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Equilibria in Aqueous Solutions of Platinum(II) Sulphoxide Complexes

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The sulphoxide complex of the $K[Pt(R_2SO)Cl_3]$ *type proved to be similar in properties to Zeise's salt* $K[Pt(C_2H_4)Cl_3]$*. The cis- and trans-influence of dimethylsulphoxide and its effect on the acid properties of platinum(II) aqua complexes are discussed in the paper. Three instability constants of the* $[PtDMSOCl_3]^-$ *complex ion are determined. They are* $K_1 = (1.3 \pm 0.3) \times 10^{-5}$, $K_2 = 6 \times 10^{-5}$, $K_3 = (2.8 + 0.5) \times 10^{-3}$.

In the last five years a number of investigations carried out in our laboratory were devoted to dialkylsulphoxide complexes of platinum metals.

The first member of the homologous series of dialkylsulphoxides – dimethylsulphoxide (DMSO) – is a remarkable aprotic solvent. In its power to dissolve organic and inorganic substances it is superior even to water. At present, sulphoxides are used not only in laboratory. They have found wide application in chemical engineering as well. Therefore, the investigation of the state of metallic salts in sulphoxide solutions is not only of theoretical but also of practical importance.

Cotton and coworkers[1] consider the properties of dialkylsulphoxides to reflect three molecular structures in equilibrium

$$R_2\overset{+}{S}\overset{-}{O} \longleftrightarrow R_2S{=}O \longleftrightarrow R_2\overset{-}{S}{\equiv}\overset{+}{O}$$

The nature of the double bond S=O depends mainly on the σ-bond $\overset{+}{S}\rightarrow\overset{-}{O}$ and the p_π–d_π back bond $\overset{-}{S}\leftarrow\overset{+}{O}$. The latter is formed by overlap of filled p_π orbitals of the oxygen atom and the corresponding vacant d_π orbitals of the sulphur atom. Coordination of sulphoxide to the positive metal ion through an oxygen atom must weaken the p_π–d_π bond and hence decrease the S–O stretching frequency. In contrast, addition of a sulphur atom from the sulphoxide molecule to the metal ion should strengthen the p_π–d_π bond of the oxide atom with sulphur and hence increase the S–O stretching frequency.

At present, coordination sulphoxide compounds have been studied for the majority of chemical elements. It has been found that sulphoxides are principally coordinated to metals through an oxygen atom. In case of platinum metals – soft acids – coordination occurs through a sulphur atom, as evidenced by IR spectroscopy. Wayland and Schramm showed[2,3] that in the palladium complex $[Pd(DMSO)_4](ClO_4)_2$ which they prepared palladium binds both S and O atoms of sulphoxide. In the diisoamylsulphoxide complex $[Pd(IACO)_4](BF_4)_2$ all four sulphoxide molecules are oxygen-coordinated.[4,5] In the rhodium compounds $[Rh(DMSO)_3Cl_3]$ and $[Rh(DMSO)_5Cl](ClO_4)_2$[6–8] two sulphoxide molecules are sulphur-coordinated and the others are oxygen-coordinated.

It was shown in our laboratory that in platinum complexes sulphur-coordinated dialkylsulphoxides exhibit a strong *trans*-influence. In this respect they resemble ethylene. Complex compounds of the $K[Pt(R_2SO)Cl_3]$ type proved to be similar in properties to Zeise's salt $K[Pt(C_2H_4)Cl_3]$. The present paper is primarily concerned with the investigation of properties of complex compounds of the $K[Pt(R_2SO)X_3]$ type.

The study of isotopic exchange of chlorine in complex ions $[Pt(R_2SO)Cl_3]^-$, where $R_2SO = (CH_3)_2SO$ and $(C_2H_5)_2SO$, showed that one of the three intrasphere chloride ions is very labile.[9,10] Its isotopic exchange occurs at the speed of "zero" exchange (Figure 1). One may suppose that the ion in question is the chloride ion in *trans*-position to the sulphoxide molecule. A similar picture was observed by Grinberg and Kuzmina[11] with Zeise's salt. In the $[Pt(C_2H_4)$

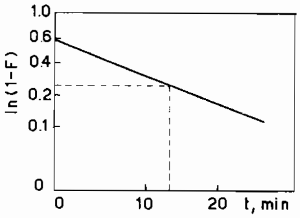

Figure 1. Relationship between ln(1-F) and time for isotopic chlorine exchange in the complex ion $[Pt(DMSO)Cl_3]^-$. Complex concentration 1.66×10^{-2}M. $[Cl^-]$ 4.98×10^{-2}M. Temperature 25°

$Cl_3]^-$ complex the exchange of the chloride in the *trans*-position to the ethylene was complete by "zero" time.

