

Mixed Ligand Co (II) Complexes: Use as Catalysts in the Hydrolysis of Esters

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Abstract: Mixed ligand metal complexes of the type $MLL' \cdot xH_2O$ ($x=1$), where M is Co(II)/Ni(II), L is deprotonated 8-hydroxyquinoline and L' is a deprotonated amino acid have been synthesized. The metal complexes have been characterized on the basis of elemental analysis and various physicochemical techniques. Hydrolysis of methyl acetate and ethyl acetate was studied by using the complexes as homogeneous catalysts. The rate constants have been obtained by using different catalysts at various temperatures. The activation energy (E) was calculated from the Arrhenius plots. The changes in the enthalpy of activation (ΔH^\ddagger), entropy of activation (ΔS^\ddagger) and free energy of activation (ΔG^\ddagger) were also calculated. A probable reaction mechanism has also been suggested.

Key words: Mixed ligand complexes, hydrolysis of esters.

I. Introduction

Some metal ligand complexes are found to catalyze reactions such as oxidation, oxidative cleavage, hydroformylation, etc. and have shown catalytic activity in decomposition of hydrogen peroxide [1]. It is well established that ternary complexes play a decisive role in the activation of enzymes and also in the storage and transport of active substances [2]. The binary and ternary transition metal complexes have shown biological activity [3]. Mixed ligand complexes of transition metals are commonly found in biological systems. During recent years metal complexes of some N-/O- donor ligands have attracted considerable attention because of their greater antifungal and antibacterial activities than those of the parent ligands [4,5]. Ternary complexes containing an amino acid as a secondary ligand are of significance as they are potential models for enzyme-metal ion substrate complexes [6]. It has been found that a majority of the metal complexes with 8-hydroxyquinoline possessing biological activities [7].

The present paper reports the synthesis and characterization of mixed ligand Co(II)/Ni(II) complexes prepared by using 8-hydroxyquinoline as primary ligand and some amino acids as secondary ligands. Hydrolysis of methyl acetate and ethyl acetate was studied by using the complexes as homogeneous catalysts. A probable reaction mechanism has also been suggested.

II. Experimental

Materials

Most of the chemicals used were of AR grade. Laboratory grade chemicals, whenever used, were purified by standard methods. Solvents ethanol, methanol and chloroform were purified and dried according to standard procedures.

Preparation of mixed ligand complexes [5]

The metal complexes were prepared from Co(II)/Ni(II) chloride hexahydrate, 8-hydroxyquinoline (HQ) and various amino acids such as L(-)-alanine, L(-)-valine, L(-)-leucine L(-)-phenylalanine, L(-)-cysteine and L(+)-glutamic acid.

To a blue-colored ethanol (10 cm^3) solution of metal(II) chloride hexahydrate (1 mmol), was added an ethanol (10 cm^3) solution of 8-hydroxyquinoline (1 mmol). The mixture was stirred and kept in a boiling water bath for 10 minutes, during which time it turned green. To this was added an aqueous (10 cm^3) solution of the amino acid (1 mmol). This mixture (1:1:1 molar proportion) was heated in a hot water bath till the temperature reached 50°C . The complexes precipitated immediately except those with alanine and cysteine, which were obtained by raising the pH of the reaction mixture from 2.9 to 6 by addition of 0.01 M NaOH solution. The mixture was cooled and the solid was filtered, washed with ice-cold water followed by 1:1 ethanol:water. The complexes thus prepared were dried under vacuum.

Instrumentation

The complexes were analysed for the metal contents, C, H and N using standard procedures. The molar conductance values were measured in methanol (10^{-3} M) on a model CM-180 Elico digital conductivity meter. Room temperature magnetic susceptibilities were measured by Guoy balance using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as the

calibrant. Electronic absorption spectra in methanol (10^{-4} M) and chloroform (10^{-3} M) solution in the ultraviolet and visible range, respectively, were measured on a Shimadzu UV-160A and Spectronic-20 spectrophotometer. Reflectance spectra of the solid complexes in the visible region were recorded against BaSO₄ on a Shimadzu UV-2100 spectrophotometer. FT-IR spectra were recorded in KBr discs on a Perkin-Elmer FT-IR spectrophotometer model 160. Thermal studies of the complexes were made on a Mettler TC 10A TA processor by recording the change in weight of the complexes on increasing the temperature upto 700⁰ C at a heating rate of 10⁰ C/min.

