Substitution of Dehydroactic Acid in Cu(II) and Ni(II) *Bis*(dehydroacetato) Complexes Using 1,4-Dihydroxyanthrquinone and Oxime in Non-Polar Solvents

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Pseudo first-order reaction conditions of excess Cu(II) and Ni(II) (dehydroacetato) Hdha, complexes concentration over second ligands such as 8-hydroxyquinoline (Hquin) or 1,4-dihydroxyanthraquinone (H_2dhaq) was employed. The ligand substitution reactions of (dha) in Cu(II) and Ni(II) complexes with 8-hydroxyquinoline or 1,4-dihydroxyanthraquinone were investigated spectrophotometrically in nonpolar solvents like cyclohexane, chloroform and dichloromethane. The reaction was performed at four different temperatures (283, 288, 293 and 298 K). The observed rate constant (k_{obs}) depends on the concentration of both leaving and entering ligands. The higher values of jobs are associated with a lower activation energy, *i.e.* the entropy is greater for the slower reaction. The solid mixed ligand complexes were isolated and characterized by elemental analysis, magnetic moments, FT-IR, ESR, molar conductivity and UV-visible spectral techniques. Square planar geometries of Cu(II) complexes and distorted octahedral for the Ni(II) complexes are suggested.

Keywords: Substitution reactions, Order reactions, Geometry shape.

INTRODUCTION

Dehydroacetic acid appeared as an attractive ligand for complexation and having biological and industrial applications [1-3]. Some transition metal complexes from Hdha proved to be valuable as bactriostatic agents and act as a model for biochemical reactions [4]. 8-Hydroxyquinoline was mainly applied for analytical purposes and separation techniques as an excellent reagent for the extraction of metal ions due to its extraordinary coordinating capabilities [5-10].

In this article, one molecule of dha in [Cu(dha)$_2$] and [Ni(dha)$_2$·2H$_2$O] complexes substituted by one molecule of 1,4-dihydroxyanthraquinine (H$_2$dhaq) or 8-hydroxyquinoline (Hquin) in nonpolar solvents such as cyclohexane, chloroform and dichloromethane at different temperatures from 283 to 298 K. The process was studied by quantitative UV-visible spectroscopy in the presence of excess [Cu(dha)$_2$] and [Ni(dha)$_2$·2H$_2$O] concentrations. The rate constants (K$_{obs}$) and the activation parameters are calculated. The solid mixed ligand metal complexes are isolated and characterized by elemental, molar conductance, magnetic moments, FT-IR, ESR and UV-visible spectral techniques. Square planar geometries of Cu(II) complexes and distorted octahedral for the Ni(II) complexes are suggested.

EXPERIMENTAL

[Cu(dha)$_2$] and [Ni(dha)$_2$·2H$_2$O] was prepared as previously described [1] and were recrystallized from chloroform. 8-Hydroxyquinoline (Hquin) and dihydroxyanthraquinone (H$_2$dhaq) were of AR grade (Merck products). Non-polar solvents (chloroform, cyclohexane and dichloromethane) were of analar grade.

The carbon, nitrogen and hydrogen of the solid metal complexes were determined by elementary analyzer system GmbH Vairo El. Conductivity measurements for the various complexes were carried out using Jenway 4320 meter Lab conductivity meter in DMF solutions at 1×10^{-3} mol L^{-1} concentrations at room temperature. Electronic spectra were run on Perkin Elmer UV/visible spectrophotometer Lambda 40 using 1 cm matched silica cells. The cell holder temperature of the instrument was held constant electronically the aid of an attached Shimadzu temperature controller. Magnetic susceptibility measurements were carried out at room temperature using a magnetic susceptibility balance of the type MSB-Auto. Molar susceptibilities were corrected for diamagnetism of the component atoms by the use of Pascal's constants. The calibrate used to be Hg[Co(SCN)$_4$]. The FT-IR spectra of the metal complexes were recorded on Shimadzu 470 infrared spectrophotometer (4000-400 cm^{-1}) using KBr discs.

ESR spectra were recorded on a Brokers Model EMX, X-band spectrometer. Metal ions were analyzed after dissolution of the solid complex in hot concentrated nitric acid diluting with distilled water. The solution was neutralized with ammonia and the metal ions were titrated with EDTA.

Solid mixed ligand complexes: The Cu(II) and Ni(II) mixed ligand complexes in the chloroform solutions of [Cu(dha)quin], [Ni(dha)quin·2H₂O], [Cu(dha)Hdhaq] and [Ni(dha)dhaq·2H₂O] after complete kinetic reaction were left for 3 h and concentrated to half the original volume. The solid mixed ligand complexes which separated out were recrystallized from chloroform.