It was shown by Grinberg and Kukushkin in 1957[12] that the lability of ligands in platinum(II) complexes depends not only upon the nature of the ligand in *trans*-position but also upon the ligand in *cis*-position. For example, ammonia in the $[Pt(NH_3)Cl_3]^-$ complex ion causes an increase in the rate of replacement of chlorine in *cis*-position as compared to replacement rates in the $[PtCl_4]^{2-}$ complex ion. In our first paper it was suggested that ligands with strong *trans*-influence exhibit weak *cis*-influence and, on the contrary, ligands with weak *trans*-influence display strong *cis*-influence.[12] Later this assumption was confirmed by experimental evidence.[13,14]

Sulphoxides proved to be an exception to this rule. They display not only strong *trans*-influence but also strong *cis*-influence. The rate of chlorine replacement in complex ions on the Cl–Pt–Cl coordination link is much higher than that on the same coordination link in any other complex, including $[Pt(NH_3)Cl_3]^-$.[9,10] From the calculation of electronic structure of DMSO molecules carried out in our laboratory[15] by MO LCAO–CNDO method (differential overlap being completely neglected) it follows that the p_π orbitals of oxygen exhibit a marked donor power. The *cis*-influence of sulphoxides in complex ions of the $[Pt(R_2SO)Cl_3]^-$ type is likely to be due to the interaction of oxygen p_y orbitals with the central atom (Figure 2), owing to which the platinum–chloride bond is labilized in *cis*-position.

Bromide complexes of platinum(II) are, as a rule, more labile than chloride ones. Therefore, in the $[PtDMSOBr_3]^-$ complex bromine ions both in *cis*- and *trans*-position to sulphoxide are practically exchanged instantaneously.[16]

Thus, coordinated dialkylsulphoxides labilise the whole inner sphere of platinum(II) complexes.

In 1955 Leden and Chatt investigated equilibria in aqueous solution of Zeise's salt. They estimated the third instability constant of the $[Pt(C_2H_4)Cl_3]^-$ ion ($K_3 = 3.0 \times 10^{-3}$) and, what is of particular significance, the acid dissociation constant of the $[Pt(C_2H_4)(H_2O)Cl_2]$ ion. The latter was found to be of the order of 10^{-5}. From the point of view of the theory of acid–basic properties of complex compounds, this exceptionally high value of the acid dissociation constant was at that time unexpected. In fact, in the fifties it was believed that the acidic properties of complex A depended on: H – the field strength of the central ion defined by the ion charge and its polarization properties; E – charge of the complex ion; α – the degree of dissociation of RH molecules in free state; β – polarizability of RH molecules:

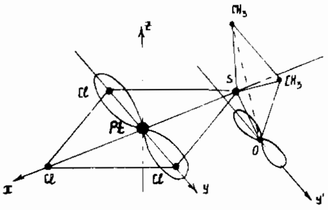

Figure 2. Interaction of oxygen p_y orbitals with the central atom.

$$A = f(H, E, \alpha, \beta)$$

In addition, the acidic properties of the intrasphere ligand RH must depend on the properties of the ligand in *trans*-position. It was believed that the acidic properties of the intrasphere group RH decrease with the enhancement of the *trans*-influence of the ligand in *trans*-position.[18]