Hydrolysis of esters

To a solution of Co(II)/Ni(II) complex, prepared by dissolving known amount of it in a solvent mixture of 20 cm³ DMF and 20 cm³ distilled water, whose pH was adjusted to 2.5, 5 cm³ of ester was added and the content stirred uniformly. The extent of the reaction was estimated by withdrawing 5 cm³ of reaction mixture at regular intervals of time and titrating it against standard NaOH solution using phenolphthalein as an indicator. Reaction was carried out at 30, 40 and 50⁰C in a thermostat with an accuracy of $\pm 0.01^{\circ}$ C. The quantity of catalysts used was in the range 0.01-0.04 g.

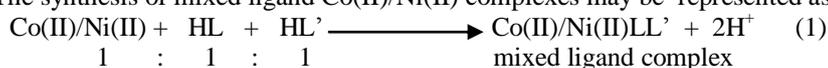
The reaction rates were compared with the rates obtained by using HCl as conventional catalyst. 40 cm³ of HCl of known strength was taken in a stoppered bottle and 5 cm³ of ester was added to it. The extent of reaction taking place was obtained as mentioned above. Reaction was carried out at 30, 40 and 50⁰C using 0.002, 0.01 and 0.05 M HCl.

The activation energy (*E*) was calculated from the Arrhenius plots. The changes in the enthalpy of activation (ΔH^{\ddagger}), entropy of activation (ΔS^{\ddagger}) and free energy of activation (ΔG^{\ddagger}) were also calculated.

III. Results And Discussion

Characterization of metal complexes

The synthesis of mixed ligand Co(II)/Ni(II) complexes may be represented as follows:



(where HL is 8-hydroxyquinoline and HL' is a secondary ligand).

All of the complexes are non-hygroscopic stable solids. They are coloured and thermally stable (Table 1), indicating a strong metal-ligand bond. The elemental analysis data (Table 1) of metal complexes is consistent with their general formulation as mixed ligand complexes MLL'.xH₂O. The molar conductance values of the complexes in methanol at 10⁻³ M concentration are very low (<1), indicating their non-electrolytic nature[8].

Magnetic studies

The observed μ_{eff} values (Table 1) are suggestive of the tetrahedral geometry for the Co(II) complexes and an octahedral geometry for the Ni(II) complex. The magnetic moments of the compounds investigated are in agreement with the conclusions based on spectral findings.

Infra-red spectra

The FT-IR spectra of the metal complexes were recorded as KBr discs over the range 4000-400 cm⁻¹. On the basis of reported infra-red spectra of ligands and their metal complexes some of the important bands have been assigned[6,9-10].

A broad band observed in the region between 3362-3315 cm⁻¹ due to asymmetric (asym) and symmetric (sym) O-H stretching modes and a strong band around 1575-1573 cm⁻¹ due to H-O-H bending vibrations are indicative of the presence of lattice water[11]. The N-H asym and N-H sym vibrations observed at ~3040 and ~2960 cm⁻¹, respectively, in the free amino acids are shifted to higher wave numbers *i.e.* in the range 3220-3174 cm⁻¹ and 3080-3050 cm⁻¹ respectively, in the spectra of the complexes, suggesting coordination of the amino group through nitrogen with the metal ion. The $\nu_{\text{asym}}(\text{COO}^-)$ band of the free amino acids *i.e.* ~1590 cm⁻¹ is shifted to higher wave number, *i.e.* in the range 1640-1630 cm⁻¹ and the $\nu_{\text{sym}}(\text{COO}^-)$ mode observed at ~1400 cm⁻¹ in the spectra of free amino acids is found to be shifted to lower wave number *i.e.* 1380-1377 cm⁻¹, in the spectra of the CML complexes indicating the coordination of the carboxylic acid group *via* oxygen with the metal ion. Nakamoto, Morimoto, and Martell showed that for a given ligand, the difference ($\nu_{\text{asym}} - \nu_{\text{sym}}$) would increase as the M-O bond becomes more covalent, since the caboxylate stretching becomes correspondingly more asymmetrical. In the present investigation, this difference being in the range 252-267 cm⁻¹ indicates that the M-O bond is purely covalent. The C-N sym stretching frequency observed at ~950 cm⁻¹ in the spectra of amino acids is found to be shifted to lower wave number *i.e.* ~908 cm⁻¹ in the spectra of the complexes, confirming coordination through the amino group of the amino acids.

