

Ligand Exchange Reactions in Some Pentaamminecobalt(III) Complexes

R. C. PAUL, O. D. SHARMA & J. C. BHATIA

Department of Chemistry, Panjab University, Chandigarh 160014

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The exchange of water with triethylphosphate (TEP) in aquopentaamminecobalt(III) perchlorate, and of dimethylsulphoxide (DMSO) in (DMSO)-pentaamminecobalt(III) perchlorate in TEP is a unimolecular reaction. The product of the exchange reaction, (TEP)-pentaamminecobalt(III) perchlorate, has been characterized. Pyridine and chloride ion displace H₂O/DMSO ligand from the pentaammine complex. The rate of the ligand exchange is a function of the [substrate].

THE kinetics of exchange of water with monodentate and bidentate ligands in aquopentaamminecobalt(III) perchlorate in aqueous medium have been reported^{1,2}. Also the pentaamminecobalt(III) complexes having DMSO, DMF and pyridine as sixth ligand have been described^{3,4}.

In this paper we report the synthesis of a new complex, (TEP)-pentaamminecobalt(III) perchlorate (TEP=triethylphosphate) and kinetics of exchange of ligand L (L = H₂O, DMSO, DMF) in [Co(NH₃)₅L](ClO₄)₃ with TEP, chloride ion and pyridine in TEP medium.

Materials and Methods

The chemicals used were of reagent grade quality and were further purified by the reported methods⁵. (Triethylphosphate)-pentaamminecobalt(III) perchlorate was prepared from aquopentaamminecobalt(III) perchlorate. The substitution of H₂O by TEP was carried out by pouring aquo-complex (3 g, 0.0065 mole) and TEP (1.187 g, 0.0065 mole) onto 150 ml of water. The contents were heated up to 85° and concentrated at 85° for 20 min with a flash evaporating system. The reactants were cooled in an ice-bath, perchloric acid (1 : 3) added and the contents kept overnight at 4°. A violet red precipitate appeared which was filtered, washed successively with small amount of cold water, ethanol, ether and TEP and dried *in vacuo* (Found: Co 9.76. Req'd: Co, 9.44%); UV: 475, 337 nm.

(Dimethylsulphoxide)-pentaamminecobalt(III) perchlorate and (dimethyl formamide) pentaamminecobalt(III) perchlorate, were prepared by the reported methods^{3,6}.

Kinetics procedure—The kinetics of ligand displacement reaction were followed conductometrically (20°-45°) as well as spectrophotometrically (at 25° only) in pure TEP. The specific rate constants and the activation parameters were calculated. *k_s* values, calculated also from the spectrophotometric data (reference at 475 nm) for the reaction at 25° (room temperature), are in good agreement with those obtained from conductometric method. The reaction could not be followed spectrophotometrically at other temperatures because of certain limitations of the instruments available.

The visible and ultraviolet spectra of the mixtures were recorded on Cary-14 and Beckmann DU spectrophotometers.

Results and Discussion

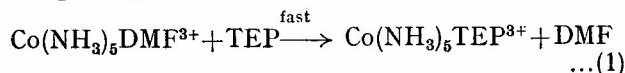
The study of kinetics of displacement of such ligands as DMSO, DMF and H₂O by TEP from the aqueous solutions of their pentaamminecobalt(III) complexes [Co(NH₃)₅DMSO](ClO₄)₃, [Co(NH₃)₅DMF](ClO₄)₃ and [Co(NH₃)₅H₂O](ClO₄)₃ (molar ratio of the complex and TEP is 1:10) is not possible because water behaves as solvent as well as the nucleophile. Also the aqueous solution of the complex [Co(NH₃)₅TEP](ClO₄)₃ always gives [Co(NH₃)₅H₂O](ClO₄)₃. Therefore, water as solvent is unsuitable for ligand exchange involving TEP. Hence, the reactions have been studied in pure TEP only.

The infrared spectra of aquo, DMSO and DMF complexes are identical with those reported earlier^{3,7}, and are reproducible in fresh TEP solutions. Evidence of the ligand character of TEP has been obtained from the IR spectrum of [Co(NH₃)₅TEP](ClO₄)₃ and of the spectra of solutions of other complexes after heating in TEP. These spectra show overlapping of perchlorate ion absorptions with $\nu_{\text{O}-\text{C}}$ and $\nu_{\text{P}=\text{O}}$ around 1000 and 1200 cm⁻¹ respectively. However, $\nu_{\text{P}-\text{O}}$ at 815 cm⁻¹ is strong and clearly defined. $\nu_{\text{P}=\text{O}}$ in free TEP at 1272 cm⁻¹ shifts to 1175 cm⁻¹ in the complex. This shift has been interpreted in terms of coordination through the oxygen atom of TEP.