Ethylene exhibits a very strong *trans*-influence. That is why one could expect the acid dissociation constant of *trans*-$[Pt(C_2H_4)(H_2O)Cl_2]$ to be close to the corresponding constant for $[Pt(H_2O)Cl_3]^-$, which equals $K \sim 10^{-7}$.[19] Actually, it proved to be two orders higher and close to the constants for *cis*-$[Pt(NH_3)_2(H_2O)_2]^{2+}$ ($K_1 = 2.8 \times 10^{-6}$) and for *trans*-$[Pt(NH_3)_2(H_2O)_2]^{2+}$ ($K_1 = 4.8 \times 10^{-5}$). It should be noted that the last two complexes are of cation type and their acidic properties are enhanced due to the positive charge of the complex ion. At present, the pronounced acidic properties of the $[Pt(C_2H_4)(H_2O)Cl_2]$ complex are accounted for by the π-acceptor properties of ethylene. The formation of a π-dative platinum–ethylene bond brings about an increase in the effective charge on the central atom and enhancement of acidic properties of the coordinated water molecule. The results of Leden and Chatt[17] were afterwards confirmed in a work[20] on $[Pt(NH_3)_2(C_2H_4)(H_2O)]^{2+}$ where ethylene is also in *trans*-position to the water molecule.

The acid dissociation constant for *trans*-$[PtDMSO(H_2O)Cl_2]$ was estimated.[21] It proved to be $K = (1.4 \pm 0.2) \times 10^{-5}$.

Thus, the acidic properties of the ethylene complex $[Pt(C_2H_4)H_2O)Cl_2]$ and the dimethylsulphoxide complex $[PtDMSO(H_2O)Cl_2]$ are very close.

In aqueous solutions of $K[PtDMSOCl_3]$ salt there are two equilibria:

$$[Pt(DMSO)Cl_3]^- + H_2O \rightleftharpoons \textit{trans-}[PtDMSO(H_2O)Cl_2] + Cl^- \; K_3 \qquad (I)$$

$$\textit{trans-}[PtDMSO(H_2O)Cl_2] \rightleftharpoons H^+ + \textit{trans-}[PtDMSO(OH)Cl_2]^- \; K \qquad (II)$$

Since they are interrelated, we can estimate the third instability constant of the $[PtDMSOCl_3]^-$ ion by determination of hydrogen ion concentration with change in chlorine ion concentration.[22] Estimation of the constant was accomplished by titration of freshly prepared solutions of the complex with KCl solution and simultaneous measurement of the pH:

$$K_3 = \frac{C_{aq}(C_{aq} + X)}{C - C_{aq}}$$

where C_{aq} and C are concentrations of the aqua complex and the starting complex corresponding to equilibrium (I) and X is the concentration of the added KCl. In accordance with equilibrium (II) C_{aq} equals

$$C_{aq} = \frac{[H^+]^2}{K} + [H^+]$$

The value of K_3 for the $[PtDMSOCl_3]^-$ complex is equal to $(2.8 \pm 0.5) \times 10^{-3}$. K_3 for the $[PtC_2H_4Cl_3]^-$ ion was determined under comparable conditions and in analogous manner. It was found to be $(3.7 + 0.5) \times 10^{-3}$. Thus, we see again that the dimethylsulphoxide complex $[PtDMSOCl_3]^-$ is similar to the corresponding ethylene compound $[Pt(C_2H_4)Cl_3]^-$.

An attempt was made to use a silver–silver chloride electrode for investigation of equilibria in solution of $K[PtDMSOCl_3]$. The electrode is used provided there is no chemical interaction between it and solution of the complex. Leden and Chatt investigated equilibria in solution of Zeise's salt with the help of a silver–silver chloride electrode. They noted that the e.m.f. of the circuit changes with time, which they attributed to oxidation–reduction interaction between the platinum salt and the electrode. The limitation of the use of a silver–silver chloride electrode for investigation of platinum and palladium complexes was shown also.[23,24]

Tentative experimental evidence indicated that slightly soluble silver salts are not formed with the $[PtDMSOCl_3]^-$ complex ion. However, addition of $K[PtDMSOCl_3]$ salt to potassium chloride solution of certain concentration leads to diminished chloride concentrations, the deviation being the greater the higher the chloride ion concentration.

