

cis and *trans* Effects of Dialkyl Sulfoxides in Complex Compounds of Platinum(II)

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The nature of *cis* and *trans* effects is shown on the example of complex compounds of platinum(II) with dialkyl sulfoxides.

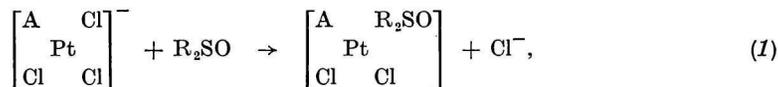
Until recently dimethyl sulfoxide was mainly used as a universal solvent for many inorganic and organic compounds. Only since 1960 great interest has been paid to dimethyl sulfoxide as a ligand.

The donor properties of dimethyl sulfoxide are due to the presence of two atoms with excessive electron density in the molecule, namely a sulfur atom and an oxygen atom. The vacant *d* orbitals on the sulfur atom may also lead to a dative π -interaction central atom—ligand.

Dialkyl sulfoxides, especially dimethyl sulfoxide (DMSO) and diethyl sulfoxide (DESO), proved to be very interesting ligands of complex compounds of platinum metals.

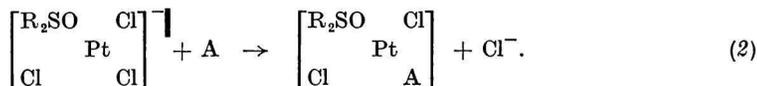
The *trans* effect is the most important characteristics of ligands. The *trans* effect in the investigated dialkyl sulfoxides was revealed primarily by chemical methods, which became possible after the synthesis of the complex compounds $K[Pt(DMSO)Cl_3]$ and $K[Pt(DESO)Cl_3]$ [1, 2].

The reaction of dialkyl sulfoxides with monoamine-type complex ions $[PtACl_3]^-$ (where A is ammonia or pyridine) should take place according to the following scheme



where the product formed is a *cis* compound. Both dimethyl sulfoxide and diethyl sulfoxide compounds were prepared according to this scheme [1, 2].

When ammonia or pyridine react with complex ions $[Pt(R_2SO)Cl_3]^-$ the compounds obtained are of the same composition as those prepared according to the scheme (1), but their properties differ. The respective compounds were found to differ in colour, crystal form, solubility, absorption and vibrational spectra, *etc.* Thus it was concluded that according to the type of reaction different isomers were produced. Hence the second type of synthesis may be represented by the following scheme



Reactions of this type were carried out not only with chloro complexes of dimethyl sulfoxide but also with analogous bromo complexes [3].

The results obtained show that dialkyl sulfoxides possess a rather high *trans* effect. Their *trans* effect is higher than that of chlorine or bromine.

When revealing the *trans* effect of dialkyl sulfoxides we succeeded in carrying out the scheme of Hel'man [4], who was the first to prove the high *trans* effect of ethylene. The scheme of Hel'man is as follows

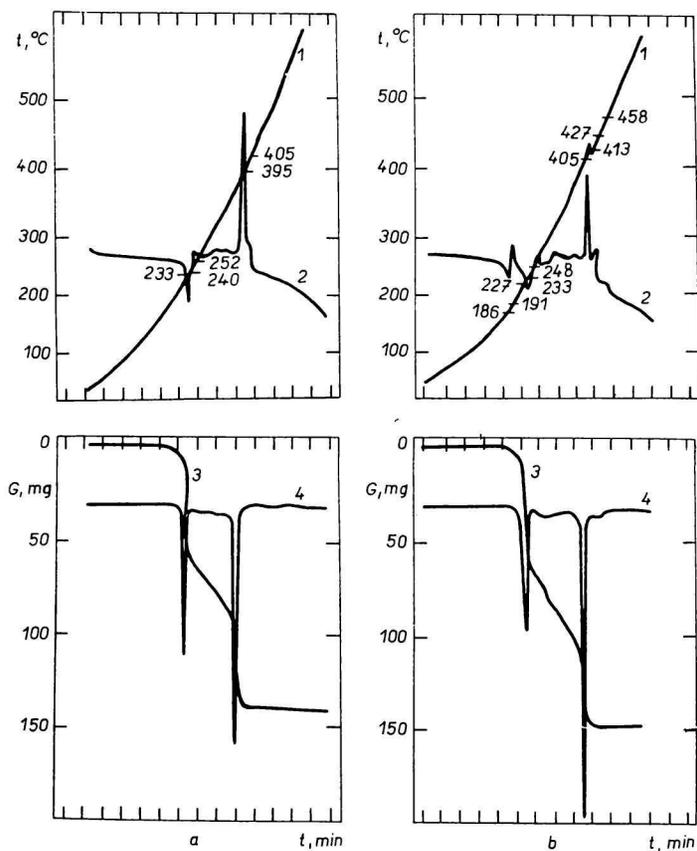
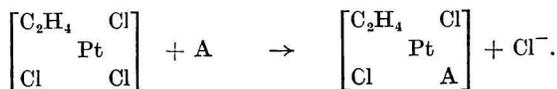
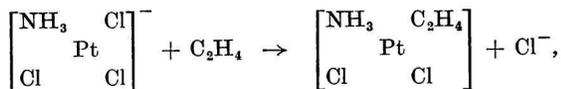


