	106.3(8)	C(1)–S(1)–C(2)	100.3(9)
Pt(2)–S(2)–O(2)	116.7(5)	Pt(2)–S(2)–C(3)	109.9(7)
O(2)–S(2)–C(3)	108.1(8)	Pt(2)–S(2)–C(4)	112.1(7)
O(2)–S(2)–C(4)	109.4(9)	C(3)–S(2)–C(4)	99.2(9)
Pt(1)–N(1)–C(5)	178.1(12)	Pt(2)–N(2)–C(7)	171.2(15)
N(1)–C(5)–C(6)	176.1(18)	N(2)–C(7)–C(8)	180.0(27)

ml, 11.9 mmol) and the mixture was kept at 20 °C for 10 h. The precipitated crystals were collected on a filter, washed with water (3 X 5 ml), ethanol (3 X 5 ml) and ether (3 X 5 ml), dried in air at 20 °C. Yield of *cis*-[Pt(Me_2SO)(MeCN)Br_2] = 0.24 g, 56% based on Pt. On heating in the solid phase at 120–125 °C acetonitrile abstraction takes place and decomposition of the resulting [Pt(Me_2SO)(μ-Br)Br$]_2$ occurs at 220 °C. *Anal.* Calc. for $C_4H_9Br_2NOPtS$: Br, 33.7; Pt, 41.2. Found: Br, 34.0; Pt, 40.9%. IR (KBr) cm^{-1}: 2321w (ν(CN)), 1150s (ν(SO)), 441m (ν(PtS)), 375m (γ(CSO)), 215w and 236w (ν(PtBr)). ^{1}H NMR, δ: 3.59 ppm (*J*(PtH) 24.1 Hz), 2.76 ppm (*J*(PtH) 9.9 Hz).

Results and Discussion

cis-[Pt(Me_2SO)(MeCN)Cl_2] (1) and *cis*-[Pt(Me_2SO)(MeCN)Br_2] (2) are found to be isostructural. In both cases, the unit cell contains two crystallographically independent molecules. In 1 and 2, the coordination polyhedrons of the Pt atom are slightly distorted square planar (Table 6, Fig. 1).

In the complexes studied, dimethyl sulfoxide is coordinated through sulfur. The finding of S-coordination of Me_2SO in 1 and 2 is in agreement with other results of the X-ray structure analysis of dimethyl sulfoxide Pt complexes (Table 7 and ref. 25). At present, only one structural study has resulted in a platinum(II) complex with O-coordinated dimethyl sulfoxide [26].

The presence of S-coordination in the Me_2SO molecules in 1 and 2 was also indicated by the infrared spectra. In this case, the ν(SO) bands (1147 cm^{-1} for 1 and 1150 cm^{-1} for 2) occur in a higher frequency range of the spectrum as compared to that of ν(SO) in the free molecule of dimethyl sulfoxide (1055 cm^{-1} [25]). Such a shift of ν(SO) frequency due to coordination is usually ascribed to metal–sulfur bonding [25]. S-coordination of Me_2SO in 1 and 2 persists also in acetone-d_6 solution. It is evidenced by the fact that in the ^{1}H NMR spectrum of complexes 1 and 2 of the above solution, the chemical shift of Me_2SO and the spin-coupling constants are characteristic of S-bonded sulfoxide ligands [25].

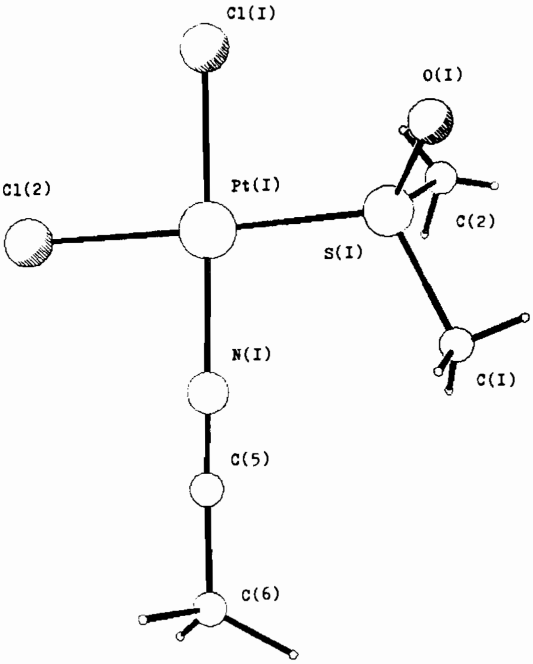

Fig. 1. View of the structure of the *cis*-[Pt(Me_2SO)(MeCN)Cl_2] complex.