Kinetic measurements: The ligand substitution reactions of dehydroacetic acid (Hdha) in [Cu(dha)₂] and [Ni(dha)₂·2H₂O] by 8-hydroxyquinoline (Hquin) and dihydroxy anthraquinone (H₂dhaq) has been investigated in different non-polar solvents such as chloroform, cyclohexane and dichloromethane at different temperature (283-298 K). Pseudo first order conditions of excess [Cu(dha)₂] or [Ni(dha)₂·2H₂O] concentration (0.5-0.7 mol L⁻¹) over second ligands (Hquin and H₂dhaq) (0.5 × 10⁻⁵ mol L⁻¹) was employed. The reaction was followed up in terms of changes of the absorbance with time using the conventional UV-visible spectrophotometer.

RESULTS AND DISCUSSION

UV-visible spectral and activation parameters: The UV-visible spectral of the pure [Cu(dha)₂] and [Ni(dha)₂·2H₂O] complex solutions show absorption bands at 500-510 and 630-660 nm, respectively. These visible bands decrease with increasing reaction time when the second ligand solutions were added (Fig. 1) and a new split band develops at longer wavelengths.
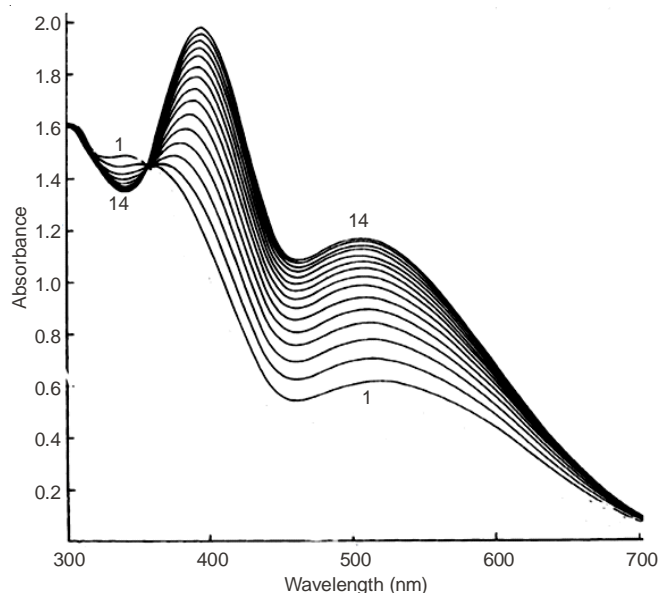

Fig. 1. Absorption spectra for the substitution of dha by quin in [Cu(dha)₂] complex (in chloroform at 20 °C, time intervals 2 min starting from 1 at 0.0 min)
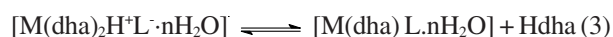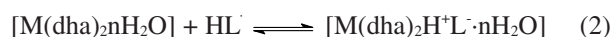
The spectral variations of [Cu(dha)quin] complex observed as a function of time on adding 8-hydroxyquinoline solution (0.5 × 10⁻⁵ mol L⁻¹) are shown in Fig. 1. The solution spectrum of Cu(II) complex changes to λ_max (470, 530 nm), (475, 540 nm) and (485, 545 nm) for cyclohexane, chloroform and dichloromethane solutions respectively. The successive absorption curves pass through isobestic points at 340, 380 and 355 nm in C₆H₁₂, CHCl₃ and CH₂Cl₂ solutions respectively, showing an equilibrium between two absorbing species. The reaction is not influenced by the elimination of the atmospheric oxygen. In case the solution spectrum of [Ni(dha)Hdhaq·2H₂O] and [Ni(dha)quin·2H₂O] complex changes to that λ_max (490-495, 680-690 nm), (490-495, 685-680 nm) and (495-500 nm) in C₆H₁₂, CHCl₃ and CH₂Cl₂ solutions, respectively. The spectral changes follow a typical first order behaviour until all dha ligand was depleted. Fine isobestic points indicating an equilibrium between the disappearing and new species. The isobestic points indicate a straight forward conversion of the reaction into a product without side or subsequent reaction spectral characteristics, the rate constants (K_obs) and activation parameter values for the substitution of dha ligand using Hquin and H₂dhaq at different temperatures are reported in Table-1.

