

Thermodynamics of Adduct Formation Between N,N'-bis(Salicylidenepropylenediiminato) Copper(II) Complex and Nitrogen Donors

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Abstract: The equilibrium constants, free energies, enthalpies, and entropies for 1:1 adduct formation of N,N'-Bis(Salicylidenepropylenediiminato)Cu(II) complex with series of nitrogen donors have been measured spectrophotometrically in benzene and in cyclohexanone and dichloroethane for comparison. The equilibrium constants for adduct formation span the range from 9.12 to 1.36 mol.l⁻¹. The order of equilibrium constants was determined by ionization potentials of the donors, as they were decrease with increasing ionization of the donor.

In a series of pyridine donors the stability of the adducts increases in the order 3-carboxaldehyde pyridine < 2-picoline < pyridine < 4-picoline.

Variation of stability of the adducts due changing bases were attributed in part to steric effects. The solvents were ranked as follows by this constant : benzene > cyclohexanone > dichloroethane.

Introduction

There is considerable interest in the field of metal chelate catalysis as well as reactions of metal chelates themselves⁽¹⁻³⁾. It has also been established that some metal chelates can act as reversible oxygen carries. Some metal chelates of some diimines undergo nonenzymatic transamination similar to that through to occur in living systems⁽⁴⁾.

The formation of adducts of metal chelates plays an important role in the synergistic enhancement of the solvent extraction of the ions⁽⁵⁻⁷⁾. Furthermore adducts of metal chelates may serve as potential models for some biologically important molecules like cobalt-alkyl complexes which have been studied as models for vitamine B12 coenzyme⁽⁸⁾.

In contrast to the considerable attention paid to adducts formed between β -diketones and porphyrines metal chelates relatively less interest paid to adducts

for metal complexes of quadridentate Schiff bases ligands⁽⁹⁻¹¹⁾.

The object of the present investigation was to study the adduct formation between bis(salicylidenepropylenediiminato)Cu(II) with variety of electron donors through determination equilibrium constants of the adducts and other thermodynamic constants in the hope of correlating the results with nature of donor and solvent.

Experimental

The Schiff base and its metal complex were prepared according to previously described methods^(12,13). All solvents and donors were of purity and were dried according to standard methods⁽¹⁴⁾. The prepared

solutions were used within 1hr period. No change in electronic spectra of the solutions used in the spectrophotometric runs was observed over

hr period. Absorption measurements were made with LKB ULTRO- 24

SPECIII 4050 UV/VIS spectrophotometer equipped with an water thermo- stated cell holder. The temperature of the solutions was maintained constant within $\pm 0.1^{\circ}\text{C}$ and measured directly by interesting a PHILIP HARRIS precision thermometer into the sample cell which was a 1-cm path length quartz cell. Measurements were made at the visible region at predetermined wavelengths and the average then taken. The concentration for the metal cheated was kept constant at $7.78 \times 10^{-3}\text{M}$ (this was determined by

the restricted solubility of the chelate) while the concentrations of the donors were not less than 10 times the concentration of the chelate for lower concentration.

Equilibrium constants were calculated using previously described method⁽¹⁴⁾. The measured value of the equilibrium constant, K , serves to determine the standard free energy ΔG° . By determining the value of k at three different temperatures and plotting k vs $1/T$ the enthalpy was calculated from the slope of the straight line obtained.

Table 1: Thermodynamic constants for 1:1 adducts of the studied chelate with nitrogen donors in benzene at 25°C .

Donors	nm	K 1.mole ⁻¹	ΔG° kcal.mole ⁻¹	ΔH° kcal.mole ⁻¹
n-propyl-amine	540	6.11	1.01	2.90
	610	6.34		
	mean	6.22		
piperidine	540	4.30	0.84	2.97
	500	4.51		
	mean	4.40		
pyridine	580	1.08	0.16	2.20
	610	1.15		
	mean	1.11		
pyridine-3- aldehyde	540	0.45	0.33	1.74
	640	0.43		
	mean	0.44		
2-picoline	550	0.60	0.18	1.82
	570	0.59		
	mean	0.59		
4-picoline	570	2.09	0.42	2.38
	650	1.79		
	mean	1.94		

Table 2: Thermodynamic constants for 1:1 adducts of the studied chelate with n-propylamine in different solvents.

solvent	K 1.mole ⁻¹	ΔG° kcal.mole ⁻¹	ΔH° kcal.mole ⁻¹
dichloroethane	1.27	0.21	2.03
cyclohexanone	3.68	0.75	2.55
benzene	6.05	1.00	2.81

Results and discussion

Visible spectra of benzene solutions of the studied complex with various amounts of n-propylamine as a donor are measured. The curves are characterized by an isosbestic point at 509 nm indicating the presence of only two absorbing species in solution. The equilibrium constant calculated from these curves (and the curves of mixtures of the chelate with other donors) are independent of wavelength as shown in spectrum, by typical data for some what widely separated wavelengths.

This indicates only 1:1 equilibria taking place between two absorbing species⁽¹²⁾

Solvent Effects : Table 1 shows that in the values of k , g_b , and H^0 unless we assume that all heats of dilution are negligible) are all suitable to discuss the donor strength effect on the adduct formation. The trends in the three constants are parallel but it is clear that the use of k values changes of the donor-acceptor reaction to assign relative base strengths is more convenient owing to the wide differences of k values at one side and to avoid of the larger variations in the enthalpy of solvation when using the enthalpy scale⁽¹⁰⁾.

Table 1 shows that for the studied chelate that the adduct formation constants increase in the order :

Pyridine , piperidine , n-propylamine , n-butylamine.

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This sequence is parallel to the decrease of the ionization potentials of these donors⁽⁹⁾ which results in an increase in the donor ability in the same sense.

For the pyridine family the adduct equilibrium constants increase in the order:

3-aldehydepyridine , 2-picoline pyridine , 4-picoline.

The higher stability of 4-picoline adducts relative to those of pyridine reflects the increase donor property of the nitrogen atom due substitution. A similar effect would be expected for substitution in the 2-position, so that the much lower stabilities observed for the adduct of 2-picoline are probably due to steric interference. The still more lower stability for the attracting effect of the aldehyde group that renders the electronic charge on the nitrogen atom relatively smaller.

These results parallel those observed by Garradon and Watton for the addition of heterocyclic bases to Cu(II)-diketonates⁽⁶⁾.

Table 2 shows the effects of solvent variation, the stabilities of the adducts increasing in the order dichloroethane, cyclohexanone, benzene. In similar study⁽⁶⁾ this was attributed to decreasing attraction between solvent molecules and the copper atom of the chelate or to decreasing solvation energy of the bases giving some importance to the later effect.

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