Bond lengths of Pt(1)–S(1) and Pt(2)–S(2) in molecules 1 and 2, are 2.216(2), 2.224(3) and 2.228(4), 2.233(5) Å, respectively. These bond lengths are less than the sum of the covalent platinum and sulfur radii (2.35 Å). The results of the X-ray structure analysis of the *cis*-[Pt(Me_2SO)LCl_2] complexes (Table 7) show that the Pt–S distances decrease following the ligand L order: Me_2SO (av. 2.234(6) Å [12] and 2.248(5) Å [13]) > MeCN (av. 2.220(6) Å) > 2-MeC_5H_4N (2.200(3) Å [14]) > NH_3 (2.186(4) Å [19]). The difference in bond lengths of Pt–S in *cis*-[Pt(Me_2SO)$_2Cl_2$] and *cis*-[Pt(Me_2SO)NH_3Cl_2] is no less than 0.048 Å which is much higher than the standard deviation of Pt–S bond lengths in the compounds mentioned (0.004–0.006 Å).

The observed variations in the Pt–S bond lengths provide a fairly rare example of the *cis*-influence of the ligands in metal complexes [27]. This may be ascribed to electronic factors due to the different

TABLE 6. Atoms deviations from least-squares planes (Å)

Complex	Atoms				
	Pt	X (*trans* to S)	X (*trans* to N)	N	S
1	0.009	−0.011	0.007	0.008	−0.012
	−0.004	0.011	−0.009	−0.010	0.011
2	0.003	−0.006	0.004	0.005	−0.006
	−0.016	0.019	−0.011	−0.012	0.020

TABLE 7. X-ray structure data (bond lengths (Å), bond angles (°)) for dimethyl sulfoxide chloride platinum(II) complexes

Compound	Pt–Cl (*trans* to S)	Pt–Cl (*cis* to S)	Pt–S	S=O	$C-\hat{S}-C$	Reference
$K[Pt(Me_2SO)Cl_3]$	2.318(5)	2.296(5) 2.302(6)	2.193(5)	1.476(15)	102.2(7)	8
$(Ph_3PCH_2Ph)[Pt(Me_2SO)Cl_3]$	2.309(5)	2.271(6) 2.275(6)	2.185(5)	1.46(1)	100.0(11)	9
$[Pt(NH_3)_4][Pt(Me_2SO)Cl_3]_2$	2.321(2)	2.282(3) 2.307(3)	2.200(3)	1.484(8)	103.4(7)	10
$[Pt(C_3H_{10}N_2)_2][Pt(Me_2SO)Cl_3]_2$	2.312(4)	2.304(3) 2.288(3)	2.189(4)	1.47(1)	101.5(9)	11
cis-$[Pt(Me_2SO)_2Cl_2]$	2.306(3)		2.244(2)	1.469(6)	99.5(5)	12
	2.312(2)		2.229(2)	1.454(9)	103.3(5)	
	2.319(4)		2.238(3)	1.46(1)	99(1)	
	2.313(3)		2.251(3)	1.47(2)	103(1)	13
cis-$[Pt(Me_2SO)(MeCN)Cl_2]$[a]	2.310(3)	2.278(2)	2.216(2)	1.465(8)	101.0(7)	this work
	2.322(3)	2.278(2)	2.224(3)	1.472(9)	102.6(6)	
cis-$[Pt(Me_2SO)(2\text{-}MeC_5H_4N)Cl_2]$	2.307(4)	2.288(3)	2.200(3)	1.470(9)	104.5(7)	14
trans-$[Pt(Me_2SO)(2\text{-}MeC_5H_4N)Cl_2]$		2.282(3) 2.295(4)	2.212(3)	1.440(10)	99.6(7)	15
trans-$[Pt(Me_2SO)PyCl_2]$[a]		2.299(3) 2.276(3)	2.224(2)	1.458(8)	100.3(6)	16
		2.305(2) 2.294(3)	2.225(3)	1.469(7)	101.5(6)	
trans-$[Pt(Me_2SO)(cytidine)Cl_2]$		2.291(5) 2.310(4)	2.220(4)	1.48(2)	100(1)	17
trans-$[Pt(Me_2SO)(NH_2Pr)Cl_2]$		2.315(2)[b] 2.290(2)	2.220(2)	1.466(7)	99.4(5)	18
cis-$[Pt(Me_2SO)NH_3Cl_2]$	2.321(5)	2.297(5)	2.186(4)	1.487(12)	101.0(10)	19
trans-$[Pt(Me_2SO)(NH_3)_2Cl]Cl$	2.312(2)		2.197(2)	1.486(6)	102.3(6)	20
trans-$[Pt(Me_2SO)(NH_3)_2Cl](ClO_4)_{0.8}Cl_{0.2}$	2.307(5)		2.204(4)	1.46(1)	103.8	21
trans-(O,S)-$[Pt(Me_2SO)$(pyridine-2-carboxylato)$Cl]$		2.289(3)	2.174(2)	1.458(7)	102.3(5)	22
$[Pt(Me_2SO)$(1.4-diaminobutane)$Cl]^+$[c]		2.307(9)	2.21(1)			23
trans-(O,S)-$[Pt(Me_2SO)(C_6H_4NO_2)Cl_2]$		2.357(8)[d]	2.178(6)	1.47(2)	105(2)	24