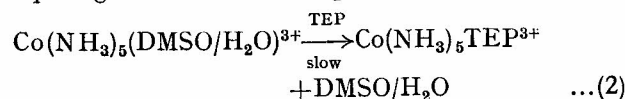
Whereas the conductivity of DMF complex in TEP remains unchanged, a gradual change in conductivity with time has been observed for aquo and DMSO complexes in TEP and $\Lambda_{\text{m}\infty}$ (molar conductance of the system after 24 hr) values are 24.0 and 20.7 ohm⁻¹ cm² mole⁻¹ respectively. There is a simultaneous increase in optical density (reference at 475 nm) of the reaction mixtures. The change in conductance of the system (which remains within the range for a 3:1 electrolyte) may be due to slow formation of [Co(NH₃)₅TEP]³⁺ ions from [Co(NH₃)₅H₂O](ClO₄)₃ and [Co(NH₃)₅DMSO](ClO₄)₃ respectively.

The complex [Co(NH₃)₅DMF](ClO₄)₃ dissolves in TEP on warming and gives [Co(NH₃)₅TEP]³⁺

ions (characteristic UV maxima at 475 and 337 nm) in solution. Δ_M (or optical density) changes very rapidly and therefore, precludes a kinetic study of the exchange reaction (1) either conductometrically or spectrophotometrically.



The electronic spectra of solutions of $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}(\text{ClO}_4)_4]$ (characteristic maxima² at 490 and 345 nm) and $[\text{Co}(\text{NH}_3)_5\text{DMSO}(\text{ClO}_4)_3]$ (characteristic maxima³ at 515 and 352 nm) in TEP do not change initially but when the solutions are allowed to stand for some time or are heated, the maxima corresponding to $[\text{Co}(\text{NH}_3)_5\text{TEP}](\text{ClO}_4)_3$ (characteristic values 475 and 337 nm) are produced. There is a slow change in conductance of the solution of aquo and DMSO complexes with time. Simultaneously the optical density (reference at 475 nm) of the reaction mixture also increases. The interchange of DMSO/aquo ligand with TEP is represented by reaction (2).



The DMSO/H₂O-TEP exchange may be due to the mass effect of TEP as solvent. At any stage of the reaction anation/aquation or TEP-DMSO/DMSO-TEP equilibrium is not proposed because the concentration of H₂O or DMSO is too low to compete with reaction (2) for an opposing reaction. The aquation of the starting ion and hydrolysis of TEP in the product is unlikely because an insignificant amount of water in the complex $[\text{Co}(\text{NH}_3)_5\text{DMSO}(\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}]$ cannot compete with a large excess of TEP as solvent. It has been shown that in aqueous or acidic conditions⁸ where formation of aquo complex from $[\text{Co}(\text{NH}_3)_5\text{TMP}]^{3+}$ (TMP-trimethylphosphate) is the principal reaction, ester hydrolysis is insignificant (only 12% compared with the lability of Co-O bond calculated as 88%).

The reaction follows a rate law

$$\text{Rate} = k[\text{Co}(\text{NH}_3)_5(\text{DMSO}/\text{H}_2\text{O})]^{3+}$$

The observed rate does not indicate whether the reaction follows an S_N1 mechanism or a compact S_N2 mechanism. The dependence of the rate on TEP concentration cannot be ascertained since its concentration is overwhelmingly large and remains almost constant throughout the reaction. However, our values of k_s (Table 1) for the reaction (2) are comparable in magnitude with those for first order specific rate constants for the systems^{8,9} $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+} - \text{H}_2\text{O}$, $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+} - \text{SO}_4^{2-}$ and $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+} - \text{H}_2\text{PO}_4^-$ which have been assigned an S_N1 mechanism. By comparison a similar mechanism has been preferred for reaction (2). However, a substantial kinetics influence of the solvent cannot be disregarded. This view is in line with the view expressed by Adamson¹⁰ and supported by Eigen¹¹.

