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Adduct Formation of Nickel(II) Chelates of 4-Methyl and 2-Methyl 8-Quinolinols with Heterocyclic Nitrogen Bases

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The formation constants of the heterocyclic N-base adducts of the nickel(II) chelates of 4-methyl and 2-methyl-8-quinolinone have been determined spectrophotometrically. Monodentate nitrogen bases gave diadducts. The formation constants of adducts of nickel-2-methyl-8-quinolinate are higher than those of nickel-4-methyl-8-quinolinate. Dibasic ligands such as 1,10-phenanthroline, 2,2′-bipyridyl etc. form monoadducts with nickel(II) chelates of 4-methyl and 2-methyl-8-quinolinol. The formation constants of these adducts are significantly high indicating the bidentate nature of the dibasic ligands, thus satisfying the hexacoordination of nickel.

INTRODUCTION

Several researchers have attempted to study systematically the role of solvent, basicity of adducting base and Lewis acidity of coordinatively unsaturated nickel (II) chelates such as dithizonate and 8-mercapto quinolinate[1], dialkythiophosphate[2–5], thio-diketonates[6], 8-quinolinates[7,8], di-*o*-tolylcarbazonate and di-*o*-tolylthiocarbazonate[9] and 2-methyl-5-nitrophenylthiocarbazonate[10]. As part of the ongoing research program dealing with the study of stability of nickel chelate adducts, we have been interested in collecting more information regarding the nature of bonding in nickel(II)-8-quinolinate self adducts as to whether it acts as a monodentate or bidentate. A survey of the literature indicated that some anomalies existed between our work and that of Bhatki *et al.*[7], about the conclusions drawn on mono and bidentate nature of the adducts formed. In order to clarify some such data, we have undertaken a detailed investigation on nickel(II)-4-methyl-8-quinolinate. To substantiate our findings we have not only repeated the earlier experiments of Bhatki *et al.*[7], but also studied a few more nitrogen bases that possess similar structures as that of 8-quinolinol but with only one donor site, namely, quinoline. In the present study, we have observed that the experimental results on adduct formation constants and the number of molecules attached to the nickel(II)-4-methyl-8-quinolinate (Ni4MQ) and nickel(II)-2-methyl-8-quinolinate (Ni2MQ) chelates are significantly different than those reported earlier[7].

EXPERIMENTAL

The method described by Phillips *et al.*[11], was used to synthesise 4-methyl-8-quinolinol. The crude product was purified by vacuum distillation. Pyridine (Fisher), picolines and quinolinol (Eastman) were purfied by distillation after drying over potassium hydroxide. Other chemicals, 2-methyl-8-quinolinol, 2,2′-bipyridyl (Eastman), 1,10-phenathroline (G. Frederick Smith Co.), neocuproin (B.D.H.), $Ni(ClO_4)_2$ (Fisher Reagent Grade) and chloroform (E. Merck) were used as such.

Preparation of nickel-4-methyl and 2-methyl-8-quinolinates

A weighed amount of nickel perchlorate (*ca.* 1 g) was dissolved in 500 ml of acetate buffer of pH *ca.* 6.0. The mixture was heated to about 50°C and to this was added an alcoholic solution of appropriate 8-quinolinol dropwise. The total amount of reagent added was slightly more than that required for 1:2 stoichiometry. The yellow precipitate formed was digested for 2 hrs and filtered hot. The precipitate was washed with hot water several times and dried at 110°C. The analysis of Ni was in good agreement with the calculated value.

Determination of formation constants of adducts

Specific amounts of chloroform solutions of the appropriate nickel chelate were pipetted into volumetric flasks containing solutions of varying amounts of adducting base in chloroform and volumes were adjusted to the mark with solvent. The absorption spectra of the solutions were recorded in the range 340–500 nm using optical path length 10 mm. The absorbance values at 450 nm and 420 nm were found to be suitable for the calculations of formation constants of Ni4MQ and Ni2MQ systems respectively because the difference in absorbance between chelate and adduct was large. The absorbance values were found to be constant for several hrs.

