COORDINATION COMPOUNDS

Ligand *trans*-Effect in Octahedral Complexes of 3d Metals and its Manifestation in the Synthesis of Metalloporphyrins in Solution

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Received December 17, 2007

Abstract—We study features of the indicator kinetic reaction of *meso*(tetraphenyl)tetrabenzoporhine with cobalt(II), nickel(II), and manganese(II) acetates in electron-donating organic solvents (*N*,*N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and pyridine (Py)) and in their binary mixtures at temperatures in the range 348–368 K. Specific features of the *trans*-effect of solvent molecules on the rate and activation parameters of formation of manganese(II), cobalt(II), nickel(II), and copper(II) complexes with porphyrin are noted.

DOI: 10.1134/S003602360907016X

The *trans*-effect of molecular and acido ligands since it was discovered by Chernyaev more than one hundred years ago in platinum(II) complexes [1] has been widely used for the synthesis of mixed-ligand complexes of the platinum-group metals and cobalt(III) [2] and substantiated theoretically [3–6]. *trans*-Effect, which consists in the labilization of the M–L (metal– ligand) donor–acceptor bond located in the *trans*-position of a square-planar [ML₄] or octahedral [ML₆] complex relative to the *trans*-influencing ligand L_T (scheme 1), is manifested only in very stable complexes of the platinum-group metals (Ru, Rh, Pd, Os, Ir, and Pt). Later [7], the *trans*-effect was discovered in very stable cobalt(III) complexes in dissociation reactions in polar electron-donating solvents.

Some kinetic features of the behavior of $[ML_mL'_p]^{2+}$ mixed solvates discovered several decades later [8–12] implied the existence of the ligand *trans*-effect in the coordination sphere of these labile complexes [13]. The *trans*-effect is a complex phenomenon; to understand it, one should study mixed coordination spheres of other metals than platinum-group metals and cobalt(III). Such complexes include mixed-ligand complexes of 3*d*, 4*d*, and 5*d* metals; these complexes have not been studied, unlike platinum metal complexes.



EXPERIMENTAL

Porphyrin for use in indicator kinetic reactions was prepared as described in [14]; solvents and salts were washed and dried after [15, 16]. The rate of the indicator reaction of metal phorphyrin formation was derived from the change of electronic absorption spectra in the visible measured on an SF-46 instrument. The experimental procedures and calculations of kinetic parameters did not differ from those described in [7].

RESULTS AND DISCUSSION

Tables 1 and 2 list effective (k_{eff}) and true (bimolecular k_v^{298}) rate constants, activation energies (E_a) , and activation entropies (ΔS^{\neq}) of reaction (1) in which phor-

Solvent	<i>Т</i> , К	$k_{\rm eff} \times 10^4$, s ⁻¹	$k_v^{298*}, L/(\text{mol s})$	E_a , kJ/mol	ΔS^{\neq} , J/(mol K)
Ру	308 318 328	3.35 7.28 15.3	0.59	63 ± 2	-43 ± 6
DMSO	308 318 328	4.18 8.19 15.85	0.77	55 ± 3	-68 ± 12
DMF	308 318 328	4.90 10.2 21.3	0.96	61 ± 4	-46 ± 13
DMF-Py (50%-50%)	308 318 328	12.4 26.2 50.1	2.50	58 ± 5	-50 ± 16
DMSO-Py (50%-50%)	308 318 328	15.8 31.2 63.8	3.0	58 ± 3	-48 ± 10
DMF-DMSO (50%-50%)	308 318 328	16.5 31.2 58.8	3.2	53 ± 2	-64 ± 7

Table 1. Rates and activation parameters of reaction (1) in which the complex CoTPTBP is formed in DMF, DMSO, Py, and their binary mixtures

* Calculated from the Arrhenius equation. Precision: $\pm 10\%$.

phyrin complexes are produced from mixed solvate complexes of cobalt(II) and nickel(II) acetates and NH-active tetraphenyltetrabenzoporphine (**I**):



$$[MAc_{2}(S_{1})_{m}(S_{2})_{n-m-2}] + H_{2}TPTBP$$

$$\longrightarrow TPTBP + 2HAc + S....$$
(1)

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The results can be interpreted on the basis of the theoretical inferences made in [17, 18], where H_2TPTBP was shown to be one of the most reactive phorphyrins in the reactions used to study the *trans*-activity of sol-



Fig. 1. *trans*-Influence in the kinetics of reaction (1) of cobalt(II) acetate in binary solvents: (1) DMSO–DMF, (2) Py–DMSO, and (3) Py–DMF.

