Spectrophotometric Study of Nitrogen Base Adducts of Nickel(II)-4-methyl-8-quinolate

T. SURESH, S. SANTOSH KUMAR, N. M. KOTTURESHAWARA,
M. REVANASIDAPPA*, SYED KHASIM[§] and SURESH[#]

Department of Industrial Chemistry,
Gulbarga University Post Graduate Centre, Bellary- 583104, India.

^{*}Department of Chemistry, [§]Department of Physics,
PES School of Engineering, Bangalore- 560100, India.

[#]Department of Chemistry, Bellary Engineering College, Bellary- 583104, India.

revum@rediffmail.com

Received 29 August 2007; Revised 26 September 2007; Accepted 20 October 2007

Abstract: Adduct formation constants have been determined by spectrophotometric study of a few typical bases with nickel(II) chelate of 4-methyl-8-quinolinol in chloroform. Bathochromic and hypsochromic shifts were observed in the visible range due to the adduct formation. Monobasic bases like pyridine, methyl substituted anilines and such other bases exhibit 1: 2 stoichiometry giving hexa – coordinated adducts. The dibasic bases such as 1,10-phenanthroline and 2,9- neocuproine exhibit 1 : 1 stoichiometry giving hexacoordinated adducts. The experimental results are discussed in terms of the basicity and steric effects of the various bases.

Keywords: Adduct formation, Steric hindrance, Formation constant.

Introduction

Nickel(II) chelates of several ligands like diphenylcarbazone, diphenylthiocarbazone, 8-quinolinol and its substituted analogues produce intense absorption in the optical spectra, in the visible range, which is characteristic of the ligand itself. Structural changes occurred in the nickel(II) chelates on addition of nitrogen bases forms adduct which gives rise to profound spectral changes. Such bathochromic and hypsochromic shifts observed in the visible region of the spectra of nickel(II) chelates of dithizone¹, diphenylcarbazone², 8-quinolinol³, methylsubstituted 8-quinolinols³, substituted diphenylcarbazones and dithizones⁴⁻¹¹ on addition of nitrogen bases. These were employed for the determination of adduct formation constants. The changes in spectra helps in confirming the structure of the

nitrogen base adducts of nickel(II) chelates. Pyridine and its methyl derivatives were used to study the role of adduct formation in the extraction of Zn(II) and Ni(II) with substituted 8-quinolinols^{12,13}, dithizones¹⁴ and dipheylcarbazon^{15,16}. Suresh *et al.*¹⁴⁻¹⁶ observed that by the addition of pyridine, 1,10-phenanthroline and 2,2'-bipyridyl to nickel(II) chelates of substituted dithizones and its analogues enhances the extraction of nickel into chloroform.

In this report, we give some results of study of the adducts of nickel(II)-4-methyl-8-quinolate (Ni4M8Q) with different nitrogen bases to gain the quantitative information about the nature and the stability of the adducts formed.

The adducts of Ni4M8Q have octahedral structures with monobasic and dibasic ligands. It may lead to better understanding of the behaviour of different donor atoms in the formation of adducts. All the reactions were carried out in chloroform as a solvent which does not add axially to the planar nickel(II) chelate.

Experimental

Apparatus

A Bausch and Lomb Spectronic 2000 UV- vis recording spectrophotometer and Systronic spectrophotometer 106 were used for the measurements of absorbance. Magnetic susceptibility measurements were carried out on the solids by Farady method¹⁷.

Reagents

The reagent 4-methyl-8-quinolinol was prepared as reported in the literature¹⁸. The product was purified by vacuum distillation (m.p. 141 °C), Pyridine (Fisher), picolines (Eastman), lutidines, aniline, 2 Me-aniline (B.D.H.), 2, 3 Di Me-aniline (Seelge-Hannover), 2,6 Di Me-aniline, (Loba), morpholine and piperidine (Merck) were dried over solid potassium hydroxide and distilled. Constant boiling fractions were collected and distilled. 1,10-Phenanthroline, 2,9-neocuprione (G.Frederick Smith Co.), 4 Me-aniline (B.D.H.), nickel perchlorate (Fisher Reagent Grade) and chloroform (Merck) were used as received.

Preparation of nickel (II)-4-methyl-8-quinolate

The nickel (II) -4-methyl-8-quinolate was prepared by dissolving a known amount of the nickel perchlorate (~ 1g) in acetate buffer (pH=6.0) and mixing it with an appropriate amount of reagent in alcoholic solution. The total amount of reagent added was slightly more than that of required for 1:2 stoichiometry. The yellow precipitate formed was digested for 2 hr and filtered hot. The complex was dried in vacuum over phosphorus pentoxide at room temperature. The nickel content of the complex was found to be 15.92% which is calculated by phenanthroline-dithizone method developed by Math *et al.*¹⁹ (Calc.15.86%).

