

NOTE

Stability Constant of Transition Metal Ions Complex with 1-Carboxamido-3,5-diaryl-4-arylopyrazoles

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The interaction of transition metal ions Co(II), Cu(II) and Ni(II) with 1-carboxamido-3-(2-hydroxy-5-chlorophenyl)-4-benzoyl-5-phenylpyrazole (L_1) and 1-carboxamido-3-(2-hydroxy-5-chlorophenyl)-4-benzoyl-5-(4-methoxy phenyl)-pyrazole (L_2) have been investigated by pH-metric technique at 0.1 M ionic strength and at $27 \pm 0.1^\circ\text{C}$ in 70% DMF-water medium. Co(II), Cu(II) and Ni(II) ions form 1 : 1 and 1 : 2 complexes with ligands L_1 and L_2 , respectively. Ligand L_1 is found a better chelating agent than L_2 because of higher values of $\log K_1$ and K_2

Key Words: Metal-ligand stability constant, Substituted pyrazoles, carboxamido derivatives, Potentiometrically.

Recent studies on complex formation have revealed that the ligand structure plays a critical role in selectivity for metal ions. Pyrazoles are weak bases and good complexing agents due to electron donor nitrogen. Very few works^{1,2} have been reported about the stability constants of transition metal complexes with pyrazoles moiety.

It was, therefore, thought of interest to study the chelating complexes of substituted pyrazoles 1-carboxamido-3-(2-hydroxy-5-chlorophenyl)-4-benzoyl-5-phenylpyrazole (L_1), and 1-carboxamido-3-(2-hydroxy-5-chlorophenyl)-4-benzoyl-5-(4-methoxy phenyl)-pyrazole (L_2) under suitable conditions potentiometrically.

The solutions of ligands were prepared in 70% DMF-water medium. The solutions of NaOH, HNO₃, cobalt nitrate, copper nitrate and nickel nitrate (BDH AnalaR) were used. The metal content in its solution was estimated by standard method³. The pH measurements were carried out with 335 Systronics pH-meter (accuracy ± 0.05 units) using glass and calomel electrodes at $27 \pm 0.1^\circ\text{C}$. The β values (pH-meter reading) in 70% DMF-water mixture were converted to H^+ proposed by Van Uiterts and Hass⁴. pH-meter was calibrated by standard buffer solutions (pH 4.00, 7.00, 9.15)

Experimental procedure involves the following three sets of titrations:

1. Free acid titration ($\text{HNO}_3 \times 10^{-2}$ M) (A)
2. Free acid + ligand titration (ligand 20×10^{-4} M) (A + L)
3. Free acid + ligand + metal ion titration (4×10^{-4} M) (A + L + M)

The titrations were carried out with standard NaOH solution (0.101 M) in presence of an inert atmosphere by bubbling a constant flow of nitrogen gas at constant temperature ($27 \pm 0.1^\circ\text{C}$). The pH-meter readings were taken for each addition of 0.2 mL. Ionic strength was kept constant at 0.1 M by adding an appropriate volume of 0.1 M KNO_3 solution.

The following systems were studied:

1. pK values of L_1 and L_2 in 70% DMF-water medium at 27°C .
2. Log k values of Co(II), Cu(II), Ni(II) with ligands L_1 and L_2 were investigated.

Both ligands are monobasic containing only one $-\text{OH}$ group, hence its dissociation is represented as below:



The deviation between acid curves and acid ligand curves started at about pH 2.0; it remained constant up to pH 3 and it increased continuously up to pH 12. This indicated the dissociation of $-\text{OH}$ group, which is present in the ligand part of complex structure. For all systems this deviation gradually increases up to pH 12.00, which shows dissociation of $-\text{OH}$ group of ligands.

Proton-ligand formation number ($\bar{\eta}_A$)

The proton-ligand formation numbers $\bar{\eta}_A$ were calculated from acid titration curves (A) and (A + L) by Irving and Rossotti's expression⁵. The pK values were estimated from formation curves ($\bar{\eta}_A$ vs. pH) by noting the pH at which $\bar{\eta}_A = 0.5$. The accurate values of pK were determined by half integral method which are presented in Table-1.

TABLE-1
DETERMINATION OF PROTON-LIGAND STABILITY CONSTANTS (pK) OF
1-SUBSTITUTED PYRAZOLES AT 0.1 M IONIC STRENGTH

System	Constant pK
1-Carboxamido-3-(2-hydroxy-5-chlorophenyl)-4-benzoyl-5-phenylpyrazole (L_1)	7.0
1-Carboxamido-3-(2-hydroxy-5-chlorophenyl)-4-benzoyl-5-(4'-methoxy-phenyl)pyrazole (L_2)	7.4

From the curve, it appears that dissociation of these ligands occurred at higher pH. All ligands showed their dissociation in the pH range 7–8. The pK value of L_2 is found to be greater (*i.e.*, 7.4) as compared to ligand 1. This may be due to the presence of $-\text{OCH}_3$ attached to phenyl ring group as an electron releasing group that decreased the dissociation increases and the dissociation constant pK values.

The pK values are found increasing in the order ligand $L_1 < \text{ligand } L_2$.

Metal-ligand stability constant ($\bar{\eta}$)

The deviation between (acid + ligand) and (acid + ligand + metal) curves started from pH 3.6 and increased continuously up to pH 12.0. It showed the commencement of complex-formation. Intense colouration was observed which also indicated the formation of complex. The formation curves were constructed

between η and pH. The metal ligand stability constants were determined by half integral method at $\eta = 0.5$ and 1.5 showing 1 : 1 and 1 : 2 formation of complex.

The values of η are estimated by applying Irving-Rossotti expression⁵. The maximum value of η was obtained at about pH 7.0 This showed the formation of 1 : 1 and 1 : 2 complexes. The values of $\log K_1$ and $\log K_2$ for 1 : 1 and 1 : 2 complexes respectively are calculated and presented in Table-2.

TABLE-2
DETERMINATION OF METAL-LIGAND STABILITY CONSTANTS ($\log k$) OF
Co(II), Cu(II) AND Ni(II) COMPLEXES WITH 1-SUBSTITUTED-PYRAZOLES
AT 0.1 M IONIC STRENGTH

Systems	Metal-ligand stability constant ($\log k$) (Half-integral method)		Metal-ligand stability constants	
	$\log k_1$	$\log k_2$	$\log k_1 - \log k_2$	$\log k_1 / \log k_2$
Co(II)-L ₁ complex	7.049877	4.55387	2.4960015	1.5481
Cu(II)-L ₁ complex	6.84473	4.45338	2.390873	1.5368
Ni(II)-L ₁ complex	6.89997	3.85397	3.0460	1.7039
Co(II)-L ₁ complex	5.8947	0.9838	4.9109	1.5358
Cu(II)-L ₁ complex	5.5499	2.00384	3.5461	2.7696
Ni(II)-L ₁ complex	5.5347	2.3042	3.2305	2.4020

It was observed from Table-2 that $\log k_1$ values are greater than $\log k_2$ values for all metal complexes.

The $\log k_1$ and $\log k_2$ values follow the order as Co(II), Ni(II), Cu(II). It could be seen (Table-2) that $\log k$ values follow increasing trend. This may be due to $-\text{OCH}_3$ group as electron releasing group.

It could be seen from data in all the cases that the differences between $\log k_1$ and $\log k_2$ are found to be greater which shows formation of stepwise complex. The value of ratio of $\log k_1 / \log k_2$ is positive in all the cases (Table-2). This implies that there is no steric hindrance to the addition of secondary ligand molecule.

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