Inorganica Chimica Acta, 26 (1978) 183–188
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Reactions of Some Nickel Chelates of 8-Quinolinols With Heterocyclic Nitrogen Bases*

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Received April 27, 1977

Adduct formation constants have been determined by spectrophotometric study of the heterocyclic base-adducts of the nickel chelates of methyl analogues of 8-quinolinol. Large bathochromic shifts were observed in the visible region on the addition of heterocyclic bases to the organic phase containing Ni-2-methyl-8-quinolinate and hypsochromic shifts were observed in the case of Ni-4-methyl-8-quinolinate, due to adduct formation. Pyridine bases formed diadducts with nickel chelates of 4-methyl-8-quinolinol, whereas monoadducts were observed in the case of 2-methyl-8-quinolinol. This is attributed to the sterically hindering methyl group in 2-methyl-8-quinolinol which maintains a pentacoordinated structure of the pyridine adduct, whereas a more stable hexacoordinated one is favoured by the 4-methyl group in 4-methyl-8-quinolinol. The stabilities of the nickel adducts increase in the following order of the bases: 2-picoline < 2,4-lutidine < 2,4,6-collidine < pyridine < 4-picoline < neocuproin < ethylenediamine < 1,10-phenanthroline ⩽ 2,2'-bipyridyl.

Introduction

In an earlier study on adduct formation, using solvent extraction [1], nickel(II) was found to extract with 8-quinolinol (HQ) in the form of a complex $NiQ_2 \cdot HQ$, termed as a self-adduct, in which the HQ was believed to be acting as a monodentate ligand involving the quinoline nitrogen atom. With 2-methyl analogue, instead of a self-adduct the extractable complex was a simple 1:2 chelate. Such behaviour indicated the sensitivity of self-adduct formation to steric influences. In an attempt to unravel the relative importance of steric hindrance and other factors in the simple chelate and in the adducting ligand, it was decided to investigate the effect of some pyridines also, including those with 2-methyl substituents, on the formation of the complexes of nickel(II) with 2- and 4-methyl analogues of 8-quinolinol.

Earlier work [2] had uncovered the tendency of nickel complexes of sulphur containing ligands such as dialkyldithiophosphates, alkylxanthates to form adducts with pyridine and other nitrogen bases whose spectra also exhibited changes. Math and co-workers [3] observed recently that the addition of phenanthroline to nickel dithizonate resulted in the formation of such an intensely pink adduct that it provided the basis for the development of the most sensitive colorimetric method for the determination of the metal. This observation was extended further to study the reaction of some low-spin nickel(II) chelates with heterocyclic nitrogen bases [4].

Chou and Freiser [5] studied the role of adduct formation in the extraction of zinc(II) with substituted 8-quinolinols. They observed that pyridine and its methyl analogues enhanced the extraction of zinc(II) into chloroform with either 8-quinolinol or its 2- or 4- methyl analogues.

This paper represents an extension of our work to the investigation of electronic influences on self-adduct formation in 8-quinolinol family of chelating agents.

Experimental

Apparatus

A Cary Model 14 spectrophotometer was used for most of the absorbance measurements. Occasionally a Beckman Model DU spectrophotometer was employed for absorbance measurements at low log B values.

Reagents

2-Methyl-8-quinolinol (Fluka) was recrystallised from absolute alcohol. A crystalline product having melting point 74 °C was obtained. 4-Methyl-8-quinolinol was synthesized from *o*-aminophenol and methyl-vinyl ketone as described by Phillips *et al.*

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*Part of the Ph.D. dissertation submitted by A. T. Rane to the University of Bombay, 1976.

[6]. The crude product was purified by vacuum distillation followed by two recrystallizations from absolute ethanol. The melting point of the purified product (140 °C) agreed well with 141 °C, reported in the literature.

Pyridine (Mallinckrodt), picolines (methyl analogues of pyridine) (Eastman), lutidines (dimethyl analogues of pyridine) (Eastman), and 2,4,6-collidine (trimethyl analogue of pyridine) were dried over potassium hydroxide and a constant boiling fraction was collected and used. Chloroform (Mallinckrodt Analytical Grade), 1,10-phenanthroline (g. Frederick Smith Co.), 2,2′-bipyridyl (Eastman),2,9-dimethyl-1, 10-phenanthroline (neocuproin, B.D.H.) and Ni-$(ClO_4)_2$ (Fisher Reagent Grade) were used without further purification.