An important feature of infrared spectra of the metal complexes is the absence of the band at $\sim 3440\text{ cm}^{-1}$ due to O-H stretching vibration of the OH group of HQ. This observation leads to the conclusion that the complex formation takes place by deprotonation of the hydroxyl group of HQ moiety. In the spectrum of free HQ ligand the $\nu(\text{C-O})$ band is observed at $\sim 1160\text{ cm}^{-1}$. It is reported that for the mixed ligand complexes of Co(II), Mn(II), Cu(II), Ni(II) and Vo(II) with HQ, this band is observed at $\sim 1125\text{ cm}^{-1}$. The position of this band undergoes variation depending on the metal complex under study. In the present investigation, a strong $\nu(\text{C-O})$ band is observed in the range $1107\text{-}1103\text{ cm}^{-1}$ in the spectra of the complexes, indicating the presence of 8-hydroxyquinolate group in the complexes coordinating through its nitrogen and oxygen atoms as uninegative bidentate ligand. The $\nu(\text{C=N})$ mode observed at 1580 cm^{-1} in the spectrum of free HQ ligand is found to be shifted to lower wave number *i.e.* $1500\text{-}1499\text{ cm}^{-1}$ in the spectra of the CML complexes, suggesting coordination through the tertiary nitrogen donor of HQ. The in-plane and out-of-plane ring deformation modes observed at ~ 500 and $\sim 780\text{ cm}^{-1}$, respectively, in the spectrum of HQ are shifted to higher wave numbers *i.e.* ~ 505 and $\sim 787\text{ cm}^{-1}$, respectively, confirming coordination through the nitrogen atom of HQ with the metal ion.

Some new bands of weak intensity observed in the regions around $657\text{-}595$ and $466\text{-}415\text{ cm}^{-1}$ may be ascribed to the M-O and M-N vibrations, respectively[12]. It may be noted that these vibrational bands are absent in the infrared spectra of HQ as well as the amino acids. Some of the important IR bands and their tentative assignments are shown in Table 2.

Electronic absorption spectra

The electronic spectra of the metal complexes in methanol solution, recorded in the ultraviolet region, exhibit intra-ligand and charge transfer transitions in the range around $25,940\text{-}48,192\text{ cm}^{-1}$ and near $26,000\text{ cm}^{-1}$, respectively. The electronic absorption spectra of Co(II) complexes in chloroform solution in the visible and near infrared region shows three transition bands in the region around $25,000\text{ cm}^{-1}$, $16,666\text{ cm}^{-1}$ and $12,000\text{ cm}^{-1}$ respectively, while that of the Ni(II) complex shows two transition bands in the region around $25,000\text{ cm}^{-1}$ and $12,195\text{ cm}^{-1}$, respectively.

The diffuse reflectance spectra of Co(II) complexes show the d-d transition bands in the region around $12,900$ and $17,500\text{ cm}^{-1}$, which are assigned to transitions ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{F})$ (ν_2) and ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{P})$ (ν_3), respectively. The Ni(II) complex shows two transition bands in the region around $12,700$ and $18,900\text{ cm}^{-1}$, which are ascribed to transitions ${}^3\text{A}_2(\text{F}) \rightarrow {}^3\text{T}_1(\text{F})$ (ν_2) and ${}^3\text{A}_2(\text{F}) \rightarrow {}^3\text{T}_1(\text{P})$ (ν_3), respectively. As the ν_1 band occurs at low energy, it is not observed in all the cases. Various spectral parameters like Dq, B' and β have been calculated by using the values of ν_2 and ν_3 transitions, according to the equations of König[13]. From the values of Dq and B', the energy of transition ν_1 has been calculated (Table 3).

The observed electronic transitional energies are suggestive of tetrahedral geometry for Co(II) complexes and an octahedral geometry for Ni(II) complex. The present β values are less than unity, suggesting an appreciable covalent character of the M-L bonds [14].

Thermal Studies

The thermograms (TG) of the complexes have been recorded in flowing nitrogen atmosphere at the heating rate of $10\text{ }^\circ\text{C}/\text{min}$ on approximately 10 mg samples. All the complexes investigated show similar behavior in their TG and Differential Thermal Analysis (DTA) studies.

The complexes, in general, show the first mass loss attributed to dehydration, in the temperature range 109 to $129\text{ }^\circ\text{C}$ (Table 4). The completion of the reaction was found to be around $555\text{ }^\circ\text{C}$.