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Solvent	<i>Т</i> , К	$k_{\rm eff} \times 10^4, {\rm s}^{-1}$	k_v^{298*} , L/(s mol)	E_a , kJ/mol	Δ <i>S</i> [≠] , J/(mol K)
Ру	348 358 368	0.825 1.71 3.51	0.010	77 ± 2	-32 ± 6
DMSO	348 358 368	2.99 6.04 13.1	0.033	78 ± 4	-18 ±15
DMF	368		Reaction does not occur		
DMF-Py (50%–50%)	348 358 368	1.88 4.11 8.10	0.023	78 ± 4	-23 ± 11
DMSO-Py (50%-50%)	348 358 368	4.84 10.3 19.9	0.063	75 ± 3	-24 ± 10
DMF-DMSO (50%-50%)	348 358 368	2.38 4.92 9.00	0.019	71 ± 4	-48 ± 12

Table 2. Rates and activation parameters of reaction (1) in which the complex NiTPTBP is formed in DMF, DMSO, Py, and their binary mixtures

* Calculated from the Arrhenius equation. Precision: ±10%

vated salts of 3*d* metals whose 3*d* shell is unfilled. *trans*-Activity was also found in Py, DMSO, and DMF molecules along S–Cu–S (homosolvates) and S₂–Cu–S₂ (mixed solvates) *trans*-coordinates in DMF–Py, DMF– DMSO, and DMSO–Py binary solvents.



Fig. 2. *trans*-Influence in the coordination sphere of $NiAc_2(S)_4$ in binary solvents: (1) DMSO–DMF, (2) Py–DMF, and (3) Py–DMSO.

A very important inference [18] is that *trans*-activity increases in going from the homogeneous coordinate L_T -M- L_T to heterogeneous coordinate L-M- L_T .

The results of our study displayed in Tables 1 and 2 and Figs. 1 and 2 imply that $[MAc_2(S)_{n-2}]$ solvated salts, where M = Co or Ni, have individual features. Whereas CoAc₂ reacts with phorphyrin at moderate and roughly equal rates in all three net solvents (avg., k_{ν}^{298} = 0.77 ± 0.12 L/(mol s)), NiAc₂ in DMF does not form Niporphyrin even at 368 K and reaction rates with Py (k_{ν}^{298} = 0.010 L/(mol s)) and DMSO ($k_v^{298} = 0.033$ L/(mol s)) differ by a factor of three. The absence of reaction (1) for NiAc₂ in DMF can arise from the dominance of $NiAc_2(DMF)_2$ tetrahedral complex in this solvent; the trans-effect cannot appear in these complex because of the absence of a *trans*-coordinate along axes x, y, and z [5, 17, 18]. In DMSO, Py, and DMSO-Py, DMF-Py, and DMF-DMSO (1:1) mixed solvents, there are sufficient concentrations of octahedral solvated salts $[NiAc_2(S)_4]$, in which the *trans*-effect is manifested. The degree of manifestation is dictated by the ratio of concentrations of octahedral and tetrahedral solvates.

In the NiAc₂–Py–DMSO(DMF) system, the *trans*influence is pronounced, especially in DMF–Py. The reaction rate in this system is about twofold the rate in net pyridine. *trans*-Activity along the Py–Ni–DMF coordinate evidently dominates in Py. In DMF–DMSO binary solvent, the *trans*-activity of DMSO along the DMF–Ni–DMSO coordinate is as along the Py–Ni–DMSO coordinate in the Py–DMSO system. These inferences are made from analysis of the data displayed in Table 2 and Fig. 2. Very close values of the activation energies (avg., 76 ± 2 kJ/mol) and activation entropies (avg., -29 ± 9 J/(mol K)) in five systems studied show that reaction (1) between porphyrin and NiAc₂ follows the same activation mechanism S_{EN}2 [19–21]. A rather similar scenario is observed in cobalt acetate (CoAc₂) systems in the same solvents (Table 1, Fig. 1), except for the fact that the reaction rate between CoAc₂ and TPTBP in net and mixed binary solvents is tens of times that for NiAc₂.

For mixed solvates of cobalt acetate based on CH₃COOH, the stability constants of $[CoAc_2(HAc)_3(DMF)]$, $[CoAc_2(HAc)_3(DMSO)]$, and [CoAc₂(HAc)₃Py] are 14.7, 15.0, and 240, respectively. For the corresponding mixed solvates of $ZnAc_2 K_{st}$ = 190, 204, and 1700. For [MnAc₂(HAc)₃(DMF)] K_{st} = 9.9, whereas for [NiAc₂(HAc)₃(DMF)] K_{st} = 5.4. From these values and the data compiled in Tables 1 and 2, the weaker the coordination link with an electrondonating solvent molecule, the weaker the trans-influence enhancing reaction (1). For this reason, the reaction rate for NiAc₂ is far lower than for CoAc₂. Probably, the same reason is responsible for the roughly equal enhancement of reaction (1) in mixed solvents, compared to net solvents, on account of trans-influence along S_1 -Co- S_2 axes; the enhancement is ~2.5-4 times in DMF-Py, ~4-5 times in DMSO-Py, and ~4 times in DMF-DMSO. Presumably, for CoAc₂ the same mechanism of the enhancing *trans*-effect on reaction (1) operates in all six solvents (Table 1), as the mean activation energy is 58 ± 3 kJ/mol and the mean activation entropy is -53 ± 8 J/(mol K). The activation energy for NiAc₂ is 18 kJ/mol higher and the activation entropy is 24 J/(mol K) higher than for CoAc₂. The solvatokinetic compensation effect strictly holds; this effect is characteristic of all phorphyrin coordination reactions [19–21] and caused by the high role of the solvent in forming the transition states of phorphyrin systems.