RESULTS AND DISCUSSION

The absorption spectrum of Ni4MQ has two bands at 450 and 340 nm in the visible region. The band at 450 nm is shifted to lower region of 400 nm by the addition of heterocyclic N-bases. The band at 340 nm does not shift significantly but its molar absorptivity decreases. This leads to the appearance of two isosbestic points around 360 and 420 nm (Fig. 1).

The absorption spectrum of Ni2MQ has a single band with λ_{max} at 375 nm and a shoulder at 345 nm. By the addition of a base, the spectrum shows two bands around 400 nm and 340 nm with two isosbestic points around 350 and 380 nm (Fig. 2).

The change in the spectrum of nickel(II) chelate upon the addition of

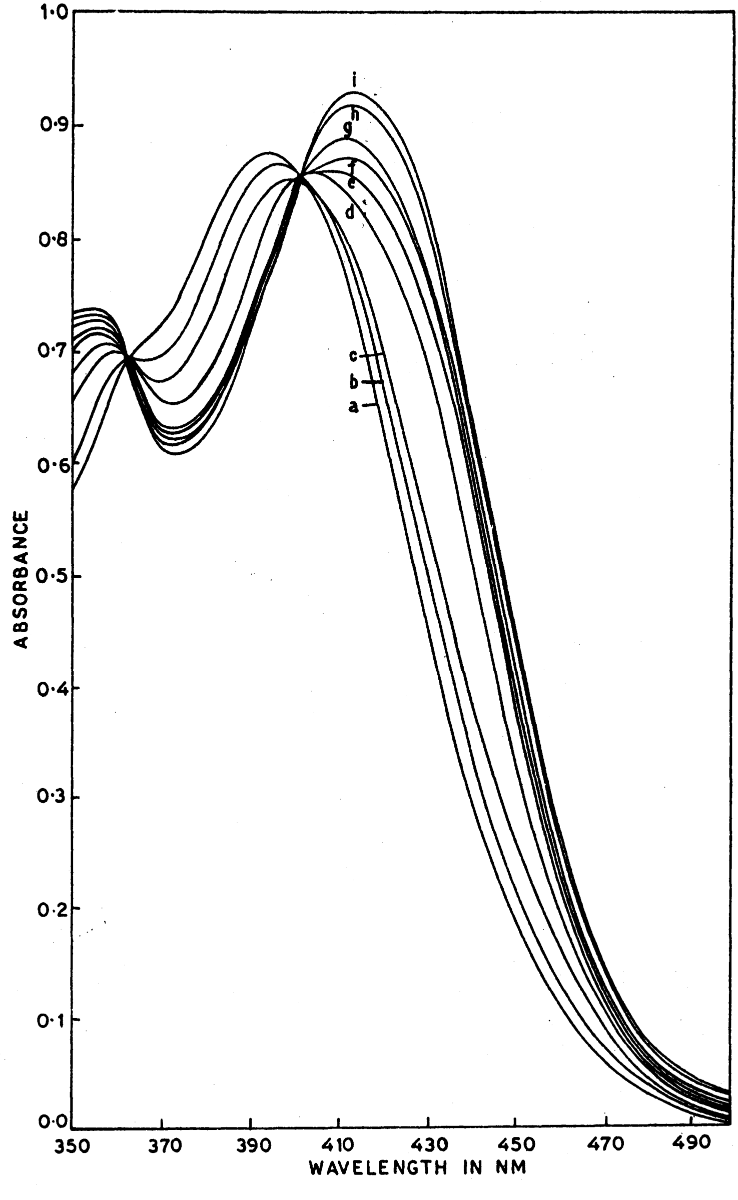

Fig. 1 Absorption spectra of Ni4MQ + pyridine mixtures in chloroform at 25°C. [Ni4MQ]: 7.75×10^{-5} M. [pyridine] $\times 10^3$ = (a) 0.00; (b) 6.18; (c) 12.36; (d) 18.55; (e) 24.73; (f) 30.91; (g) 37.09; (h) 43.27; (i) 55.64; (j) 74.18 and (k) 98.91.