On the basis of the results of the physico-chemical studies, the bonding and structure in the metal complexes can be represented as shown in Figure 1.

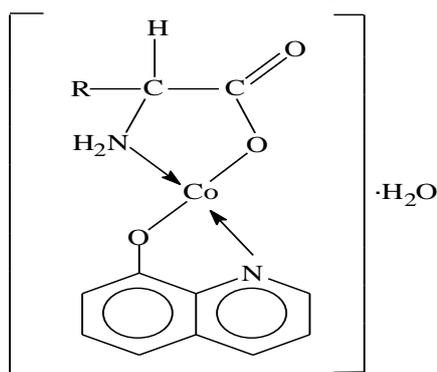


Fig.1. Proposed structure of metal complexes

Hydrolysis of esters

Hydrolysis of methyl acetate and ethyl acetate was studied by using complexes as homogeneous catalysts.

Keeping the quantity of ester and the temperature constant, when the quantity of catalyst was varied in the range 0.01-0.04 g, the value of k increased with increase in the quantity of the catalyst (Table 5).

Table 5. Influence of the amount of catalyst on the hydrolysis of ethyl acetate by a representative complex [Co(Q)(Val)].H₂O

Amount of catalyst (g)	Specific reaction rate, $k \times 10^{-4} \text{ (min}^{-1}\text{)}$
0.010	0.52
0.020	0.80
0.030	1.25
0.040	1.64

^aTemperature: 313 K, volume of ethyl acetate: 5.0 cm³.

The plot of rate constant versus the amount of catalyst (Fig. 2) is linear showing that the rate constant is directly proportional to the amount of catalyst used in the reaction. A similar correlation has been established in the case of aliphatic esters by Walvekar *et al*[15].

Hammett *et al*[16] have shown that the hydrolysis of ethyl acetate in presence of HCl is first order in [ester]. In the present study, it is found that with the present Co(II) complexes also the hydrolysis is first order in [ester] as shown by the linear plot of $\log(a-x)$ against t . The rate constants for the hydrolysis of methyl acetate and ethyl acetate obtained by using different catalysts at various temperatures are given in Table 6 and 7 respectively. Keeping the quantity of the catalyst and ester constant, when the temperature was varied in the range 30-50°C, the value of k increased with increase in temperature. As a catalyst, however, HCl is more efficient as compared to the mixed ligand complexes.

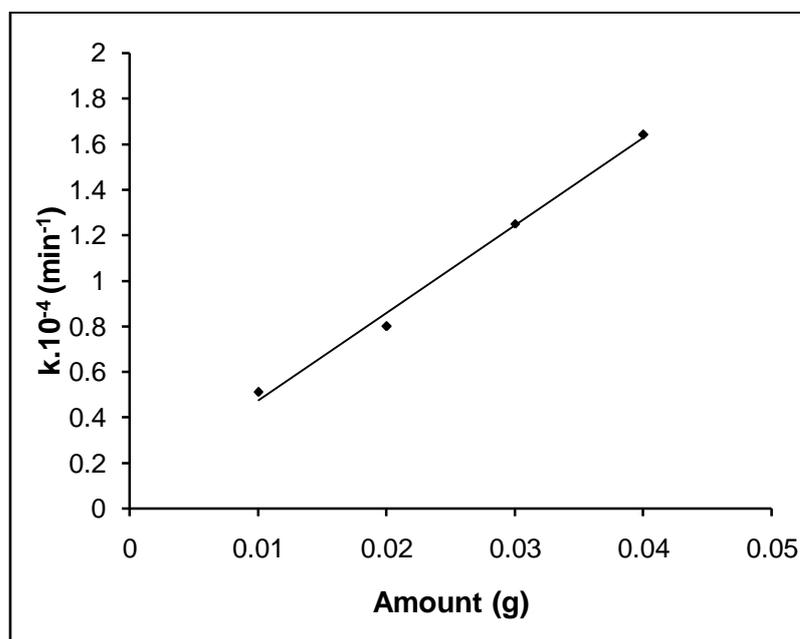


Fig. 2. Plot of rate of reaction versus amount of catalyst [Co(Q)(Val)].H₂O (Temperature: 313 K, volume of ethyl acetate: 5.0 cm³)

It has been found that the rate of hydrolysis of methyl acetate is higher than that of ethyl acetate for all the catalysts, indicating that steric hindrance affects the rate of the reaction. The rate is reduced by the bulkier ethyl group near the reaction site [17], in addition to which there would be contribution due to normal inductive and resonance effects of the substituent.