The rate data at different temperatures yield for the parameters ΔH^\ddagger and ΔS^\ddagger the values 27.8 kcal mole⁻¹ and 22.3 e.u. for water complex and 23.5 kcal mole⁻¹ and 26.9 e.u. for DMSO complex. The ΔH^\ddagger values require that cobalt(III)-OH₂ and cobalt(III)-DMSO bonds in the activated complex be

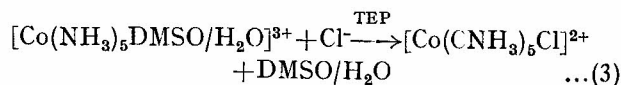
TABLE 1 — AVERAGE VALUES OF k_s AND ACTIVATION PARAMETERS FOR THE LIGAND EXCHANGE REACTIONS

L	$(M_s = 0.2-0.8 \text{ mmole/litre})$				ΔH^\ddagger kcal mole ⁻¹	ΔS^\ddagger e.u.
	$10^5 k_s \text{ (sec}^{-1}\text{) at}$					
	30°	35°	40°	45°		
	$(\text{NH}_3)_5\text{CoL}^{3+} + \text{TEP} \rightarrow (\text{NH}_3)_5\text{Co}(\text{TEP})^{3+} + \text{L}$					
H ₂ O	4.63	11.07	30.12	78.86	27.8	22.3
DMSO	3.87	9.34	25.59	74.60	23.5	26.9
	$(\text{NH}_3)_5\text{CoL}^{3+} + \text{Cl}^- \xrightarrow{\text{TEP}} (\text{NH}_3)_5\text{CoCl}^{2+} + \text{L}$					
H ₂ O	—	3.21	11.40	27.40	26.0	23.3
DMSO	—	7.33	12.79	30.27	29.3	-4.0

SD of $k_s = 1.25$; $\Delta H^\ddagger = 0.27$; and $\Delta S^\ddagger = 1.2$. Temperatures maintained with an accuracy of $\pm 0.1^\circ$.

stretched to a critical value. There is no basis for deciding whether a true intermediate is formed on decomposition of the activated complex or some use is made of the entering TEP molecule in the activation process. Positive values of ΔS^\ddagger are as large as would be expected if the activated complex were to have the properties of S_N1 process.

In the presence of CH_3COCl or $(\text{C}_2\text{H}_5)_4\text{NCl}$ solutions of $[\text{Co}(\text{NH}_3)_5\text{DMSO}/\text{H}_2\text{O}](\text{ClO}_4)_3$ in TEP finally exhibit maxima at 500 and 341 nm which are characteristic for the cation $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$. Besides the principal reaction (3)



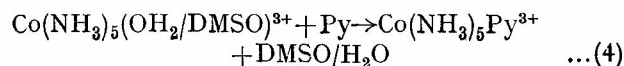
there exists a reduction process involving conversion of some octahedral Co(III) species to tetrahedral cobalt(II) species. This has been substantiated by the slow development of a blue tinge and also by the appearance of absorption bands⁵ at 660, 610 and 595 nm.

The first order specific rate constant for different mole ratios of the substrate and chloride ion (Table 1) have been calculated. At lower $[\text{Cl}^-]$, deviations are insignificant and the reaction appears to be first order in $[\text{Co}(\text{NH}_3)_5(\text{DMSO}/\text{H}_2\text{O})]^{3+}$. The rate law for the entire range is

$$\text{Rate} = (k_1 + k_2[\text{Cl}^-])[\text{complex}]$$

ΔH^\ddagger and ΔS^\ddagger for the replacement of H₂O and DMSO between $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ and chloride ion, and $[\text{Co}(\text{NH}_3)_5\text{DMSO}]^{3+}$ and chloride ion are 26.0, 29.3 kcal mole⁻¹ and 23.3 and -4.0 e.u. respectively. The entropy values favour the involvement of chloride ion in the activated complex. Thus the values of ΔS^\ddagger does not rule out an S_N2 mechanism in which a seven-coordinate activated complex may be formed. However, stronger solvation of chloride ion compared to H₂O or DMSO might have some contribution to the overall ΔS^\ddagger values for the reaction.

The reaction (4)



appears to follow a path similar to reactions (1) and (2). For the dilute solutions of $[\text{Co}(\text{NH}_3)_6(\text{DMSO}/\text{H}_2\text{O})](\text{ClO}_4)_3$ in pyridine an immediate change in colour has been observed. The resulting spectrum shows absorption maxima at 479 and 341 nm which have been assigned to $[\text{Co}(\text{NH}_3)_6\text{Py}]^{3+}$ ion. However, the reaction could not be followed kinetically because both conductivity and spectrophotometric methods failed to register the rapid change in conductance/absorbance as a function of time. The reaction has also been investigated as a function of [pyridine] in TEP as solvent. The shifts in the positions of absorption bands appear to depend on [Py]. However, the overall reaction does not seem to be a simple one because the results are not reproducible within permissible limits of error. Hence the possibility of competitive equilibria involving pyridine and TEP cannot be disregarded.

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