[a] Data given for two crystallographically indepdendent molecules. [b] *trans*-lengthening of the Pt–Cl bond due to a hydrogen bond. [c] In the cited paper, X-ray structure data are limited due to low accuracy of the results obtained. [d] *trans*-lengthening of the Pt–Cl bond is due to a high aryl ligand *trans*-influence.

donor–acceptor properties of L ligands in the *cis*-$[Pt(Me_2SO)LCl_2]$ complexes. The Pt–S distances may be also affected by steric factors. The latter are due to repulsion of the *cis*-localized ligands in the complex molecule resulting in variation of the metal–ligand bond lengths.

Apparently, the Pt–S bond in *cis*-$[Pt(Me_2SO)LCl_2]$ is mainly affected by electronic factors. An argument for the assumption is that the above order of ligands corresponds approximately to a decrease in the π-acceptor and an increase in the σ-donor ability of the same ligands. It also suggests that it is electronic rather than steric factors that affect the Pt–S bond lengths. In fact, Pt–S bonds in various (including bulky) ligands of dialkyl sulfoxide and dialkyl sulfoxide amine complexes approximately correspond to Pt–S bonds in *cis*-$[Pt(Me_2SO)_2Cl_2]$ and *cis*-$[Pt(Me_2SO)NH_3Cl_2]$. For example, in *cis*-$[Pt(R_2SO)_2Cl_2]$, the average Pt–S bonds are 2.265(11) (MeEtSO [28]), 2.255(11) (Pr_2SO [28]) and 2.238(14) (C_4H_8SO [29]) Å. In the chelate $[Pt(MeS(O)NH_2)Cl_2]$ complexes, the above Pt–S bonds are 2.202(3) ($MeS(O)C_3H_6NH_2$ [30]), 2.182(3) ($MeS(O)CH_2CH(CO_2H)NH_2$ [31]) and 2.198(2) ($MeS(O)C_2H_4CH(CO_2H)NH_2$ [32]) Å.

The geometry of the dimethyl sulfoxide ligand in complexes **1** and **2** changes with coordination. The sulfur atom is close to tetrahedral in configuration. The O–S–C bond angles fall within the range 106.3–110.8° which is consistent with a value of ~107° for the O–S–C bond angle in a free dimethyl sulfoxide molecule [33]. The C–S–C angles (99.2–102.6°) are also consistent with the C–S–C bond angles in a free molecule of Me_2SO (97.4°). The data presented in Table 7 and ref. 25 show a slight increase in the C–S–C bond angle in the Me_2SO coordinated molecule characteristic of all dimethyl sulfoxide platinum(II) complexes subject to X-ray structure analysis.

In the dimethyl sulfoxide Pt(II) complexes (Table 7), the coordination most strongly influences the S=O bond. The S=O bond in Me_2SO is known to be equal to 1.531(5) Å [33] and in complexes **1** and **2** the bond length S=O falls in the range 1.454(12)–1.482(14) Å.