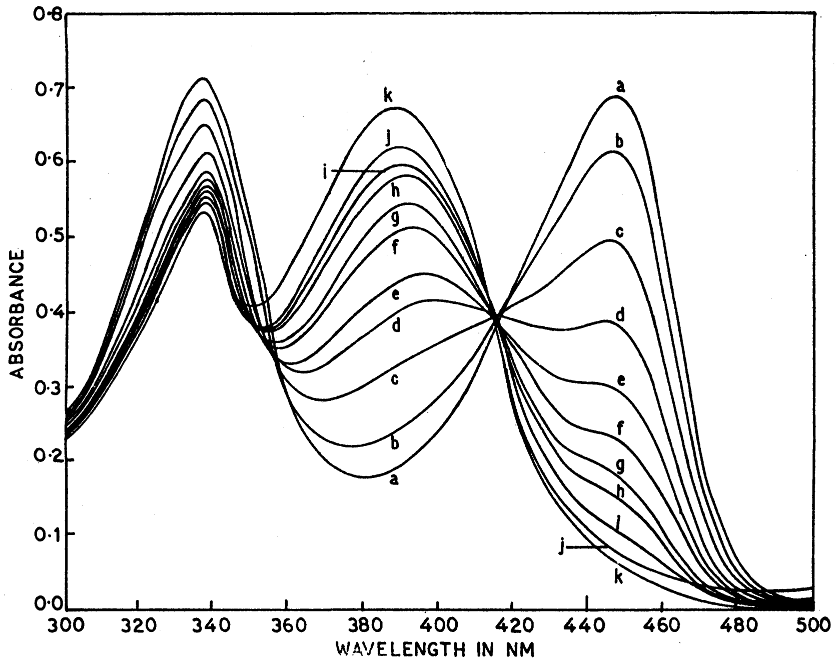

Fig. 2 Absorption spectra of Ni2MQ + pyridine mixtures in chloroform at 25°C. [Ni2MQ]: 1.25×10^{-4} M. [pyridine] $\times 10^4$ = (a) 0.00; (b) 0.25; (c) 0.49; (d) 1.00; (e) 1.51; (f) 1.99; (g) 2.51; (h) 5.01 and (i) 12.59.

heterocyclic N-bases can be used to determine the equilibrium constant of adduct formation.

The over-all formation constant β_n^{ad} of the adduct for the reaction of the nickel(II) chelate, NiL_2, with n molecules of base, B, to form the adduct, NiL_2B_n, is given by:

$$\beta_n^{ad} = \frac{[NiL_2B_n]}{[NiL_2][B]^n} \tag{1}$$

If the initial concentrations of the chelate and base are C_{ch}^o and C_B^o respectively, then

$$C_{ch}^o = [NiL_2] + [NiL_2B_n] \tag{2}$$

and

$$C_B^o = [B] + n[NiL_2B_n] \tag{3}$$

The absorbance A, of a solution, at a wavelength at which both the adduct and the nickel chelate are the absorbing species, is given by:

$$A = \varepsilon_{ch}[NiL_2] + \varepsilon_{ad}[NiL_2B_n] \tag{4}$$

where, ε_{ch} and ε_{ad} are the molar absorptivities of the chelate and adduct respectively. Substituting for $[NiL_2]$ and $[NiL_2B_n]$ from equations (2) and (4) into equation (1), one gets

$$\beta_n^{ad} = \frac{\varepsilon_{ch}C_{ch}^o - A}{A - \varepsilon_{ad}C_{ch}^o} \cdot \frac{1}{[B]^n} \tag{5}$$

Since the initial optical density (A_{ch}) in the absence of base and the final optical density (A_{ad}) in the presence of large excess of base (i.e., when all complex is in the adduct form) are related as follows:

$$A_{ch} = \varepsilon_{ch}C_{ch}^o \qquad \text{and} \qquad A_{ad} = \varepsilon_{ad}C_{ch}^o$$

from equations (2) and (4).