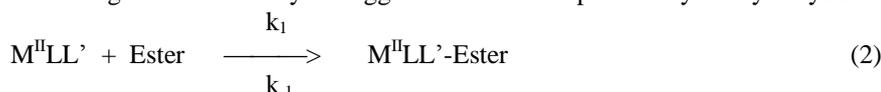
The influence of the amino acid side chain of the mixed ligand Co(II) complex in the hydrolysis of the ester is of interest because the information so obtained can contribute to an understanding of the chemical function of these groups in more complicated systems especially the biological ones. Any substituent on the α -carbon of the amino acid, which repels the electrons, is found to decrease the general acid properties of the

complex. The side chains of L-alanine, L-leucine and L-valine are electron repelling; the corresponding complexes catalyze the reactions with slower rates. The effect of steric hindrance due to amino acid side chain in the complexes on the ester hydrolysis reaction is visible when the side chain of the amino acid is varied from the least hindered alanine to the most hindered valine. The steric hindrance thus enhances the rate of the reaction. Another reason may be that the electron repelling methyl group is closer to the coordinated Co(II) ion (inductive effect) in alanine as compared to that in leucine and valine. Activation energy values are found to decrease as amino acid moiety varies from alanine to valine in the mixed ligand complexes, further indicating comparatively higher reaction rate with valine complex.

It is observed that ΔH^\ddagger values are closer to E values in accordance with absolute reaction rate theory for solution. The value of ΔG^\ddagger has been found to be higher in all the cases and not much difference has been found in two systems. The values of ΔS^\ddagger were found to be negative in all the cases indicating that molecules in transition state are more ordered than the reactants in ground state.

In the hydrolysis of esters, the activated complexes are probably quite polar, owing to the ionization of the carbonyl group. Owing to the electrostriction of the solvent by the activated complexes in such reactions, the entropies of activation are low. Such reactions are accelerated by an increase in the dielectric constant of the solvent. Another reason for strongly negative values may be the partial immobilization of water molecules in the activated state, brought about as a result of the distribution of charges on activated complex.

Following mechanism may be suggested for the complex catalyzed hydrolysis of esters.



On the basis of steady state approximation,

$$[M^{II}LL'-Ester] = \frac{k_1 [Ester] [M^{II}LL']}{k_{-1} + k_2 [H^+]} \quad (4)$$

The rate of the reaction is given as

$$\frac{dx}{dt} = \frac{k_1 k_2 [Ester] [M^{II}LL']}{k_{-1} + k_2 [H^+]} \quad (5)$$

Under the present experimental conditions, $[Ester]$ is much larger than $[H^+]$. Hence, $k_{-1} + k_2 [H^+]$ can be neglected. Eq. (5) then changes to Eq. (6).

$$\frac{dx}{dt} = k_1 k_2 [Ester] [M^{II}LL'] \quad (6)$$

The hydrolysis of ester seems to be bimolecular as ester and catalyst are involved in the reaction kinetics. The above mechanism predicts a first order dependence on $[M^{II}LL']$. According to Eq. (6), a plot of rate of the reaction against $[M^{II}LL']$ should be linear. This is found to be so, as seen from the plot in Figure 2, indicating the validity of the rate law (6) and hence of the proposed mechanism.

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Table 1. Observed Color, Decomposition Temperature, Magnetic Moment and Elemental Analysis Data of the Metal Complexes^a

Complex	Empirical formula (Formula Wt.)	Yield, %	Color	Decomp. Temp. (°C)	Elemental Analysis, % Found (Calculated)				μ_{eff} (B.M.)
					M	C	N	H	
[Co(Q)(Ala)]·H ₂ O	C ₁₂ H ₁₄ CoN ₂ O ₄ (308.93)	83	Light green	210	19.18 (19.07)	46.79 (46.61)	9.16 (9.06)	4.63 (4.53)	4.05
[Co(Q)(Val)]·H ₂ O	C ₁₄ H ₁₈ CoN ₂ O ₄ (336.93)	89	Light green	225	17.35 (17.49)	49.68 (49.86)	8.21 (8.31)	5.19 (5.34)	4.05
[Co(Q)(Leu)]·H ₂ O	C ₁₅ H ₂₀ CoN ₂ O ₄ (350.93)	81	Light green	213	17.92 (16.79)	51.16 (51.29)	7.60 (7.97)	5.75 (5.69)	4.12
[Co(Q)(Phe)]·H ₂ O	C ₁₈ H ₁₈ CoN ₂ O ₄ (384.93)	89	Light green	251	15.38 (15.30)	55.95 (56.11)	7.41 (7.27)	4.59 (4.67)	4.52
[Co(Q)(Cys)]·H ₂ O	C ₁₂ H ₁₄ CoN ₂ O ₄ S (340.99)	85	Light green	>300	17.48 (17.28)	42.41 (42.23)	7.99 (8.21)	4.25 (4.10)	4.03
[Ni(Q)(Phe)]·H ₂ O	C ₁₈ H ₁₈ NiN ₂ O ₄ (384.69)	93	Green	200	15.41 (15.25)	56.01 (56.11)	7.25 (7.27)	4.50 (4.67)	2.82