Fig. 1. Thermal analysis curves: a) *cis*-[PtNH₃(DMSO)Cl₂]; b) *trans*-[PtNH₃(DMSO)Cl₂]. 1. change of temperature with time; 2. differential curve of temperature change; 3. change of mass with time; 4. differential curve of mass change.

In spite of the fact that DMSO or DESO in complexes of Pt(II) direct the exchange reaction in *trans* position, it is the *cis* isomer that possesses lower free energy and not the *trans* isomer. This follows from the thermal analyses. In the case of $[\text{PtNH}_3(\text{DMSO})\text{Cl}_2]$ it is seen from Fig. 1 that while endo-exothermic effects are observed, there is no corresponding loss of weight. It is proved experimentally that the endothermic effect is due to the melting of the compound. A reaction of isomerization accompanied by release of energy takes place in the molten state. The melting point of the *cis* isomer thus obtained is higher than that of the *trans* isomer; hence, in spite of the slight increase of temperature the *cis* isomer crystallizes from the molten mass. The thermal analysis curve of a corresponding *cis* isomer shows neither endo- nor exothermic effects which are not accompanied by loss of weight. It is to be noted that after the endo-exo-effect in the *trans* isomer the thermal analysis curves for both isomers are practically identical. Thus these facts confirm that the rule of *trans* effect of Chernyaev is mainly of kinetic nature.

An attempt was made [5] to find out the reaction rate of ammonia or methylamine with complex ions $[\text{PtC}_2\text{H}_4\text{Cl}_3]^-$ and $[\text{Pt}(\text{DMSO})\text{Cl}_3]^-$. As these reactions take place very fast, it was possible to compare them only qualitatively. It was found that both these complexes react with amines with nearly the same rate. It was concluded that the *trans* effect of DMSO is very close to that of ethylene.

In 1957 *Grinberg* and the author showed that the lability of ligands in complex compounds of Pt(II) depended not only on the *trans* partner but also on the nature of *cis* ligand [6].

For example, ammonia in the complex ion $[\text{PtNH}_3\text{Cl}_3]^-$ accelerates the exchange reaction of chlorine ions in the *cis* position as compared to the rate of the exchange in the complex $[\text{PtCl}_4]^{2-}$. Even in this first paper [6] it was suggested that the ligands having a high *trans* effect possess a low *cis* effect and, on the contrary, the ligands having a low *trans* effect are characterized by a high *cis* effect. Actually, ammonia and pyridine have a low *trans* effect but a comparatively high *cis* effect.

Special reference must be made to the paper of *Grinberg* and *Kuzmina* [7] who investigated the isotopic exchange of chlorine in complex ion $[\text{PtC}_2\text{H}_4\text{Cl}_3]^-$. In this paper it was shown that ethylene having a high *trans* effect actually stabilized the chlorine atoms in *cis* position in the complex ion.

The opposition of the *trans* effect and the *cis* effect in a series of ligands C_2H_4 , Cl , NH_3 , py is shown by the data of the rate of isotopic chlorine exchange presented in Table 1.

Bersuker [8] suggested an electronic mechanism which explains the experimental data of the *cis* effect. He came to the conclusion that the empirically established series of the *trans* effect (activity) can be used as the series of *cis* effect if one reverses the signs of inequality in the opposite direction. The *cis* effect of dialkyl sulfoxides on the exchange of chloride ions was investigated in [9, 10].

In the paper [9] it was shown that the chloride ion located against the DMSO in the complex $[\text{Pt}(\text{DMSO})\text{Cl}_3]^-$ was actually exchanged instantaneously. This is seen in Fig. 2. Such a behaviour of the complex $[\text{Pt}(\text{DMSO})\text{Cl}_3]^-$ concerning the exchange of the *trans*-chloride ion is analogous to that of the complex $[\text{PtC}_2\text{H}_4\text{Cl}_3]^-$ [7].

