

Spectroscopic Study of Lewis Bases Coordinating to Vanadyl-N,N,N,N-Bis (Benzil) Azomethine Bis (1,2-Ethylene Diamine)

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ABSTRACT

Formation constants for the coordination of aniline, pyridine, dimethyl sulfoxide, dimethyl formamide, ethanol, dimethylamine and triethylamine to vanadyl-N,N,N,N-Bis (benzil) azomethine bis (1,2-ethylene diamine) have been determined. The coordinating ability and steric constraints were discussed.

INTRODUCTION

It has been known that transition-metal-oxo-complexes are useful reagent for the oxidation of organic molecules [1]. Studies are explained that coordinating ability of oxo-metaloporphyrin are differ from each other depending on the type of lewis base and the steric effect of porphyrin and they have not been shown to be effective-oxidizing agent [2-4], on other hand , oxoiron (IV) porphyrin complexes are extremely reactive species and have only been detected spectroscopically in solution at low temperature when iron (II) porphyrin react with oxygen in the presence of a lewis base [5]. Most of studies focused on oxometalloporphyrins with lewis bases [6-8].

In this paper we report the relative affinities of lewis bases to VO-N,N,N,N-Bis (benzil) azomethine bis (1,2 ethylene diamine) in order to obtain detail information regarding formation constant and factors effecting on the coordinateg ability of these complexes.

EXPERIMENTAL

The compound of N,N,N,N-Bis (benzil) azomethine bis (1,2-ethylene diamine) was prepared as described by Khahawar___[9]. The complex [VOBAED] was prepared by dissolving (6.3×10^{-6} mol) of VOSO_4 and (5.3×10^{-6} mol) of N,N,N,N-bis (benzil) azomethine bis(1,2 ethylene diamine) in 30 ml H_2O , the solution then mixed at room temperature for 30 minutes . The precipitate was filtered, washed,and then collected by filtration . A 5.35×10^{-4} g (1.1×10^{-6} mol) then dissolved in 4ml of CH_2Cl_2 and the lewis base was added with ratio 1:1 .

UV-visible absorption spectra were recorded on UVIDC-650 double beam spectrophotometer at room temperature. In general reaction of VOBAED to lewis bases was represented by equation 1.

RESULTS AND DISCUSSION

The solutions of pure VOBAED in dichloromethane were showed absorption bands at 392,571 and 740 nm . Table I show the visible bands maxima of VOBAED (base) in CH_2Cl_2 .

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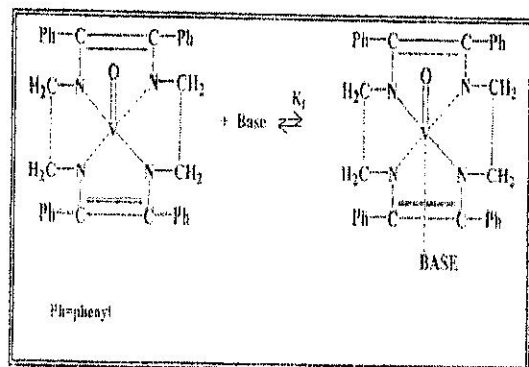


Table 1
Visible bands maxima (nm) of VOBAED(base) in CH₂Cl₂ at room temperature

Complex	Band(logε)		
	1 st	2 nd	3 rd
VOBAED	392(4.92)	571(5.31)	740(4.26)
VOBAED(pyridine)	389(4.38)	567(5.51)	735(4.00)
VOBAED(Aniline)	410(4.47)	588(5.90)	755(3.49)
VOBAED(DMF)	400(4.49)	579(5.28)	747(3.99)
VOBAED(EtOH)	388(4.41)	566(4.52)	710(4.38)
VOBAED(DMSO)	387(4.42)	565(4.51)	712(4.39)
VOBAED(Diethylamin)	385(4.40)	563(4.65)	744(4.72)
VOBAED(Triethylamin)	408(4.31)	587(5.11)	763(3.81)

The data listed in table 1 show that the addition of lewis bases of aniline, DMF and triethylamine to VOBAED will cause a shift to higher wavelengths (red shift), while the other lewis bases were caused a shift to lower wavelengths (blue shift), the nearly appear the same wavelengths for the first and second bands but the third one different. This exported to destabilize the a₁^{*} level as shown in figure 1.

Since the energy of the b₂ level is expected to be insensitive to such changes. The blue shift is assignment that was a high distance between a₁^{*} and b₂ levels. Coordinating of aniline, DMF and trimethylamine to VOBAED are characterized a new level 2a₁ is formed between 1a₁ and a₁^{*}, the energy was lowered, the absorption would appear in a high wavelengths. Formation constant (K_f) presented in equation (1) was calculated from spectrophotometric data by use of modified Drago's method [10], it's represented in equation 2.