Rewriting equation (5) in the logarithmic form, we obtain

$$\log \beta_n^{ad} = -n \log [B] + \log \left[\frac{A_{ch} - A}{A - A_{ad}}\right] \tag{6}$$

If chelate alone absorbs at the wavelength used, for calculations of $\log \beta_n^{ad}$, then equation (6) will take the form:

$$\log \beta_n^{ad} = -n \log [B] + \log \left[\frac{A_{ch} - A}{A}\right] \tag{7}$$

From the plot of $\log \left[\frac{A_{ch} - A}{A - A_{ad}}\right]$ versus—log [B] as required by equation (6), it should be possible to determine $\log \beta_n^{ad}$ from the intercept and n, the number of moles of base added to the chelate, from the slope.

If the adduct is weak, then the total base concentration C_B^o will be large compared to the amount of base used in the adduct formation. In such cases,

$$C_B^o = [B] \tag{8}$$

Otherwise, correction for the amount of base used in the adduct formation should be made. Equation (3) after substitution for $[NiL_2B_n]$, using equations (2) and (4) gives

$$[b] = C_B^o - n\left[\frac{A - \varepsilon_{ch}C_{ch}^o}{\varepsilon_{ad} - \varepsilon_{ch}}\right] \tag{9}$$

In the case of 1,10-phenanthroline and 2,2′-bipyridyl, it was observed that their adducts are highly stable and the magnitude of total base concentration (C_B^o) and concentration of the base bound to the chelate ($n[NiL_2B_n]$) were of the same order. Therefore [B] calculated by using equation (9) is sensitive to the experimental errors (often yielded meaningless negative values). In such cases, stoichiometry of adduct was established using mole-ratio and/or Job's method.

Under these conditions only approximate log β_n^{ad} values were reported and these values were obtained as

$$\log \beta_n^{ad} = -\log [C_B^o] \text{ when } \left[\frac{A_{ch} - A}{A - A_{ad}}\right] = 1$$

The results of the present experiments are shown in Table 1, together with the values reported by Bhatki *et al.*[7] A close look at the magnitudes of log β_1^{ad} values* for the bases with only one donor site and those of two donor sites namely 2,2′-bipyridyl, 8-quinolinols etc., reveals that the latter bases appear to act as bidentate due to their high log β_1^{ad} values. The monodentate nature of these ligands having two donor sites has been reported earlier by Bhatki *et al.*[7] for Ni4MQ and Ni2MQ adducts and by Chou and Freiser[12] for zinc-8-quinolinate self-adducts. In the former case, the argument was based on the fact that the slopes of the plot of log $\left[\frac{A_{ch} - A}{A - A_{ad}}\right]$ versus—log [B] was found to be 2. This might have been due to the incorrect use of equation (6). If one accepts the proposition of Bhatki *et al*[7]. and Chou and Fresier[12] regarding the monodentate nature of the bases having two donor sites, then one can visualize on steric grounds that log β_n^{ad} values would be smaller than quinoline which has a similar structure and very much smaller than other monodentate bases like pyridine. This appears to contradict our results. A value of 2 for the slope as observed by Bhatki *et al.*[7] might have been erroneously interpreted in order to retain the hexacoordination for nickel(II). On the contrary, our data indicate a value of unity for n** (slope) and the high log β_1^{ad} values imply the bidentate nature of the reagents with two donor sites, at the same time retaining the normal hexacoordination of the nickel(II). It may be further noted that Bhatki *et al.*[7] have tried indirectly to suggest both monodentate and bidentate nature of the adducts formed from 1,10-phenanthroline and 2,2′-bipyridyl etc.