Preparation of Nickel-2-methyl-8-quinolinate

A weighed amount of nickel perchlorate (<1 g) was dissolved in about 500 ml of distilled water. To this was added ~5 g of sodium acetate. A little turbidity developed, which was got rid of by adding a few drops of acetic acid. The mixture was then heated to about 50 °C and to this was added an alcoholic solution of 8-quinaldine (2-methyl-8-quinolinol) dropwise from a separatory funnel. The total amount of the reagent used was in slight excess over that required for complete precipitation of nickel as nickel-8-quinaldinate. A distinct yellow precipitate was formed.

The yellowish complex was digested on a low heat for two to three hours and filtered hot through a sintered-bed glass funnel. The precipitate was washed with hot water and dried at 110 °C for several hours to constant weight. The nickel content of the complex was determined by the usual dimethylglyoxime method and also by a method developed by Math and co-workers [3]. Found Ni = 15.58%; calculated for Ni-8-quinaldinate = 15.65% Ni.

In a similar manner the nickel complex of 4-methyl-8-quinolinol was prepared and analysed for nickel content. Found Ni = 15.61%, calculated Ni = 15.65%.

Determination of Equilibrium Absorbance Measurements

Specific amounts of chloroform solutions of the appropriate nickel complex were pipetted into standard volumetric flasks containing solutions of varying amounts of adducting base in chloroform and the volumes were adjusted to the mark with chloroform. The absorption spectra of the solutions were taken on the Cary 14 spectrophotometer in the range 300–500 nm employing 10 mm cuvettes. The wavelength selected for subsequent absorbance measurements was 450 nm in case of Ni-4-methyl-8-quinolinate and 375 nm for 2-methyl-analogue. They were used for the equilibrium calculations. The absorbance values were found to be constant for several hours. Typical plots are shown in Figures 1 and 2.

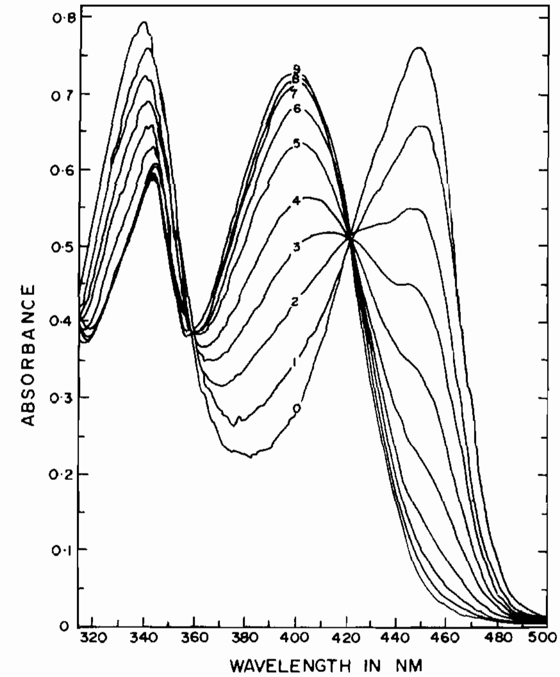

Figure 1. Absorption spectra of mixture of Ni-4Me-8Q + 2,2′-Bipyridyl in chloroform. 1 = 1.334×10^{-5}, 2 = 2.669×10^{-5}, 3 = 4.003×10^{-5}, 4 = 5.337×10^{-5}, 5 = 6.677×10^{-5}, 6 = 8.006×10^{-5}, 7 = 9.34×10^{-5}, 8 = 1.067×10^{-4}, 9 = 6.671×10^{-4} *M* 2,2′-bipyridyl.

Results and Discussion

The spectrum of the pure 4-methyl nickel chelate in chloroform (Fig. 1) in absence of any heterocyclic base shows two absorption bands, one at 340 nm and the other at 450 nm in the visible region. The spectrum undergoes a profound change upon the addition of pyridine or other similar nitrogen base. A new band with an absorption at 400 nm develops in the visible region with two isosbestic points around 360 and 420 nm. In general a chelate formation leads to changes in spectra [7].

The spectral behaviour of nickel-2-methyl-8-quinolinate in chloroform is shown in Figure 2. On addition of a base, the spectrum resolves into two bands, one at ~340 nm and the other at ~400 nm, with two isosbestic points at 350 and 380 nm.

The change in the spectrum of a nickel complex under investigation that accompanies the addition of pyridine or other bases can be used to determine the equilibrium constant of adduct formation. As it is not entirely unlikely that the chelates might exist as polymers, these possibilities are also taken into account in the following derivation of the equilibrium constant.