The isotopic exchange of the chloride ion in *trans* position to ethylene takes place in the same way with the speed of "zero exchange". This again shows the close proximity of the *trans* effect of DMSO and C_2H_4 .

The exchange rate of chloride ions in *cis* position in the complex $[\text{Pt}(\text{DMSO})\text{Cl}_3]^-$ was found to be unexpectedly very high. In spite of this high *trans* effect DMSO does not stabilize but labilizes the chloride ions in *cis* position. In addition it is to be noted

Table 1

Rate constants of chlorine exchange in complex ions of Pt(II)

Complex ion	Cl—Pt—Cl [s ⁻¹]	L—Pt—Cl [s ⁻¹]	References
$\begin{bmatrix} \text{Cl} & \text{Cl} \\ \text{Pt} \\ \text{Cl} & \text{Cl} \end{bmatrix}^{2-}$	1.04×10^{-5}	1.04×10^{-5}	[14]
$\begin{bmatrix} \text{NH}_3 & \text{Cl} \\ \text{Pt} \\ \text{Cl} & \text{Cl} \end{bmatrix}^{-}$	2.91×10^{-5}	4.16×10^{-6}	[15]
$\begin{bmatrix} \text{py} & \text{Cl} \\ \text{Pt} \\ \text{Cl} & \text{Cl} \end{bmatrix}^{-}$	3.82×10^{-5}	2.68×10^{-6}	[15]
$\begin{bmatrix} \text{C}_2\text{H}_4 & \text{Cl} \\ \text{Pt} \\ \text{Cl} & \text{Cl} \end{bmatrix}^{-}$	4.92×10^{-4}		[7]
$\begin{bmatrix} \text{DMSO} & \text{Cl} \\ \text{Pt} \\ \text{Cl} & \text{Cl} \end{bmatrix}^{-}$	4.96×10^{-4}		[9]
$\begin{bmatrix} \text{DESO} & \text{Cl} \\ \text{Pt} \\ \text{Cl} & \text{Cl} \end{bmatrix}^{-}$	1.65×10^{-4}		[10]

that the process of isotopic exchange of the chloride ions along the coordinate Cl—Pt—Cl is accompanied by previous hydration. This seems to be a common phenomenon for isotopic exchange reactions in complex compounds of Pt(II).

In the complex ion $[\text{Pt}(\text{DESO})\text{Cl}_3]^{-}$ the exchange of *trans* chlorine occurs instantaneously. The chloride ions along the coordinate Cl—Pt—Cl in DMSO complexes are labile, but the lability is nearly 3-times smaller than that in DMSO compounds.

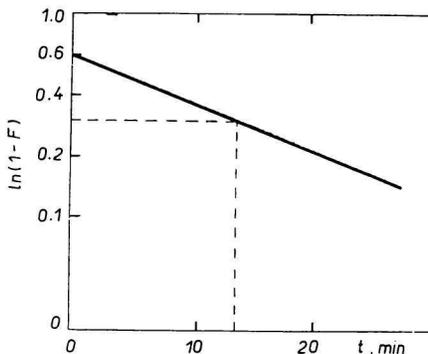


Fig. 2. Relationship between $\ln(1 - F)$ and time for isotopic chlorine exchange in the complex ion $[\text{Pt}(\text{DMSO})\text{Cl}_3]^{-}$.

Complex concentration 1.66×10^{-2} M; $[\text{Cl}^{-}]$ 4.98×10^{-2} M; temperature 25°C.

The low lability of *cis* chloride ions in DMSO complexes in comparison to DMSO may be explained by the high screening of chloride ions which is connected with the size of the alkyl groups.

The fact that in sulfoxides there is no complete opposition of the series of *trans* and *cis* effects seems to be due to different nature of the *cis* effect, which is intermolecular and not intramolecular.

In the paper [11] we showed some of the properties of *cis* ligands to be due to their interaction with the oxygen atom of sulfoxide. In this case the lability of chloride ions along the coordinate Cl—Pt—Cl can be explained by the effect of the oxygen atom. Since the oxygen atom has lone electron pairs, it may promote the exchange of chloride ions in *cis* position. This is due to the fact that the oxygen atom gives up its lone electron pairs to the central atom as temporary compensation for the loss of electrons taking place when the ligand leaves the complex compounds.

Our point of view resembles little that of *Ingold et al.* [12, 13] who postulated the double mechanism of ligand exchange in cobalt complex compounds.

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