The results display that the K_obs of the formed [Cu(dha)quin]; [Cu(dha)Hdhaq], [Ni(dha)quin·2H₂O] and [Ni(dha)Hdhq·2H₂O] solutions decreases as the dielectric constant of the solvent increases [C₆H₁₂ = 2.023, CHCl₃ = 4.8 and CH₂Cl₂ = 9.08]. This can be explained on the principle that the formed mixed ligand complexes are of strong character. Thus, increasing polarity of the medium leads to dissociation of the dative structure owing to the expected high dipole-dipole or dipole-induced dipole interaction along the same direction [11]. On mixing the second ligand (Hquin or H₂dhaq) with [Cu(dha)₂] or [Ni(dha)₂·2H₂O] complex solution the colour of the latter becomes deeper with time. The increase in the colour intensity (as measured by higher absorbance) by a spectrophotometer equipped with a thermostatic cell holder and is plotted against time as given in Fig. 2. The rate constant (K_obs) of these substitution reactions were measured under pseudo first order conditions the experimental data were fitted to the eqn. 1 [12].

$$\ln A_t = \ln A_0 - k_{obs}t \qquad (1)$$

where A_0 is the absorbance at time t = 0 and A_t is the absorbance at t = t. The plot of $\ln A_t$ various times (t) gives a straight line whose slope equal to the substitution rate constant (K_obs) (Fig. 2). The rate constant (K_obs) values were determined and listed in Table-1. The spectral data and kinetic result are consistent with the mechanism as show in below:

$$[M(dha)_2nH_2O] + HL \rightleftharpoons [M(dha)_2H^+L^-\cdot nH_2O] \qquad (2)$$

$$[M(dha)_2H^+L^-\cdot nH_2O] \rightleftharpoons [M(dha) L\cdot nH_2O] + Hdha \qquad (3)$$

where M = Cu(II) or Ni(II), n = 0 in case Cu(II) = 2, in case Ni(II) complexes, L = quin or dhaq

The short-lived intermediate [M(dha)₂H⁺L·nH₂O] represents reversible formation. When L is present, the reaction 3 becomes the rate-controlling and the rate of this reaction depends on the identity of L but little on dha.

The rate constant (K_obs) is smaller for 1,4-dihydroxyanthraquinone than of 8-hydroxyquinoline complexes, indicating faster substitution one molecule dha in a metal complex in solutions (Table-1). Fig. 1 shows that the bands of the reaction and product does not overlap and remains well resolved during the whole reaction. Therefore, the two bands are selected

TABLE-1
RATE CONSTANT (K_{obs}) AND THE ACTIVATION PARAMETERS OF THE SUBSTITUTION OF
dha IN Cu(II) AND Ni(II) COMPLEXES USING Hquin AND H_2dhaq AS SECONDARY LIGAND

Compound	Solvent	λ_{max} (nm)	Rate constant, K_{obs} (10^6 S^{-1}), Temp. (°C)				Activation parameters		
			10	15	20	25	ΔH^* (K J mol^{-1})	ΔS^* (K J mol^{-1})	ΔG^* (K $J^{-1}mol^{-1}$)
[Cu(dha)quin]	C_6H_{12}	470; 530	5.65	5.50	5.25	5.01	6.11	-10.00	4.30
	$CHCl_3$	475; 540	7.14	6.95	6.46	6.12	6.00	-11.00	4.50
	CH_2Cl_2	485; 545	8.23	8.01	7.55	7.25	5.80	-9.00	4.80
[Cu(dha)Hdhaq]	C_6H_{12}	475; 540	4.45	4.25	4.13	3.85	4.32	-8.00	3.20
	$CHCl_3$	475; 550	6.25	6.10	5.90	5.65	4.15	-6.50	3.60
	CH_2Cl_2	490; 560	7.12	6.86	6.45	6.25	3.95	-7.0	4.00
[Ni(dha)quin·$2H_2O$]	C_6H_{12}	490; 680	4.15	4.00	3.75	3.65	6.15	-8.50	4.60
	$CHCl_3$	490; 685	6.36	6.15	6.00	5.78	6.00	-9.00	4.90
	CH_2Cl_2	495; 700	7.25	7.13	7.01	6.83	5.85	-9.00	5.10
[Ni(dha)Hdhaq,$2H_2O$]	C_6H_{12}	495; 690	3.12	3.00	2.87	2.55	4.50	-7.50	3.50
	$CHCl_3$	495; 700	5.38	5.32	5.05	4.77	4.80	-7.00	3.80
	CH_2Cl_2	500; 710	6.45	6.40	6.32	6.22	5.22	-7.00	4.20