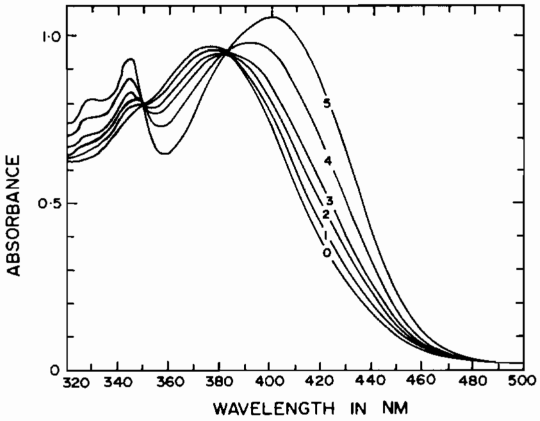

Figure 2. Absorption spectra of mixture of Ni-2Me-8Q + 1,10-Phenanthroline in chloroform. 1 = 1.112×10^{-5}, 2 = 2.224×10^{-5}, 3 = 3.336×10^{-5}, 4 = 4.448×10^{-5}, 5 = 5.560×10^{-5} *M* 1,10-phenanthroline.

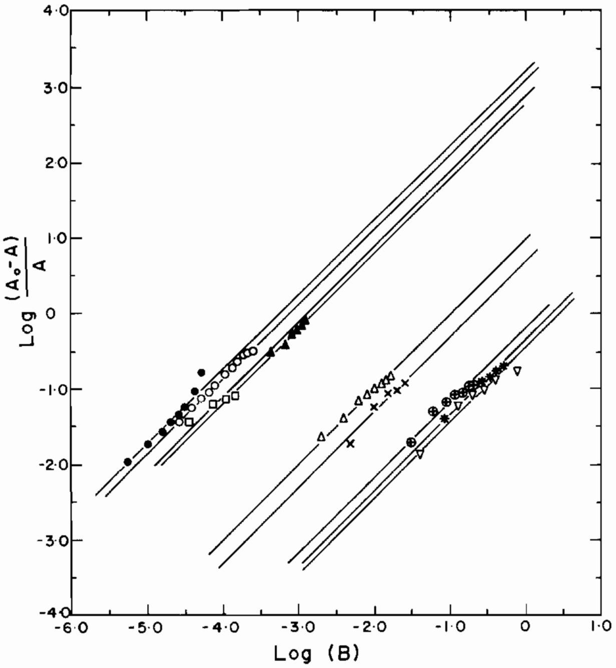

Figure 3. Plot showing adduct formation between Ni-2-Me-8 Quinilinate and various heterocyclic nitrogen bases in chloroform. ● 1,10-Phenanthroline, ○ 2,2′-Bipyridyl, □ Ethylenediammine, △ 4-picoline, X Pyridine, ⊕, 2,4,6-Collidine, * 2,4-Lutidine, ▽ 2-Picoline, ▲ 2,9-Neocuproin.

The formation of a monomeric chelate adduct can be represented by eq. (1)

$$\mathrm{NiQ_2} + n\mathrm{B} \overset{K_{AD}}{\rightleftharpoons} \mathrm{NiQ_2 \cdot nB} \tag{1}$$

where B represents the heterocyclic nitrogen base added. Equation (2) represents a case when the complex is polymeric but the adduct a monomeric species

$$(\mathrm{NiQ_2})_x + nx\mathrm{B} \overset{K_{AD}}{\rightleftharpoons} x\mathrm{NiQ_2 \cdot nB} \tag{2}$$

When both the original complex and the adduct are polymeric, they are represented by eq. (3)

$$(\mathrm{NiQ_2})_x + nx\mathrm{B} \overset{K_{AD}}{\rightleftharpoons} (\mathrm{NiQ_2 \cdot nB})_x \tag{3}$$

Expressions based on these formulae are:

$$\log K_{AD} = npB + \log \frac{A_o - A}{A} \tag{4}$$

$$\log K_{AD} = nxpB + x \log (A_o - A) - \log A + \log \frac{x}{e^{x-1}} \tag{5}$$

and

$$\log K_{AD} = nxpB + \log \frac{A_o - A}{A} \tag{6}$$

respectively, where A_o is the absorbance in the absence of adducting base B, and A the absorbance in the presence of B, whose concentration is denoted by its negative logarithm, pB.

