

The stepwise weight loss observed in T.G.A. studies indicates that there is (i) loss of water associated with the decomposition of the chelated ligand at low temperatures (90–170° C). and (ii) drastic decomposition above 300° C. The low temperature decomposition appears to involve the loss of nitrogen. We find that although the polychelate could be obtained, it has low thermal stability.

The magnetic susceptibility of the chelate is found to be 5.12×10^{-6} C.G.S. unit at 29° C. Hence magnetic moment of the chelate per nickel atom is calculated at 2.75 B.M. It indicates octahedral nature of the chelate. Taking into consideration the formula and low value of the magnetic moment, we suggest the interlinking of chains, leading to some spin-spin interaction.

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NUCLEAR MAGNETIC RESONANCE STUDIES OF HYDROGEN BONDING

THE present paper deals with the results obtained by NMR spectroscopic studies of the equilibrium constants for the systems pyrazine, 2,2'-bipyridyl and 1,10-phenanthroline as proton acceptors with methanol, ethanol and piperidine as donors. Incidentally, the equilibrium constants for the chloroform-pyrazine, chloroform-acetone, hydrogen bonded systems have been reported^{1,2}.

Experimental

B.D.H. spectrograde carbon tetrachloride, cyclohexane and chloroform were used after further purification by standard methods³. E. Merck grade 2,2'-bipyridyl was used after recrystallizing from benzene and cyclohexane. E. Merck grade

1,10-phenanthroline monohydrate is dehydrated at 105° C and then recrystallized from benzene and then from carbon tetrachloride. It had an m.p. 117° C⁴. Fluka grade pyrazine was used without further purification.

All the spectra were recorded employing Varian Associates A 60-D NMR spectrometer (Analytical Instrument) operating in the field sweep mode equipped with temperature control. Chemical shifts of the Lewis acids were measured relative to TMS or cyclohexane. The precision of the chemical shifts is ± 0.5 Hz. The probe temperature is $37 \pm 0.5^\circ$ C. Each NMR tube was fitted with a cap to prevent evaporation of the solvent.

Procedure

The hydrogen bonding chemical shifts for the alcohols and piperidine were determined along with K by measuring the chemical shifts of the -OH proton of alcohols and NH proton of piperidine under very dilute conditions of these Lewis acids and varying amounts of donors.

In order to evaluate the equilibrium constant (K) and the H-bonding chemical shift (ΔW°), the following relations were used⁵⁻⁹:

$$1/\Delta W_{\text{observed}} = 1/K \cdot \Delta W^\circ [B]_0 + 1/\Delta W^\circ \quad (1)$$

$$\Delta W_{\text{observed}}/[B]_0 = -\Delta W_{\text{observed}} \cdot K + \Delta W^\circ \cdot K \quad (2)$$

where K is the equilibrium constant, $[B]_0$ the initial concentration of the base, $\Delta W_{\text{observed}}$ is the difference between the observed chemical shift and that of free acid and ΔW° the difference between free and complexed acid. All the computations were carried out in a single operation on an IBM 1130 computer using the general least squares method.

Results and Discussion

The hydrogen bonding chemical shifts ΔW° for methanol, ethanol, piperidine with a series of Lewis bases and the corresponding equilibrium constants are given in Table I along with acid concentration and base concentration range. Measurements were made on five concentrations in each case.

The concentrations of acids, methanol, ethanol, piperidine and chloroform are such that the self-association does not compete with the given Lewis bases¹⁰⁻¹².

From the results of Table I it can be seen that variations in the estimates of ΔW° using equation (1) obviously affect the value of K. The modified equation (2) directly gives K and hence the values of K so obtained may reasonably be accepted to be more accurate than those obtained with equation (1)⁹.

TABLE I

| Sl. No. | Lewis acid | Lewis base | Acid concentration | Base concentration range | From W° | equation (1) K.1/mol. | From W° | equation (2) K.1/mol. |
|---------|------------|---------------------|--------------------|--------------------------|---------|-----------------------|---------|-----------------------|
| 1. | Methanol | Pyrazine | 0.19708 | 0.1428-0.6422 | 136.2 | 1.22 | 149.1 | 1.08 |
| 2. | Ethanol | Pyrazine | 0.27412 | 0.1428-0.6422 | 62.6 | 0.44 | 42.3 | 0.59 |
| 3. | Piperidine | Pyrazine | 0.16171 | 0.1428-0.6422 | 152.5 | 0.092 | 32.5 | 0.376 |
| 4. | Methanol | 2,2-bipyridyl | 0.19708 | 0.20146-0.92672 | 214.2 | 0.98 | 212.9 | 0.98 |
| 5. | Ethanol | 2,2-bipyridyl | 0.27412 | 0.20146-0.92672 | 108.5 | 2.04 | 120.7 | 1.67 |
| 6. | Piperidine | 2,2-bipyridyl | 0.16171 | 0.20146-0.92672 | 17.6 | 1.62 | 21.8 | 1.14 |
| 7. | Methanol | 1:10 phenanthroline | 0.19708 | 0.01663-0.07982 | 243.0 | 6.88 | 245.7 | 6.80 |
| 8. | Ethanol | 1:10 phenanthroline | 0.27412 | 0.01663-0.07982 | 276.9 | 5.00 | 227.0 | 6.40 |
| 9. | Piperidine | 1:10 phenanthroline | 0.16171 | 0.01663-0.07982 | 15.07 | 8.00 | 33.2 | 4.17 |
| 10. | Chloroform | Pyrazine | 0.04998 | 0.1428-0.6422 | 138.0 | 0.105 | 97.7 | 0.151 |
| 11. | Chloroform | Acetone | 0.1247 | 0.6808-6.808 | 64.6 | 0.43 | 64.1 | 0.43 |

The values of K increase from pyrazine to 1:10 phenanthroline. This may be expected from their structures. Pyrazine obviously gives a weaker intramolecular hydrogen bonded complex. The two nitrogens of 1,10-phenanthroline are cis-planar which adds to the feasibility of the intramolecular exchange of hydrogen bond. Work is in progress to test this suggestion.

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