For estimation of the stepwise constants we used Bjerrum's method.[25] The equilibrium concentration of chloride ions corresponding to K_3 of the $[PtDMSOCl_3]^-$ complex (when $\bar{n} = 2.5$) is rather high, and under these conditions the error introduced by the silver–silver chloride electrode is considerable. The value of K_3 determined in this way proved to be one order of magnitude lower. When $\bar{n} = 1.5$, the equilibrium chloride concentration is equal to K_2, but since K_2 is much lower than K_3, the electrode functioned normally over the range of corresponding chloride ion concentrations. In the same manner we estimated the approximate value of $K_2 = (5 \div 8) \times 10^{-5}$.[26] To check the value obtained for K_2 we made also use of another method for determining equilibrium concentrations of components in solution of platinum salts taking into consideration the acidic properties of aquacomplexes.[26]

When the $K[PtDMSOCl_3]$ complex is dissolved in water, in addition to equilibria (I) and (II) there are established equilibria (III) and (IV):

$$[PtDMSO(H_2O)Cl_2] + H_2O \rightleftharpoons [PtDMSO(H_2O)_2Cl]^+ + Cl^- (K_2) \quad (III)$$

$$[PtDMSO(H_2O)_2Cl]^+ \rightleftharpoons H^+ + [PtDMSO(H_2O)(OH)Cl]\,(K\text{ acid}) \quad (IV)$$

Knowing the acid dissociation constants of $[PtDMSO(H_2O)Cl_2]$ and $[PtDMSO(H_2O)_2Cl]^+$ aquacomplexes and K_3 for the $[PtDMSOCl_3]^-$ ion one can calculate the constant K_2 relating to equilibrium (III).

For the calculation it was necessary to determine the equilibrium concentrations of platinum mono- and diaqua complexes and the chloride ions. The procedure used consisted in titration of a monoaqua complex solution of known concentration with KCl solution and simultaneous measurement of the pH. The determination of the pH was carried out, as before, with an instrument of the LP–58 type at 25 °C and ionic strength $\mu = 0.5(KNO_3)$. Equilibrium was established in 1–2 min. The calculations were made by the following equations:

$$K_3 = \frac{[aq][C_{Cl} - (C_{aq} - [aq])]}{C_{aq} - [aq]} = 10^{-3} \quad (1)$$

where [aq] is the equilibrium concentration of *trans*-$[PtDMSO(H_2O)Cl_2]$; C_{Cl} and C_{aq} are the initial chloride and monoaqua complex concentrations. The equilibrium concentration [aq] was calculated from eqn 1. $[H^+]_a$ – the active concentration of H^+ ions obtained on dissociation of the monoaqua complex was determined from [aq]:

$$[aq] = \frac{[H^+]a}{1.4 \times 10^{-5}} + [H^+]a, \text{ where } K_a = 1.4 \times 10^{-5} \quad (2)$$

$$[H^+]_d = [H^+]_{exp} - [H^+]a \quad (3)$$

where $[H^+]_{exp}$ and $[H^+]_d$ are the active H^+ ion concentration determined experimentally and that of the diaqua complex.

From $[H^+]_d$ we calculated the equilibrium concentration of the diaqua complex (equilibrium IV):

$$[PtDMSO(H_2O)_2Cl^+] = \frac{[H^+]^2}{3.1 \times 10^{-4}} + [H^+]_d$$

$$\text{where } K_{acid(1)} = 3.1 \times 10^{-4}\,* \quad (4)$$

$$[Cl^-] = C_{Cl} - (C_{aq} - [aq]) + [PtDMSO(H_2O)_2Cl^+] \quad (5)$$

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* The second step of acid dissociation of the diaqua complex is negligible, since $K_{acid(2)}$ is four orders of magnitude lower.

TABLE I. Estimation of K_2 for $[PtDMSOCl_3]^-$; $\mu = 0.5(KNO_3)$, t = 25° C.