^awhere Q represents the deprotonated primary ligand 8-hydroxyquinoline whereas Ala, Val, Leu, Phe, Cys and Glu represent the deprotonated secondary ligands alanine, valine, leucine, phenylalanine, cysteine and glutamic acid, respectively.

Table 2. Some Important Infrared Spectral Bands (cm^{-1}) of the Complexes^a

Complex	$\nu(\text{O-H})$ (H_2O)	$\nu(\text{N-H})$ (asym) (A.a.)	$\nu(\text{N-H})$ (sym) (A.a.)	$\nu(\text{COO}')$ (asym) (A.a.)	$\nu(\text{COO}')$ (sym) (A.a.)	$\nu(\text{HOH})$	$\nu(\text{C=N})$ (HQ)	$\nu(\text{C-O})$ (HQ)	$\nu(\text{C-N})$ (sym.) (A.a.)	$\nu(\text{C-H})^a$ (HQ)	$\nu(\text{C-H})^b$ (HQ)	$\nu(\text{M-N})$	$\nu(\text{M-O})$
[Co(Q)(Ala)]·H ₂ O	3315 w	3174 w	3055 w	1630 s	1378 s	1573 s	1499 s	1104 s	907 w	786 w	506 w	602 ^c w 646 ^d w	420 ^e w 450 ^d w
[Co(Q)(Val)]·H ₂ O	3362 w	3218 w	3058 w	1639 s	1380 s	1575 s	1500 s	1106 s	907 w	788 w	505 w	603 ^c w 648 ^d w	435 ^e w 465 ^d w
[Co(Q)(Leu)]·H ₂ O	3322 w	3210 w	3075 w	1645 s	1378 s	1573 s	1500 m	1104 s	906 w	787 w	505 w	595 ^c w 657 ^d w	425 ^e w 450 ^d w
[Co(Q)(Phe)]·H ₂ O	3320 w	3178 w	3050 w	1638 s	1377 s	1574 m	1499 m	1104 s	906 w	787 w	505 w	602 ^c w 646 ^d w	425 ^e w 460 ^d w
[Co(Q)(Cys)]·H ₂ O	3360 w	3210 w	3080 w	1640 s	1380 s	1575 m	1500 s	1107 s	909 w	788 w	506 w	602 ^c w 648 ^d w	420 ^e w 466 ^d w
[Co(Q)(Glu)]·H ₂ O	3325 w	3178 w	3055 w	1640 s	1377 s	1573 m	1499 s	1103 s	908 w	787 w	507 w	597 ^c w 649 ^d w	415 ^e w 455 ^d w
[Ni(Q)(Phe)]·H ₂ O	3320 w	3210 w	3075 w	1638 s	1379 s	1577 m	1499 m	1107 s	907 w	786 w	505 w	602 ^c w 646 ^d w	405 ^e w 460 ^d w

Table 3. Diffuse Reflectance Spectral Data for the Complexes

Complex	ν_1 (cm^{-1}) ^a	ν_2 (cm^{-1})	ν_3 (cm^{-1})	$\frac{Dq}{(\text{cm}^{-1})}$	B (cm^{-1})	β
[Co(Q)(Ala)]·H ₂ O	6,285	12,903	17,391	628.5	762.5	0.785
[Co(Q)(Val)]·H ₂ O	6,231	12,820	17,241	623.1	757.7	0.780
[Co(Q)(Leu)]·H ₂ O	6,231	12,820	17,241	623.1	757.7	0.780
[Co(Q)(Phe)]·H ₂ O	6,290	13,157	17,391	629.0	778.3	0.801
[Co(Q)(Cys)]·H ₂ O	6,126	12,195	16,949	612.6	717.7	0.739
[Co(Q)(Glu)]·H ₂ O	6,252	12,820	17,301	625.2	757.5	0.780
[Ni(Q)(Phe)]·H ₂ O	6,901	12,706	18,939	690.1	729.4	0.700

^aCalculated values.