In all the systems studied, it was possible to measure the absorbance of the mixtures at wavelengths where the only significant absorption was due to the simple chelate (450 nm for the nickel oxinate of the 4-methyl analogue) so that the absorbance A could be considered to be directly proportional to the concentration of the simple chelate in the equations. By plotting the data as log $\{(A_o - A)^x/A\}$ *vs.* log B as called for in equation (5), it should be possible to distinguish between Reactions 1, 2 and 3, particularly if sufficiently precise absorbance measurements at low pB values can be obtained. Curves were then drawn in which x was assigned the values of 1, 2 and 3. Only the curve in which x = 1 was linear throughout (Fig. 3). In contrast, the other curves with x = 2 and x = 3 deviated significantly from linearity, specially in the low log B range. These curves are not shown here. The linear curve which was obtained with x = 1 is given in Figure 4 for 4-methyl-8-quinolinate of nickel and pyridine. Also given in this figure are the plots obtained in presence of other nitrogen bases such as phen, 2,2′-bipyridyl, 2-picoline and 4-picoline, *etc.* The curves for 2-picoline (2-methyl-pyridine) in both the cases are to the extreme right of pyridine *i.e.* towards high log B values showing that these adducts are very weak, whereas, the adducts formed in presence of phen (1,10-phenanthroline) are very stable as they appear to the left of the pyridine curve, *i.e.* at very low log B values. However, some steric hindrance was observed when the dimethyl analog of *o*-phenanthroline was employed instead of phen itself. The adduct formed was weak as indicated by the shift in the curve (Fig. 3) to higher log B values. The stabilities of the nickel adducts, in both the cases, were found to increase in the following order of the bases:

TABLE I. Adduct Formation Constants for Nickel(II) Chelates.

Base	pK	log K_{AD} in Chloroform		
		2-methyl-8-quinolinate	4-methyl-8-quinolinate	Dithiozonate[e]
Pyridine	5.2[a,b]	0.65	3.40	1.08
2-Picoline	5.9[a,b]	−0.48	0.05	−0.42
4-Picoline	6.08[c]	0.94	3.73	1.45
2,4-Lutidine	6.72[a]	−0.33	0.28	–
2,6-Lutidine	4.95[d]	No adduct formation	No adduct formation	−0.60
2,4,6-Collidine	7.48[a,b]	−0.18	1.65	–
Ethylenediamine	6.84[d]	2.87	8.47	3.86
2,2′-Bipyridyl	4.40[c]	3.13	8.65	4.63
1,10-Phenanthroline	4.95[d]	3.23	8.47	5.96
2,9-Neocuproin	5.85[d]	2.75	–	–

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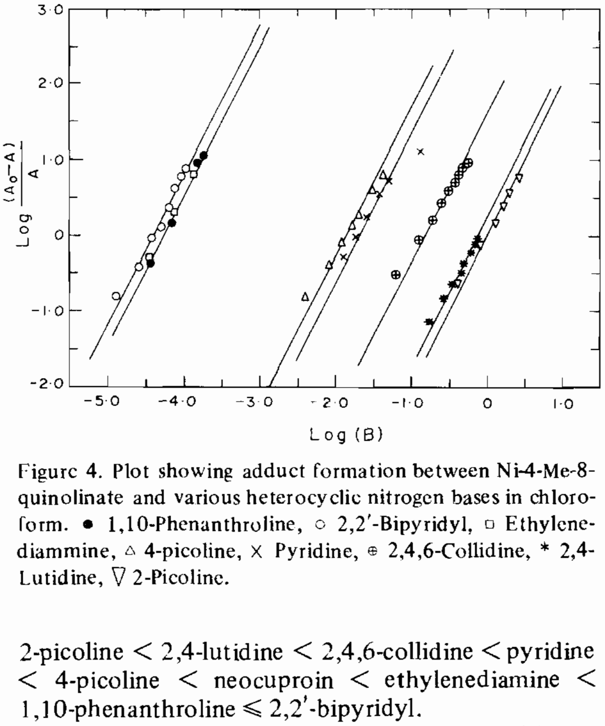

Figure 4. Plot showing adduct formation between Ni-4-Me-8-quinolinate and various heterocyclic nitrogen bases in chloroform. ● 1,10-Phenanthroline, ○ 2,2′-Bipyridyl, □ Ethylenediammine, △ 4-picoline, X Pyridine, ⊕ 2,4,6-Collidine, * 2,4-Lutidine, ▽ 2-Picoline.

2-picoline < 2,4-lutidine < 2,4,6-collidine < pyridine < 4-picoline < neocuproin < ethylenediamine < 1,10-phenanthroline ⩽ 2,2′-bipyridyl.