$C_{Cl} \times 10^3$ M	$C_{aq} \times 10^3$ M	pH	$[H^+]_{exp} \times 10^4$	$[H^+]_a \times 10^4$	$[H^+]_d \times 10^5$	$K_2 \times 10^5$
3.99	4.99	3.65	2.44	1.71	7.3	5.9
7.95	4.97	3.91	1.23	1.68	1.5	6.3
9.90	4.95	3.97	1.07	0.96	0.9	7.0
					average	6.10

Thus, the value K_2 obtained agrees very closely with that found with the use of a silver–silver chloride electrode.

$$K_2 = \frac{[PtDMSO(H_2O)_2Cl^+][Cl^-]}{[PtDMSO(H_2O)Cl_2]^- [PtDMSO(H_2O)_2 Cl^+]} \quad (6)$$

K_2 was determined over a concentration range $(3.9–9.9) \times 10^{-3}M$ of the added chloride, where the concentrations $[H^+]_{exp}$, $[H^+]_a$ and $[H^+]_d$ are commensurable. The results of titrating 50 ml of solution of *trans*-$[PtDMSO(H_2O)Cl_2]$ (5×10^{-3} mole) and the estimates of K_2 are listed in table I.

When using the indicator silver–silver chloride electrode we failed to determine K_1, since the chloride concentration, corresponding to $\bar{n} = 0.5$, was beyond the range of application of the method. It was only found that $K_1 < 5 \times 10^{-5}$.

For estimation of K_1 of the $[PtDMSOCl_3]^-$ complex ion, a sensitive potentiometric method[27–29] permitted determination of halide ions in concentrations up to $(1 \div 5) \times 10^{-6}$ g/l. The procedure consists in measuring the changes in the e.m.f. (ΔE) of a flow concentration cell with two similar silver–silver halide electrodes on replacement in the indicator semielement of the reference solution containing no ions to be determined by the analyzed solution with a halogenide ion concentration C_2. Within the range of low chloride ion concentrations the dependence of ΔE on C_2 is linear. The concentration measured was determined from equation $C_2 = \Delta E/K$ where K is the proportionality factor obtained experimentally with the use of standard solutions. The investigation was carried out with an apparatus described earlier.[26]

The constant K_1 was determined during the investigation of the following equilibrium

$$[PtDMSO(H_2O)_3]^{2+} + Cl^- \rightleftharpoons [PtDMSO(H_2O)_2Cl]^+ + H_2O \quad (V)$$

It was found that the introduction of $[PtDMSO(H_2O)_3]^{2+}$ ions (in concentrations from 5 to 20 mM) into the solution exerts practically no influence on the potential of the silver–silver chloride electrode. This can be accounted for by the fact that the rate of diffusion of chloride ions from the continuously dissolving electrode (AgCl) into the laminar flow of solution is much higher than the rate of interaction between $[PtDMSO(H_2O)_3]^{2+}$ ion and Cl^-. Therefore, the chloride ions from the electrode have no time to cause tangible changes in the system under investigation. Platinum complex ions are found to be adsorbed on the electrode surface. The adsorption somewhat increases the time necessary for the potential to be established but it has practically no influence on the results of determination of chloride ions in solution. The K_1 value was calculated from Bjerrum's formation function ($\bar{n} = 0.5$). For this, $\bar{n}$ was plotted against the equilibrium chloride ion concentration. K_1 proved to equal $(1.3 \pm 0.3) \times 10^{-5}$.[31]

Thus, the successive instability constants of the $[PtDMSOCl_3]^-$ complex ion are: $K_1 = (1.3 \pm 0.3) \times 10^{-5}$; $K_2 = 6 \times 10^{-5}$; $K_3 = (2.8 \pm 0.5) \times 10^{-3}$.

In conclusion we shall turn again to the comparison of properties of dimethylsulphoxide and ethylene as ligands of platinum(II) complexes. The comparison of stability of Zeise's salt and its dimethylsulphoxide analogue in aqueous solution shows their stabilities to be close. The somewhat lower instability constant of the $[PtDMSOCl_3]^-$ ion may be evidence of the somewhat higher effective positive charge on platinum(II) in the sulphoxide complex. The comparison of acid dissociation constants of $[PtDMSO(H_2O)Cl_2]$ and $[Pt(C_2H_4)(H_2O)Cl_2]$ also indicates that the effective charge in the sulphoxide complex is somewhat higher than that in ethylene. The author together with Baranovsky and Panina estimated the σ-donor and π-acceptor properties of these ligands from the overlap integrals of DMSO and C_2H_4 orbitals.[32] DMSO proved to be both a better σ-donor and a better π-acceptor than ethylene. This is in accord with experimental evidence.

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