Acetonitrile in complexes **1** and **2** is actually linear. N–C–C bond angles amount to 177.5(11), 179.3(12)° and 176.1(18), 180.0(27)° for complexes **1** and **2**, respectively. Pt–N bonds are close to those in other organonitrile compounds of platinum(II) [3, 34–39]. The N-coordination of the MeCN molecule in complexes **1** and **2** is feasible since the ν(CN) absorption in the IR spectrum of **1** at 2339 and 2312 cm^{-1} and **2** at 2321 cm^{-1} is shifted to a high frequency region of the spectrum as compared to the ν(CN) absorption at 2266 cm^{-1} [40] in an acetonitrile free molecule.

An X-ray structure study of the complexes containing the L–Pt–X coordinate allows the *trans*-influence of the L ligand as compared to that of the X^- acidoligand to be determined. The latter can be considered as 'reference points' in most structural studies relevant to the *trans*-influence of coordinated ligands in complexes. Based on the data given in Table 7, the Pt–Cl bond in complexes of different types with the $Me_2(O)S$–Pt–Cl coordinates occurs in the range 2.31–2.32 Å while the Pt–Cl bond (*cis* to S) in complexes with the [Pt(Me_2SO *trans*-influence is close to that of the bromide ion. the *trans*-influence of dimethyl sulfoxide in the platinum(II) complexes is stronger than that for the chloride ion. This finding is in agreement with conclusions discussed in refs. 41 and 42 on the *trans*-influence of dimethyl sulfoxide in palladium and ruthenium complexes.

In complex **2**, the Pt–Br bond lengths are 2.429(2) and 2.427(2) Å. These are slightly lower than the Pt–Br bond lengths in $K_2[PtBr_4]$ [43] and $Rb_2[PtBr_4]\cdot H_2O$ [44] where they are 2.445(2) and 2.435(3) Å, respectively. This suggests that the Me_2SO *trans*-influence is close to that of the bromide ion. However, to make the conclusions more valid additional X-ray structure data on the $[Pt(R_2SO)Br_3]^-$ and *cis*-$[Pt(R_2SO)_2Br_2]$ complexes should be obtained.

The Pt–X bonds in **1** (2.278(2) and 2.278(2) Å) and **2** (2.397(2) and 2.394(2) Å) on the N–Pt–X coordinates are consistent with those of Pt–X_{trans} in $(Et_4N)[Pt(MeCN)Cl_3]$ (2.266(2) Å [3]), *cis*-$[Pt(MeCN)_2Cl_2]$ (av. 2.264(1) and av. 2.274(5) [34]) and $(Et_4N)[Pt(MeCN)Br_3]$ (2.393(1) Å [36]). In the above complexes, the Pt–X_{trans} bonds are shorter as compared to the bond lengths in complexes with $[PtX_4]^{2-}$ anions. Such a shortening of the Pt–X bonds in acetonitrile complexes is ascribed to a stronger *trans*-influence of the Cl^- and Br^- ions as compared to MeCN.

Conclusions

In refs. 1 and 2 the *trans*- and *cis*-effect of different ligands with respect to chloride ion was compared. It has been established that Me_2SO, unlike most other ligands, exhibits a strong *trans*- and *cis*-effect. Comparison of the experimental and published data shows that the *trans*-influence weakens in the order $Me_2SO \sim Br > Cl >$ MeCN and the *cis*-influence in the order $Me_2SO >$ MeCN $>$ 2Me-$C_5H_4N > NH_3$. Hence, dimethyl sulfoxide in platinum(II) complexes of *cis*-$[Pt(Me_2SO)(ligand)X_2]$ exhibits a relatively high *trans*- and *cis*-influence.

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Note Added in Proof

(i) Since the time of paper submission, we have synthesized and obtained the X-ray structure of the two complexes *cis*-Pt(Me$_2$SO)(PhCH$_2$CN)Cl$_2$] (Pt–S 2.215(1) Å) and *cis*-[Pt(Me$_2$SO)(pyridine)Cl$_2$] (Pt–S 2.209(4) Å). Therefore, the *cis*-influence order is as follows: Me$_2$SO > MeCN $\geqslant$ PhCH$_2$CN > Py > 2-MeC$_5$H$_4$N > NH$_3$.

(ii) All studies carried out by L. Manojlović-Muir research group dealing with structural *cis*-influence are presented in the review: L. Manojlović-Muir, *Izv. Jugoslav. Centra Krist., 13* (1978) 21.