Determination of equilibrium constants

Known volume of chloroform solutions of Ni4M8Q were pipetted into standard flasks containing various amounts of the nitrogen base (dissolved in chloroform) and the mixtures were diluted to the mark with solvent. The absorption spectra of the solutions were obtained in the range 300-500 nm, with an optical path length of 10 mm. The absorbance value at 450 or 380 nm was found to be suitable for the study of formation of the Ni4M8Q adducts, The difference in absorbance between chelate and adduct being largest at these wave lengths. The absorbances were found to be constant for at least 1 hr, unless otherwise stated. Typical plot is shown in Figure 1.

Figure 1. Absorption spectra of Ni4M8Q + 4-methyl aniline mixtures in chloroform at 25°C. [Ni4M8Q]: 12.10×10^{-5} M, [4-Me-aniline] $\times 10^2$ M: (a) 0.00 (b) 0.99 (c) 1.99 (d) 2.99 (e) 3.98 (f) 5.98 (g) 7.97 (h) 9.96 and (i) 11.95

Results and Discussion

The absorption spectra were measured in the visible region around 300-500 nm using chloroform as a reference at a concentration of 10^{-5} M. A typical spectrum for Ni4M8Q is shown in Figure 1. The light yellow coloured chloroform solution of Ni4M8Q has two bands in 450 ($\epsilon_{\text{mol}} \sim 8.09 \times 10^4 \text{ l.mole}^{-1} \cdot \text{cm}^{-1}$) and 340 nm ($\epsilon_{\text{mol}} \sim 8.21 \times 10^4 \text{ l.mole}^{-1} \cdot \text{cm}^{-1}$) with two isosbestic points around 360 and 420 nm (Fig.1.). The addition of nitrogen bases to Ni4M8Q produced dark yellow coloured adduct having a single absorption band at 400 nm. Measurements at wavelengths 450 and 380 nm gave similar results. However, the absorption at 450 nm only chelates absorbs which is suitable for analysis. Therefore, the absorption values at 450 nm was plotted as a function of pB to obtain sigmoidal curves. The values of A_{ad} was obtained from the extrapolation of these curves which are used in the calculation of $\log \beta_n^{\text{ad}}$ using

$$\log \beta_n^{\text{ad}} = -n \log [B] + \log [A_{\text{ch}} - A / A - A_{\text{ad}}] \quad (1)$$

where n is the number of base molecules, B , attached to chelate; A_{ch} and A_{ad} are respectively, the absorbances due to chelate and adduct and A is the absorbance due to the chelate and adduct equilibrium mixture.

In case of bidentate ligands, in addition to the slope of unity found from equation (1), the mole-ratio²⁰ and Job's method²¹ were also used to confirm the ratio of base to chelate. The experimental data is given in Table 1.

Table 1. Adduct formation constants of nickel(II)-4-methyl-8-quinoline with nitrogen bases in chloroform

Base	pKa	Slope(n)	$\log \beta_n^{\text{ad}}$
Pyridine	5.20 ⁺	2	3.48
2-Picoline	5.90 ⁺	2	-0.12
4-Picoline	6.08 ⁺	2	3.82
2,6-Lutidine	4.95 ⁺	2	1.54
2,4-Lutidine	6.72 ⁺	2	2.32
Aniline	4.63 [*]	2	1.74
2 Me-aniline	4.44 [*]	2	1.02
4 Me-aniline	5.08 [*]	2	1.32
2,3 Di Me-aniline	4.64 ^{**}	2	1.26
2,6 Di Me-aniline	4.10 ^{**}	2	0.86
2-Nitroaniline			NAF
3-Nitroaniline			NAF
4-Nitroaniline			NAF
1,10-phenanthroline	4.95 [*]	1	5.90
2,9- Neocuproin	5.85 [*]	1	2.96
Morpholine	8.33 [*]	2	2.46
Piperidine	11.12 [*]	2	2.88
Ethyl alcohol		2	1.18

References : ⁺ [1] ^{*} [28] ^{**} [29], NAF -No Adduct Formation.

The stabilities of nickel(II) adducts with monodentate bases, increases with pKa for the conjugated acid of the base. These adducts contain two moles of bases with slope of 2 for the plots of $\log [A_{\text{ch}} - A/A_{\text{ad}}]$ vs $-\log [\text{Base}]$. This accounts for six coordination sites around nickel. The formation of such six-coordinate nickel(II) chelates has also been observed in the case of oxygen containing ligands^{4,10,11}.

The stabilities of Ni4M8Q – adducts were found to increase in the following order of bases: 2-picoline < 2,6 Di Me-aniline < 2 Me - aniline < 2,3 Di Me - aniline < 4-Me - aniline < 2,6-lutidine < aniline < 2,4-lutidine < morpholine < piperidine < 2,9-neocupron < pyridine < 4 –picoline < 1,10-phenanthroline. The lower stabilities of 2-picoline, 2,6 Di Me - aniline, 2Me - aniline, 2,6 Di Me - aniline and 2,9-neocupron may be attributed to steric hindrance offered by methyl groups present at nitrogen donor group even though their pKa values are much more higher than pyridine, aniline and 1,10-phenanthroline. The high values of $\log \beta_n^{\text{ad}}$ for nitrogen heterocyclic bases^{22,23} are compared to low values of $\log \beta_n^{\text{ad}}$ for aniline bases which indicate that anilines are probably the weaker bases. It may be anticipated²⁴ that the stronger the basic character the stronger will be the bonding in Ni4M8Q – nitrogen base adducts. Hence it may be concluded that Ni4M8Q – pyridine adducts have stronger bonding than Ni4M8Q – aniline adducts as evident from $\log \beta_n^{\text{ad}}$ values in Table 1.

