CHARGE TRANSFER COMPLEXES BETWEEN SOME CRYPTANDS WITH TETRACYANOETHYLENE AND 2-HYDROXY-1,4-NAPTHOQUINONE

Sabri Mohammed.Hussain   **Khalid Jamal**

College of medicine-University of Anbar.

A R T I C L E   I N F O

A B S T R A C T

The intermolecular charge transfer (CT) complex of two cryptands , viz , K221 and K222 (as donors) and tow acceptors, viz , tetracyanoethylene (TCNE) and 2-hydroxy-1,4-napthoquinon were studied ion Uv-visible region in dichloromethane (DCM)as solvent at 298.2k .It was found that the basicity of cryptand played an important role in the formation constant Kc value obtained. The nature of CT complexes formed were achieved by calculation of oscillator strength.

Introduction

Since the discovery of crown compound(1) there has been remarkable expansion in the research on characteristics and application of particular group of compounds within of only few years(2-6) .

Among the multicyclic crown compounds are the cage type bicyclic crown compounds, whose two bridge heads consist of two N $\in$ group , synthesized by lehn et at (2) . compared to crown ethers , these compound bind metal ion slightly into the space in their lattices with higher ion selectivity and greater stability of the resulting complexes .

For these reasons , considerable attention has been paid to these compounds , as well to crown ethers(3-5) . these cage type bicyclic crown compounds were named (cryptands) and their complexes (cryptates) .

In this research we present some results concerning the complex formation between two cryptands ,i.e,K221 and K222 with two acceptors TCNE and 2-hydroxy-1,4-napthoquinone.

Experimental:

All uv-visible spectral, measurements were carried out on Du-7 spectrophotometer, using (1 cm) fused silica cells. Donor concentration were kept within (1*10-1- 1*10-2 M) while acceptor concentration was kept constant (1*10-3 M) .

All solvents (BDH) were of spectroscopic grade and they were dried over molecular sieve. cryptands were of pure grade (fluka).

Calculation :

Calculation of the equilibrium constant for complex formation Kc , and molar absorptivity ε , were based on Benesi-Hildebrand (7) equation :

$$[A^{\circ}]/(A) = \frac{1}{Kc} \frac{1}{[D]} + \frac{1}{\varepsilon c}$$

―――――* Corresponding author at: College of medicine-University of Anbar, Iraq.E-mail address: **sabri_1956@yahoo.com**

where A is the absorbance due to complex formation , [A°]   and [D°] are the initial concentration of the acceptor and donor respectively .

RESULTS and DISCUSSION :

A new broad band in the visible region (552-554 nm) of the spectrum   appeared after mixing solution of cryptands K221 or K222 with (TCNE) in (DCM) , while (540- 548 nm)in the case of mixing solution of cryptands with (2-hydroxy-1,4-napthoquinone) , these bands must be associated with the formation of CT   complex (8) since nether donor (cryptand) nor acceptor (TCNE) or (2-hydroxy-1,4-napthoquinone) absorbed in this region .

The linear plots of the Benesi-Hildebrand equation (7) fig.(1) , indicated that the stoichiometric ratio of CT complexes under examination were 1:1 .

Table 1 shows the values of Kc and εc for these complexes .

From this table , it is interesting to observe that while Kc and εc   per oxygen atom of the ring showed little increase in going from K221 to K222 , the value of εc Kc per oxygen atom increased markedly on adding one oxygen atom in macro cyclic ring .

Attempts were made to obtain solid complexes by mixing equimolar quantities of the donor with the acceptor dissolved in (DCM) and allowing the solution to evaporate slowly at room temperature but not successful .

Oscillator strengths (f) calculation are of interest to showing the extent of the transfer of electron charge between the donor and acceptor molecules . thus their values are of interest in the study of the nature of the CT-complexes (8) .

For this purpose , we calculate the oscillator strength . the relation employed for the calculation of oscillator strength was of general formula :

$$f = 1.35 \times 10^{-8} \quad \varepsilon (v_{max} - v_{\frac{1}{2}})$$

The results given in table (2) , show quite that the complex formed were not highly polar .

REFERENCES:

1- C. J. pederson ; J. amer. chem..soc.; 89,2495A, 1967. melson; coordination chemistry of macro cyclic compounds; 1979 , plenum press , new York.

2- Y. Jaya thirtha and V. Krishnan; Indian journal of chemistry; 27A,316, 1999.

3-S.R.Salman and S.M .Al-marsoumi; spectrochem. Acta ; 49A,453,(1993) .

4-M.K.Amini and M. shamsipur ; J. solution Chem.. ; 21,275,(1992).

5-Gazi A. W. derwish , S. R. salman and S. M. Al-marsoumi ; J. of Inclusion phenomena and molecular recognition in chem.. ;   20,123-129, 1995.

6-H. A-benesi and J. H. Hildebrand; J. Am. Chem. Soc. ; 71,2703,1949.

7-R.Foster; Organic Charge Transfer Complexes; Academic press, 1969 .

Table (1) : Maximum absorption wave length λ nm, molar itiesabsorptiv εc (mol-.cm-.l) , formation constant Kc (dm3.mol-) and products of εc Kc (l2.mol-2.cm-) of the complex formed between cryptands and acceptors in DCM at 298 k

Donor	Acceptor	λMax	Kc	εc	εcKc
K221	TCNE	554	2.33	166.7	388.41
K222	TCNE	552	2.74	222.2	608.83
K221	2-hydroxy-1,4-napthoquinone	548	3.86	250	965
K222	2-hydroxy-1,4-napthoquinone	542	21.75	116.3	2529.53

Journal of University of Anbar for Pure Science (JUAPS)   Open Access

	napthoquinone	
K222	2-hydroxy-1,4-napthoquinone	0.201

Table (2) : Oscillator strength (f) of the absorption band of CT-complexes between cryptands and acceptors .

Donors	Acceptors	f
K221	TCNE	0.241
K222	TCNE	0.296
K221	2-hydroxy-1,4-	0.190

معقدات انتقال الشحنة لبعض الكربتانات مع رباعي سيانوالاثيلين و ٢-هايدروكسي – ١،٤ نافثوكوينون

خالد جمال   صبري محمد حسين

E.mail: sabri_1956@yahoo.com

الخلاصة

تضمن البحث دراسة معقدات انتقال الشحنة لبعض الايثرات التاجية (الكربتاند) كمواد واهبة للالكترونات مع مستقبلين للشحنة هي رباعي سيانواثيلين و ٢-هيدروكسي –١-٤ نافثوكوينون في درجة حرارة الغرفة باستخدام ثنائي كلوريد الميثان كمذيب .

اظهرت النتائج ان قاعدية الكربتان تمثل دورا مهما في قيمة ثابت تكوين المركب تم التعرف على طبيعة المعقدات الناتجة من خلال حساب الشدة الاهتزازية.