We also studied reaction (1) with manganese acetate $MnAc_2$ in the same solvents as we chose for NiAc₂ and CoAc₂. Unexpectedly, $MnAc_2$ was completely inert in Py, DMSO, and DMF. The destruction of the H₂TPTBP ligand was observed in all three solvents at 360°C, with the disappearance of strongest Soret band in the electronic absorption spectrum in the presence of $MnAc_2$ (Fig. 3). The ligand in DMF or DMSO was half-destructed in 2 h; in DMSO–DMF (1 : 1), the ligand was far more stable; and in Py, its destruction was the



Fig. 3. Destruction of the H_2 TPTBP ligand in DMF in the presence of MnAc₂ in 120 min.

slowest. Destruction reasons and mechanisms have not been studied.

The inertness of MnAc2 in complex-formation reaction (1) with tetraphenyltetrabenzoporphine is unexpected, the more so as Golubchikov et al. [22] found the trans-influence in the coordination sphere of $[MnAc_2(HAc)_{4-m}(DMF)_m]$ in the complex-formation reaction with tetraphenylporphine. Where 1.2 mol/L DMF is present in CH₃COOH, the MnTPP complex is formed three times as rapidly as in glacial CH₃COOH. Golubchikov et al. [22] concluded that, in the MAc₂-H₂TPP-CH₃COOH-DMF systems, the *trans*-influence of DMF along coordinates x and y in the octahedral complex changes in the order $Mn^{2+} < Co^{2+} > Ni^{2+}, Cu^{2+} \gg Zn^{2+}$ (for Zn^{2+} , it is zero). Toldina et al. [23] suggested that the trans-influence is impossible in high-spin manganese(II), cobalt(II), iron(II), and nickel(II) solvated salts. trans-Influence is manifested in these cations only in the low-spin state, which can appear in the transition state of reaction (1) and similar reactions with other phorphyrins. Avoiding the transition state, phorphyrin-coordinated manganese(II) and other metal(II) cations can return to the high-spin state.

The *trans*-influence mechanism in the coordination sphere of octahedral complexes has not been discussed in the literature. Bersuker and Ablov [5] assumed that the stronger steric crowding of the reaction site (M^{2+}), enhanced influence of *cis*-ligands, and the like are characteristic of this type of complex. However, Bersuker and Ablov [5] dealt with very strongly bound complexes of cobalt(III), ruthenium(III), rhodium(III), platinum(IV), and other metals.

In [17, 18, 22, 23], we studied the *trans*-influence of solvent molecules in the octahedral coordination sphere of solvate complexes of 3*d*-metal salts [13] with a labile, highly flexible inner sphere.

Proceeding from the mechanism of the formation of metal phorphyrin complexes from salt monosolvates $[MX_2(S)_{n-2}]$ and phorphyrins H_2P

$$[MX_{2}(S_{n-2})] + H_{2}P$$

$$\xrightarrow{-2S} [H_{2}P...MX_{2}(S)_{n-4}]^{\neq} \longrightarrow MP + 2HX + S...,^{(2)}$$

and from the structure of the transition state $[H_2P...MX_2(S)_{n-4}]^{\neq}$ [19–21], we propose the following scheme of the activation mechanism of *trans*-influence for octahedral salt heterosolvates in reaction (1):



The transition state is formed in the course of the attack of two labile solvent molecules (S) on the reaction site of phorphyrin H_2N_4 under the *trans*-effect of solvent molecules ($S_T = Py$, DMSO, DMF). N–H bonds are polarized and extended in the field of the cation and two solvent molecules (both S, and S_T ; as a result, two N \longrightarrow M donor–acceptor bonds are formed. As protons are removed from the phorphyrin plane, two more M \leftarrow N bonds are formed with the elimination of two acetate anions (Ac⁻) on account of solvation and their binding with protons. The entire kinetic system is in an isolated solvent cage [24], where phorphyrin parts with protons, the salt solvate is destroyed, and metal phorphyrin is formed.

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