The smaller formation constants of the adducts of Ni4M8Q with morpholine may be attributed due to decrease in basicity of the nitrogen atom in the morpholine ring. From the study of adduct formation of Ni4M8Q with saturated heterocyclic nitrogen bases, it is clear that the structural and electrostatic rearrangements in the donor, as well as, in the acceptor molecules must be considered in the interpretation of adduct formation²⁵. Fernando²⁶ has

shown that there is considerable distortion in nickel(II) chelates when these adducts are formed with stronger nitrogen bases. The donor molecules themselves have undergone structural changes²⁷, for example piperidine, in chair configuration, the hydrogen on nitrogen atom in the equatorial position. When the adduct formation occurs the hydrogen atom probably shifts to the axial position to allow the nickel atom to bond to the nitrogen and occupy the equatorial position.

Polar solvent like ethyl alcohol also form stable adduct like nitrogen bases. It is surprising to find that the absorption spectrum of Ni4M8Q does not change upon the addition of 2,3 and 4-nitroanilines. This may be due to the fact that these ligands do not form adducts with Ni4M8Q under these experimental conditions.

It is, however, interesting to note that, the adduct formation constants for Ni4M8Q are significantly higher to its sulphur and nitrogen nickel(II) chelates which indicates that, the adducts of nickel(II) chelates^{4,5} with O & N atoms prefer higher coordination number than four.

References

1. Math K S and Freiser H, *Anal. Chem.*, 1969, **41**, 1682.
2. Suresh T, Dheerendra T and Kulkarni V H, *Acta Cienca Indica*, 1992, **18C**, 113.
3. Bhatki K S, Rane A T and Freiser H, *Inorg. Chim. Acta*, 1978, **26**, 183.
4. Math K S and Suresh T, *Talanta*, 1985, **32**, 811.
5. Math K S, Suresh T and Aminabhavi T M, *Spectrochemica Acta*, 1986, **42A**, 693.
6. Suresh T, Math K S and Kulkarni V H, *Asian J. Chem.*, 1993, **5**, 296.
7. Suresh T, Kulkarni V H and Hippargi S S, *Nat. Acad. Sc. Letters*, 1994, **17**, 141.
8. Suresh T and Basavaraj B, *Proc. Nat. Acad. Sc. India*, 1998, **68A**, 121.
9. Suresh T and Biradar V and Kulkarni V H, *J. Chemtracks*, 1999, **01**, 1.
10. Suresh T, Kottureshwara N M and Suresh, *J. Ind. Counc. Chem.*, 2004, **21**, 38.
11. Suresh T, Nagesh Shastry D, Revanasiddappa M and Suresh, *J. Ind. Chem. Soc.*, 2006, **83**, 1.
12. Fa-Chun Chou and Freiser H, *Anal. Chem.*, 1968, **40**, 34.
13. Bhatki K S, Rane A T and Freiser H, *Inorg. Chem.*, 1978, **17**, 2215.
14. Suresh T, *Acta Cienca Indica*, 1994, **XXC**, 58.
15. Suresh T and Kulkarni V H, *J. Ind. Chem. Soc.*, 1995, **72**, 887.
16. Suresh T, *J. Ind. Coun. Chem.*, 2002, **19**, 47.
17. Landott – Bornstein, *Zahlenwerte Und Funktionen (Magnetic Properties II)*, Springer-Verlag, Berlin, 1965.
18. Phillips J D, Elbinger R L and Merritt L, *J. Amer. Chem. Soc.*, 1949, **71**, 3987.
19. Math K S, Fernando Q and Freiser H, *Anal. Chem.*, 1964, **36**, 1762.
20. Joe J A and Jones A L, *Ind. Eng. Chem., Anal. Ed.*, 1944, **16**, 11.
21. Job P, *Anal. Chim. Phys*, 1928, **9**, 113.
22. Suresh T, *Ph.D. Thesis*, Karnataka University, Dharwad, India, 1985.
23. Suresh T and Kottureshwara N M, *Gulbarga University Research Journal (Sc. & Tech.)*, *Vijana Ganga*, 2005, **04**, 18.
24. Albert A and Serjeant E P, *The Determination of Ionization Constants*, Chapman and Hall Ltd., London, 1971.
25. Marshall T and Fernando Q, *Anal. Chem.*, 1972, **44**, 1346.
26. Fernando Q, *Separ. Sci.*, 1969, **01**, 575.
27. Gartio A F and Wayland B B, *J. Amer. Chem. Soc.*, 1969, **21**, 866.
28. Robert C Weast, *Hand Book of Chemistry and Physics*, Cleveland, Ohio, 1976.
29. Pollock J R A and Stevens R, *Dictionary of Organic Compounds*, Chlor-Dim, London 1965.