ΔG^* measured at 25 °C.
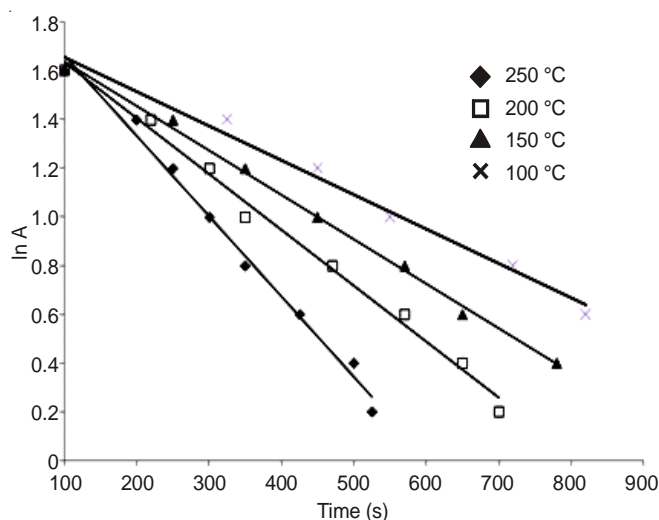

Fig. 2. First order plot for the reaction of [Cu(dha)$_2$] complex with Hquin at different temperature (25, 20, 15 and 10 °C)

to follow the consumption of the adduct 2 and growth of the product in eqn. 3.

The activation parameters are determined from the temperature dependence (283-298 K) of the rate constant. A plot of the log (K_{obs}/T) *versus* $1/TK^{-1}$ (eqn. 4), where k_{obs} are the observed rate constant, K is the Boltzman constant, h is plank's constant.

$$\ln\left(\frac{K_{obs}}{T}\right) = \ln\left(\frac{K}{h}\right) - \frac{\Delta H^*}{RT} + \frac{\Delta S^*}{R} \ldots \quad (4)$$

The enthalpy, ΔH^* and entropy ΔS^*, of activation was determined from the slope and intercept, respectively and listed

in Table-1. The free energy of activation (ΔG^*), was determined from eqn. 5.

$$\Delta G^* = \Delta H^* - T\Delta S^* \quad (5)$$

The higher value K_{obs} are associated with a lower activation energy, *i.e.* the entropy is greater for the slower reaction. This suggests that the reaction is controlled by the entropy of activation [13,14].

Characterization of solid complexes: Elemental analysis data indicate that the [Cu(dha)$_2$] and [Ni(dha)$_2$·$2H_2O$] complexes are reactive towards the 8-hydroxyquinoline and 1,4-dihydroxyanthraquinone ligands affording mixed ligand complexes by a substitution reaction which are formulated as given in Table-2. Table-2 reveal clearly that one the anion of the binary chelates is replaced by monovalent anion of 8-hydroxyquinoline or 1,4-dihydroxyanthraquinone ligand. The second ligand (8-hydroxyquinoline or 1,4-dihydroxy-anthraquinone) coordinate to the metal ion as monovalent bidentate ligand. Electronic spectra of the mixed ligand complexes were recorded in DMF solution from 200-800 nm. Table-2 lists the electronic spectral bands, molar conductivities in DMF solutions and magnetic moments of the complexes in the solid state.

The two bands in all metal complexes located at 210-270 and 350-380 nm are assigned to the ($\pi \rightarrow \pi^*$) transitions within the organic ring [15,16].

The electronic spectra of the dark green [Ni(dha)quin·$2H_2O$] and [Ni(dha) Hdhaq·$2H_2O$] showed a band due to $^3T_{ig}$ (P) $\leftarrow$ ^3A(F) in the range 680 and 710 nm respectively. The magnetic moment Ni(II) complexes lie in the range 2.9-3.5 BM for Ni(II) octahedral complexes [17]. The molar conductivity of Ni(II)

TABLE-2
ELEMENTAL ANALYSIS, ELECTRONIC SPECTRA BANDS, MAGNETIC MOMENTS
AND MOLAR CONDUCTIVITY OF METAL COMPLEXES

Complex	m.f.	Colour	Elemental analysis (%): Calcd. (Found)			d-d (λ_{nm}) Transition	Λ_m (Ohm^{-1} cm^2 mol^{-1})	μ (BM)
			C	H	M			
[Cu(dha)quin]	$CuC_{17}H_{14}NO_5$	Dark blue	54.32 (54.30)	3.75 (4.25)	16.90 (17.30)	530	37	1.90
[Cu(dha)Hdhaq]	$CuC_{22}H_{15}O_8$	Dark blue	56.11 (56.35)	3.21 (3.50)	13.49 (13.60)	560	32	2.00
[Ni(dha)quin·$2H_2O$]	$NiC_{17}H_{18}NO_7$	Dark green	50.16 (50.62)	4.45 (4.60)	14.45 (14.30)	710	20	2.90
[Ni(dha)Hdhaq·$2H_2O$]	$NiC_{22}H_{19}O_{10}$	Green	52.62 (52.20)	3.81 (4.25)	11.69 (11.75)	680	25	3.50