Monodentate bases such as pyridine and picolines have been studied in the present investigation as well as by Bhatki *et al.*[7] It is found that the value of slope ($n = 2$) and the formation constants for Ni4MQ adducts were found to be the same between our work and that of Bhatki *et al*[7]. However, the data for Ni2MQ adducts were quite different; we have observed a slope of 2, while they have obtained a slope of unity. Even the magnitudes of formation constants are considerably different. The present data show that the Ni2MQ adducts are significantly more stable. This might be due to the fact that Bhatki *et al.*[7] have

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*$\log \beta_1^{ad} \approx \frac{1}{2} \log \beta_2^{ad}$

**n values were obtained by mole ratio and Job's method for 2,2′-bipyridyl and 1,10-phenanthroline.

TABLE 1

ADDUCT FORMATION CONSTANTS FOR NICKEL (II) CHELATES

Base	Nature	2-Methyl-8-quinolinate					4-Methyl-8-quinolinate				
		n		log β_1^{ad}		log β_2^{ad}	n		log β_1^{ad}	log β_2^{ad}	
		Present	Reported*	Present	Reported*	Present	Present	Reported*	Present	Present	Reported*
Pyridine	Monodentate	2	1	—	0.65	4.10	2	2	—	3.48	3.40
2-*Picoline*		2	1	—	–0.48	1.72	2	2	—	–0.10	0.05
4-*Picoline*		2	1	—	0.94	4.90	2	2	—	3.80	3.73
Quinoline		No adduct formation					1	—	0.90	—	—
4-*Me*-8-quinolinol	Bidentate	No adduct formation					1	—	2.92	—	—
2-*Me*-8-quinolinol		No adduct formation					1	—	2.70	—	—
2,2′-Bipyridyl		1	1	> 4.8	3.13	—	1	2	> 4.80	—	8.65
1,10-Phenanthroline		1	1	> 4.8	3.23		1	2	> 4.80	—	8.40
Neocuproin		1	1	2.62	2.75		1	—	2.96	—	—

n corresponds to number of base molecules attache to nickel(II) chelate.

*K.S. Bhatki, A.T. Rane and H. Freiser, *Inorg. Chim. Acta*, **26** 183 (1978).

used equation (7) instead of equation (6). It should be realized that equation (7) ignores the absorption due to the adducts formed. However, the *necessity of the* term A_{ad} in the discrimination of equation (6) is mandatory especially when the two systems absorb greatly in the region used. Unfortunately, one can see that this mistake was repeatedly committed in all the subsequent publications of Bhatki and Rane[8].

The relatively higher stability of monobasic adducts of Ni2MQ than Ni4MQ may be attributed to the formation of a weak bond such as Ni–N due to the steric stretch in Ni2MQ. On the other, hand, in the case of Ni4MQ, due to its high stability[13], the base cannot approach the metal as closely as in Ni2MQ.

In the case of dibasic ligands, it is surprising to note that the present values of formation constants of Ni2MQ do not agree and n = 1 is seen in both the data. The stabilities observed in the present work (log $\beta_1^{ad} > 4.8$ for 2,2′-bipyridyl and 1,10-phenanthroline are higher than those of Bhatki *et al.*[7] This is because correction for [B] in equation (6) was not made for base consumed in the formation of adducts. For neocuproin, since the adduct is weak and hence the base used in adduct formation is small, equation (8) becomes valid. Thus, the close agreement between the two data can be seen.

For Ni4MQ-bidentate bases, a slope of 1 is observed in the present studies as compared to a value of 2 in Bhatki *et al.*[7] In the latter work, a value of n = 2 indicates coordination number of nickel to be 8. Neocuproin, 2-methyl-8-quinolinol and 4-methyl-8-quinolinol adducts of Ni4MQ are less stable. One possible explanation for such a behaviour may be due to the presence of bulky methyl group in *ortho* position in neocuproin or a proton from OH in 4-methyl-8-quinolinol or both in 2-methyl-8-quinolinol adducts.

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