Table 4. Thermal Data for the Complexes

Complex	Temperature Range ($^{\circ}\text{C}$) ^a	Weight loss due to H ₂ O (%)	
		Calculated	Observed
[Co(Q)(Ala)]·H ₂ O	109-186	5.8	6.1
[Co(Q)(Val)]·H ₂ O	129-183	5.4	5.3
[Co(Q)(Leu)]·H ₂ O	116-200	5.1	5.2
[Co(Q)(Phe)]·H ₂ O	114-183	4.7	4.9
[Co(Q)(Cys)]·H ₂ O	117-175	5.2	4.9
[Co(Q)(Glu)]·H ₂ O	123-197	4.9	4.8
[Ni(Q)(Phe)]·H ₂ O	119-169	4.7	5.7

^aFirst mass loss step during decomposition.

Table 6. Kinetics of hydrolysis^a of methyl acetate in presence of complexes as homogeneous catalysts^b

Complex	T (K)	$k \times 10^{-2}$ (min ⁻¹)	E (kJ.mol ⁻¹)	ΔH^{\ddagger} (kJ.mol ⁻¹)	ΔS^{\ddagger} (J.K ⁻¹ .mol ⁻¹)	ΔG^{\ddagger} (kJ.mol ⁻¹)
[Co(Q)(Ala)]·H ₂ O	303	0.71	56.16	53.56	-172.44	107.53
	313	1.38				
	323	2.80				
[Co(Q)(Val)]·H ₂ O	303	1.20	30.23	27.63	-254.47	107.28
	313	1.77				
	323	2.42				
[Co(Q)(Leu)]·H ₂ O	303	0.73	44.67	42.07	-209.87	107.76
	313	1.35				
	323	2.39				
[Co(Q)(Phe)]·H ₂ O	303	0.81	47.86	45.26	-198.92	107.52
	313	1.42				
	323	2.68				
[Co(Q)(Cys)]·H ₂ O	303	1.02	33.29	30.69	-244.47	107.20
	313	1.58				
	323	2.94				
[Co(Q)(Glu)]·H ₂ O	303	0.60	57.44	54.84	-169.60	107.92
	313	1.18				
	323	2.42				
[Ni(Q)(Phe)]·H ₂ O	303	0.47	32.90	31.30	-252.17	109.00
	313	0.82				
	323	1.15				

^aVolume of ester taken : 5 cm³

^bAmount of catalyst : 40 mg

Table 7. Kinetics of hydrolysis^a of ethyl acetate in presence of complexes as homogeneous catalysts^b

Complex	T (K)	$k \times 10^{-2}$ (min ⁻¹)	E (kJ.mol ⁻¹)	ΔH^\ddagger (kJ.mol ⁻¹)	ΔS^\ddagger (J.K ⁻¹ .mol ⁻¹)	ΔG^\ddagger (kJ.mol ⁻¹)
[Co(Q)(Ala)].H ₂ O	303	0.62	53.61	51.01	-182.2	108.06
	313	1.15				
	323	2.22				
[Co(Q)(Val)].H ₂ O	303	0.82	39.22	36.62	-226.3	107.48
	313	1.64				
	323	2.52				
[Co(Q)(Leu)].H ₂ O	303	0.69	46.80	44.20	-203.9	108.04
	313	1.24				
	323	2.09				
[Co(Q)(Phe)].H ₂ O	303	0.76	50.14	47.54	-192.2	107.69
	313	1.27				
	323	2.56				
[Co(Q)(Cys)].H ₂ O	303	0.78	33.29	30.69	-246.4	107.81
	313	1.48				
	323	2.13				
[Co(Q)(Glu)].H ₂ O	303	0.56	9.56	56.96	-163.0	107.98
	313	1.15				
	323	2.39				
[Ni(Q)(Phe)].H ₂ O	303	0.42	33.41	30.81	-248.09	109.19
	313	0.69				
	323	0.99				

^aVolume of ester taken : 5 cm³

^bAmount of catalyst : 40 mg