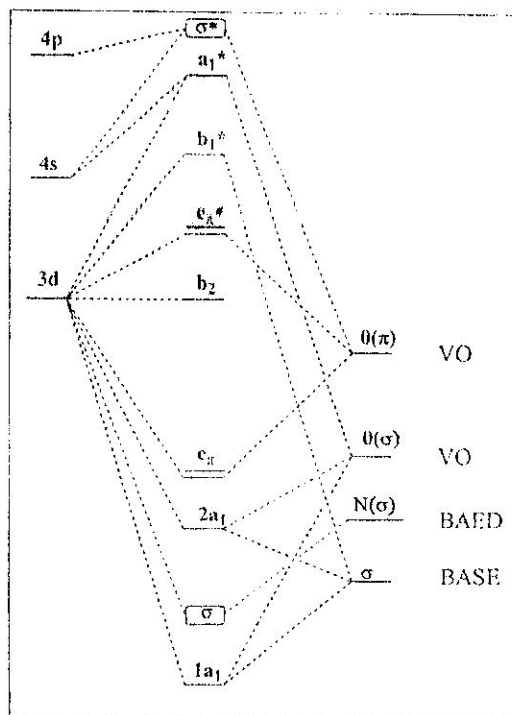


Fig.1
Molecular orbital energy levels of VOBAED (base)

$$\frac{A}{\Delta A} = \left[\frac{1}{K \Delta \epsilon} \times \frac{1}{B} \right] + \frac{1}{\Delta} \dots \dots \dots (2)$$

Where K_f is the formation constant of the adduct, Δε is the extinction coefficient between VOBAED and the adducts, ΔA is the absorbance difference between VOBAED and the adducts, A_T is the initial concentration of VOBAED and B_T is the initial concentration of the base.

A typical of A_T / ΔA versus 1/B_T was to be shown in fig.2 for coordination of aniline to VOBAED. A linear line was obtained, Δε and K_f can be calculated from the intercept the ordinate and the slope respectively. The K_f values were listed in table 2.

The coordinating ability of lewis bases to VOBAED was found to follow the sequence in decreasing order oxygen donor > nitrogen donor

> sulfur donor. It was also observed that the axial ligation is sensitive to steric bulkiness of the ligand as shown in table 2 for diethylamine and triethylamine bases. Finally we would be reported that the axial interaction of lewis bases to vanadium are very strong .

Table 2
Formation constants for the coordination of lewis bases to VOBAED

Lewis base	K_f
Pyridine	0.143
Aniline	0.182
DMF	0.360
EtOH	1.480
DMSO	0.041
Diethylamine	1.180
Triethylamine	0.050

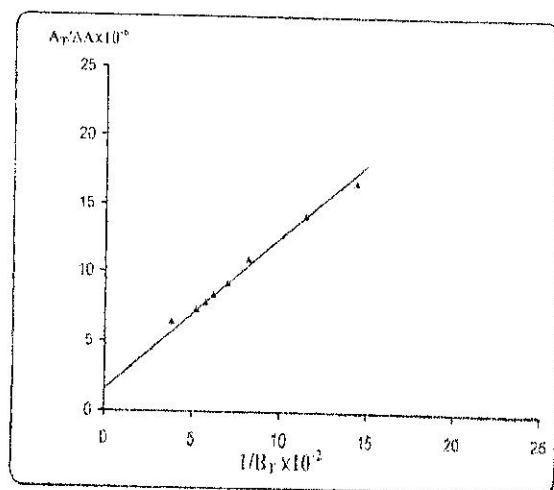


Fig.2

Plot of $\Delta T/\Delta A$ vs. $1/B_T$ for the coordination of aniline to VOBAED

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دراسة طيفية لقواعد لويس المتعلقة بفناديل-N,N,N-بز (بنزيل) ازوميثاين
بز (٢,١) اثيلين داي امين

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الخلاصة

يتضمن البحث دراسة طيفية حول طبيعة التناسق بين بعض قواعد لويس مثل الانيلين ، البيريدين ، ثنائي مثيل سلفوكسايد ، ثنائي مثيل فورمامايد ، الايثانول ، ثنائي اثيل امين ثلاثي اثيل امين مع معقد الفناديل ن،ن،ن-بنز بنزيل ازوميثاين بس(٢,١) اثيلين ثنائي امين) .
استخلصت ثوابت التكوين لهذه المركبات حيث وضحت الدراسة اختلاف القدرة التناسقية والتاثيرات الفراغية للمركبات المدروسة.