Confirmation of the validity of equations (1) and (4) in addition to the linear plots for $x = 1$ was obtained from the observation that values of the equilibrium constant, K_{AD}, were independent of the initial concentration of NiQ_2 over a twenty-five-fold concentration range. Hence, it is reasonable to eliminate the possibility that NiQ_2 is polymeric in chloroform solution on the basis of these spectrophotometric measurements.

Values of log K_{AD} calculated according to equation (4) for the systems under investigation are listed in Table I. These values exhibit the expected increase with increasing adducting ligand basicity. The values obtained by Math and Freiser [4] for other systems are also shown in this table for comparison.

In the cases of pyridine and 4-picoline for both 2-methyl-8-quinolinate and 4-methyl-8-quinolinate there is a linear increase of log K_{AD} with pK_a values of the adducting bases. For 2-picoline, however, steric hindrance results in weaker adducts, 2-methyl-8-quinolinate showing less stability than the 4-methyl-8-quinolinate chelate. In the former case, the adducts contain only one mol of base, accounting for the five coordination sites around nickel. Such five-coordinate nickel chelates have been observed in 1:1 adducts of nitrogen bases with nickel chelates of sulphur-containing ligands [4, 8].

Although some of the increased stability (Table I) arises from a more favourable entropy change [4], it is not unlikely that certain ligands such as phenanthroline and bipyridyl which are bidentate can form adducts with nickel chelates as a six-coordinate octahedral complex. Further confirmation requires the thermodynamic calculations of entropy and enthalpy changes.

The plots of log K_{AD} values for nickel quinolinate adducts in the cases of 2-methyl and 4-methyl analogues *vs.* nickel dithizonate adducts of reference 4 are shown in Figure 5. These give two straight lines which intersect each other.

A decrease in the adduct stability was observed wherever steric hindrance was encountered. For example (see Table I), the adduct formation constants for the 2-methylpyridine (2-picoline) adducts were lower than those for the corresponding pyridine adducts. Likewise, in comparing the chelating ligands, the adduct formation constants for the pyridine adducts of 2-methyl-8-quinolinate were lower than those of the corresponding adduct of 4-

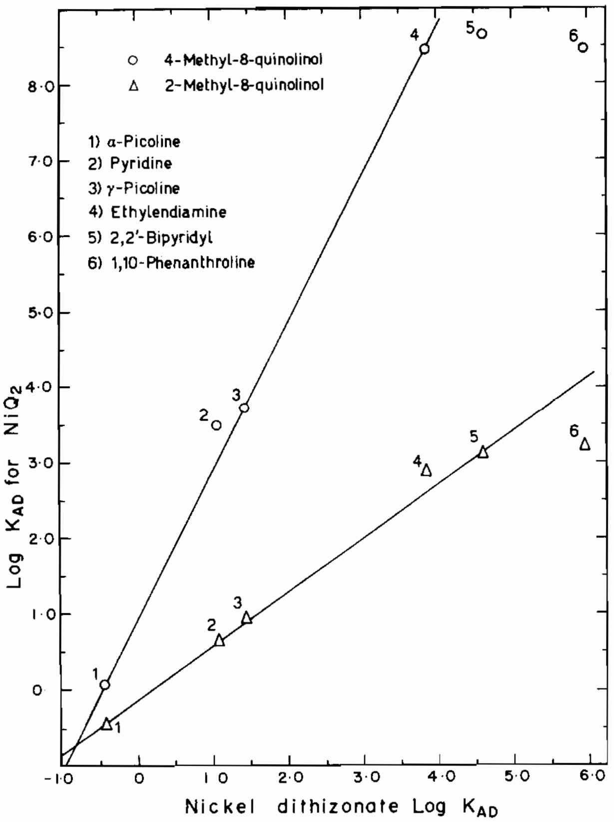

Figure 5. Plot of log K_{AD} for Ni-8-quinolinate adducts *vs.* that of Ni-dithizonate. △ Ni-2-Me-8Q; ○ Ni-4-Me-8Q. (1) 2-Picoline, (2) Pyridine, (3) 4-Picoline, (4) Ethylenediammine, (5) 2,2'-Bipyridyl, (6) 1,10-Phenanthroline.

methyl-8-quinolinol chelates. If we go on increasing the methyl groups by fixing them in 2 and 6 positions *etc.* of the pyridine molecule such as 2,6-lutidine or 2,4,6-collidine or as in 2-methyl-8-quinolinol system, two to three methyl groups come adjacent in the 1:1 adduct and this resultant crowding has an adverse effect on adduct formation. That this was really so was seen when nickel chelates of methyl analogue of 8-quinolinol were treated with 2,6-lutidine. No shifts in the spectra were observed in both the methyl analogues, indicating the absence of adduct formation. Both the methyl groups in 2,6-lutidine are very close to the nitrogen in the ring and this crowding causes a very strong steric effect on the adduct formation.