TABLE-3
CHARACTERISTIC OF FT-IR FREQUENCIES (cm^{-1}) OF Cu(II) AND Ni(II) COMPLEXES

Complex	$\nu(H_2O)$	ν(O-Phenyl)	ν(C=N)	ν(C=O) (dha)	ν(C=O) (Hdhaq)
[Cu(dha)$_2$]	–	1240	–	1700	–
[Cu(dha)quin]	–	1290; 1270	1620	1760	–
[Cu(dha)Hdhaq]	–	1290	–	1710	1610
[Ni(dha)$_2$·2H$_2$O]	3495	1285	–	1705	–
[Ni(dha)quin·2H$_2$O]	3480	1285; 1265	1615	1720	–
[Ni(dha)Hdhaq·2H$_2$O]	3485	1285; 1285	–	1715	1615

complexes in DMF lies in the range 20-25 Ohm^{-1} cm^2 mol^{-1}, indicating non electrolyte [18].

The electronic spectrum of the dark blue [Cu(dha)quin] and [Cu(dha)Hdhaq] complexes in DMF solutions showed one unsymmetrical band in range 530-560 nm due to $^2A_{1g} \leftarrow ^2B_{1g}$, $^2B_{2g} \leftarrow ^2B_{1g}$, $^2E_g \leftarrow ^2B_{1g}$ transitions in a square planar geometry [15]. The magnetic moments for Cu(II) complexes lies in the range of 1.90-2.0 BM for square planar structure [19]. The molar conductivity of Cu(II) complexes in DMF solution lies in the range 32-37 Ohm^{-1} cm^2 mol^{-1}, indicating non electrolyte [18].

X-band ESR spectra of Cu(II) complexes were recorded in the solid state at 298 K. The unresolved hyperfine splitting for Cu(II) can be attributed to the bipolar effect caused by mutual interactions between nuclear spin of the organic moiety (I = 1) with the unpaired of electron density of Cu(II). The spin Hamiltonian Parameters for Cu(II) complex square planar (S = 1/2, I = 3/2) were calculated. The g-tensor values can be used to derive the ground state. In square planar or square pyramidal complexes, the unpaired electron in the $d_{x^2-y^2}$ orbital gives $g_{11} > g_1 > 2.00$, while $g_1 > g_{11} > 2.00$, if the unpaired electrons lies in d_{z^2} orbit, the observed values of g_{11} (2-2811) $> g_1$ (2.2321) > 2.00 indicate and x^2-y^2 grounds state characteristic for square planar [20].

The ligands (Hquin and H$_2$dhaq) display a broad IR band in the high frequency region due to the stretching vibration of H-bonded OH group at 3200 and 3330 cm^{-1} respectively, (this band disappears in the IR spectra of the resultant quinoline complexes (Table-3).

The band found at 1625 cm^{-1} in the spectra of 1,4-dihydroxyanthraquinone is assigned to the stretching vibration of C=O group [13,21]. These band shifts markedly to lower frequencies in the mixed ligand complexes also the band due to ν(O-phenyl) found at 1300 cm^{-1} in the IR spectra of 1,4-dihydroxyanthraquinone are shifted to lower frequencies in the complexes. These shifts can be considered as strong evidence for the participation of both the C=O and OH groups in complex formation [21,22]. The band due to ν(O-phenyl) found at 1280 cm^{-1} for free 8-hydroxyquinoline shifted to lower values on complexation [23]. This shift illustrates the participation of the quinoline oxygen in complex formation. The strong band at 1630 cm^{-1} for the free Hquin are characteristic of the quinoline ν(C=N). This band shifts to lower frequency in the spectra of the complexes. The presence of coordinated water molecules in Ni(II) complexes with a broad absorption at 3495-3480 cm^{-1} due to stretching of OH, also, a band near 1600 cm^{-1} is due to deformation of water and bands at 950 and 790 cm^{-1} may be attributed to rocking and westing modes of a coordinated water molecule [23].

Conclusion

In summary, pseudo first order reactions of Cu(II) and Ni(II) (dehydroacetato) complexes concentration over second ligands such as 8-hydroxyquinoline and 1,4-dihydroxyanthraquinone was employed. The observed rate constant (K$_{obs}$) calculated and it depends on the concentration of both leaving and entering ligands. The K$_{obs}$ decrease with the increase dielectric constant of the solvents. Square planar and distorted octahedral geometry of Cu(II) and Ni(II) complexes respectively are suggested.

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