The 1:1 adduct stoichiometry raises some interesting questions about the nature of these complexes. Nickel(II) often has coordination number of four or six [9]. Because the extraction-data in the previous study [1] yielded information about only five coordination sites around nickel ion, it was decided to extend this study to adducting system of heterocyclic nitrogen bases.

Although the curves of log $(A_o - A)^x/A$ *versus* log B are linear when plotted with x = 1, their respective slopes are one and two in the case of 2-methyl and 4-methyl-8-quinolinol, respectively (Figs. 3 & 4). This is an indication that pyridines probably form mono-adducts with the nickel chelate of 2-methyl-8-quinolinol of the formula NiQ_2P, whereas they form diadducts with Ni-4-methyl-8-quinolinate as $NiQ_2 \cdot 2P$.

A great deal of information is available [10] on the magnetic properties of octahedral and square-planar nickel complexes, including measurements of temperature dependence and crystal anisotropy. Moments of the octahedral complexes are mostly between 2.9 and 3.3 B.M. For the square-planar complexes χ_{Ni} is negative or if positive, is very small. It seems more probable that usually the paramagnetic form is hexacovalent. In pyridine and other coordinating solvents the moments tend to be higher and to depend less on temperature and concentration than for "inert" solvents. For such solvents the hexacovalency is attained by coordination of the solvent into the octahedral positions of the square-planar form. The theory of the nickel(II) ion under the influence of ligand fields intermediate between square-planar and octahedral has been discussed in detail by Figgis and Lewis [10].

Hydrated nickel-8-quinolinate, $NiQ_2 \cdot 2H_2O$ and even the anhydrous NiQ_2 are yellowish green high spin compounds. The value for χ_{Ni} in the quinolinate chelate has been reported to be 4640 e.m.u. mol^{-1} and the magnetic moment for the pyridine adduct as 2.8 B.M. [11].

Recently Patel *et al.* [12] isolated various pyridine adducts of nickel-8-quinolinate and studied the magnetic susceptibilities of the complexes. They observed magnetic moment values of 3.2 B.M. for these adducts suggesting an octahedral symmetry for these high spin nickel(II) complexes. They also studied their spectra in visible and infra-red regions, in alcohol and in the corresponding base medium. They, however, did not succeed in isolating an adduct with 2-picoline. This explains the steric hindrance observed in such cases when adjacent positions to the nitrogen atom in the ring are blocked by bulky groups (see Table I).

On the basis of this discussion it can be said with confidence that the adducts formed by pyridines with nickel-4-methyl-8-quinolinate are hexacoordinated, whereas those in the nickel-2-methyl-8-quinolinol system are pentacoordinated. The sterically hindering methyl group in the 2-methyl chelate favours such pentacoordinated adduct with square base pyramidal structure.

In the nickel complex crystals isolated from solution, the fifth and sixth sites are occupied by water molecules which X-ray analysis shows to be rather distant from the metal ion [13]. According to the X-ray study, this complex is octahedral consisting of two transcoplanar chelate rings with water molecules located at axial positions. The formation of a diadduct would just involve the replacement of the axial water molecules by pyridine molecules.

It is not unlikely that nickel(II) would form a monosolvate adduct $NiQ_2 \cdot P(S)$ with chloroform as in the case of zinc(II) [14]. Since chloroform is not a Lewis base, it is difficult to rationalize its coordination to the central metal ion (it may attach to the 8-quinolinol molecule through hydrogen bonding).

From a practical point of view, adduct formation in general significantly enhances the extraction of a metal ion. In many cases, it also supplies valuable information about the coordination number. The adduct stability is enhanced by an increase in the basicity of the adducting base and an increase in the residual Lewis acidity of the metal atom, *i.e.* after chelation. In the self-adduct system these factors tend to compensate for each other so that the overall effect is very small (0.5 log unit) over a wide range of reagent basicities.

Acknowledgement

The authors gratefully acknowledge the financial support from the U.S. Atomic Energy Commission, when one of them (K.S.B.) was awarded a post-doctoral fellowship to work at the University of Arizona at Tucson during 1968–69, where part of this work was carried out.

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