The above mentioned product was washed with tungsten hexafluoride to remove the impurities. The final product gave the following analysis: [Found: Re, 61-90; F, 12-50; Calc. for Re(CO)3F2: Re, 60-41; F, 12-32%]. The reaction between rhenium carbonyl and xenon difluoride in perfluoro 1,3-dimethylcyclohexane solvent the evacuation was continued for 12 hr was purified by washing repeatedly with WF6. As stoichiometry close to Re(CO)3F2. The product was transferred to a steel bomb and reacted with Re, 60.41; F, 12.32%. The product was purified by washing repeatedly with WF6 as well as with HF. The impure carbonyl fluoride was transferred to a steel bomb and reacted with CO at 50 atmospheric pressure and 100° when product with the stoichiometry Re(CO)3F2 was obtained.

The infrared spectrum of the present compound, in the carbonyl stretching region, shows a close similarity with the spectra of molybdenum and tungsten-2 fluoride, while the positions of these bands in the carbonyl halides are shown below:

[Re(CO)4Cl]2: 2043, 2010, 1964 Refs. (12, 13)
[Re(CO)4Br]2: 2044, 2012, 1970 Refs. (12, 13)
[Re(CO)4F2]: 2170(w). 2065(ms), 2040(m), 2012(s), 1980(m), 1912(s). The existence of dimeric species in mass spectrum supports our contention that rhenium carbonyl fluoride most probably has tetrameric structure with fluorine bridges.

The stability of the complexes of lead(II) with pyridine, α-picoline, β-picoline, and γ-picoline has been studied potentiometrically in 50% (v/v) aqueous ethanolic solution with potassium nitrate as the supporting electrolyte at 25°. The introduction of methyl group into the pyridine ring intensifies the basic property which is also influenced by its position in the ring. To compare the stability of metal-ligand and proton-ligand complexes the values of the first stability constants have been determined.

The literature reveals that a large number of attempts have been made to prepare the tertiary amine-metal complexes under different conditions. However the studies of formation constants in solution are scanty. In this investigation the formation constants of the complexes of lead(II) with the tertiary bases, i.e. pyridine, 2-picoline, 3-picoline and 4-picoline, have been computed using Musgrave and Humberg titration procedure.

Pyridine, 2-picoline, 3-picoline and 4-picoline (BDH reagents) were fractionally distilled over barium oxide and used. Lead(II) was used as nitrate. All the solutions were made in 1:1 (v/v) aqueous ethanolic solution of 0-5M KNO3. The ligand concentration was 0.25M. A standard nitric acid solution was used throughout with other reagents.

All the pH measurements were made in a precision pH-meter equipped with glass-calomel electrode assembly. Titrations were performed at 25°±0.1°. pH-meter was calibrated with aqueous buffer solution following the procedure of Van Uttert and Hase.

The relation \( \log [H^+] = B + \log U_H = B + \log (\gamma_+ + U_H) = B + \log \gamma_+ + U_H \) is valid for water and other mixed solvents like water-dioxane and water-ethanol where \( B \) is the pH-meter reading, \( \gamma_+ \) is the mean activity coefficient of the acid in the solvent mixture at the same temperature and ionic strength and \( U_H \) is the correction appropriate to zero ionic strength. The value of the pH-meter correction factor log \( U_H \), i.e. log \( (\gamma_+ U_H) \), was obtained as the intercept of the linear plot of \( B \) against \( B \) using solutions of known hydrogen ion concentration and this was used to correct practical constants into stoichiometric constants. The value of log \( U_H \), i.e. log \( (\gamma_+ U_H) \), has been obtained as \(-0.125\) for
The acid dissociation constants \( \text{p}K_a \) of the pyridines were determined following the methods of Musgrave and Humberg. The method for the determination of the stability constants of lead(II) complexes of pyridine and substituted pyridines was very similar to that of the acid dissociation constants of the pyridines. In this case the metal solution of equal volume and same acidity was titrated with the ligand solution maintaining the same ionic strength. Besides this, a given volume of the acid (of the same strength) was titrated with the solvent used. The total complexed \([L]\) was calculated from the difference in total concentration of ligand \(C_L\) and the sum of the concentrations of the free ligand \([L]\) and that of the protonated ligand \([HL^+]\).

The degree of formation of the metal-ligand complexes at a particular points is given by Eq. (1)

\[
\bar{n} = C_L - [L] - [LH^+] = \frac{C_L}{\sum_{n=0}^{\infty} n^2 \beta_n [L]^n} \quad \ldots(1)
\]

The acid dissociation constants of the ligands are listed in Table 1 along with the relevant values in different media. The lower \(\text{p}K_a\) values of the ligands obtained in the present study (Table 1) are probably due to the increase in the dielectric constant of the medium and change in the solvent composition.

Under the experimental conditions, it cannot be said with certainty what would be the maximum number of ligands bound to the metal ion. With all the pyridines, determination of the stability constants of the 1:1 complex species have been calculated, but the determination of the stability constants of still higher species could not be made as addition of more reagent resulted in the precipitation of the respective complexes. After proper rearrangement of the expression for \(\bar{n}\) the stability values were calculated and are recorded in Table 2.

The coordination strengths based on the position of the electron-releasing substituents in the pyridine ring are calculated by the sequency: \(\gamma\)-picoline \(>\alpha\)-picoline \(>\beta\)-picoline \(>\text{pyridine}\).

The plot of \(\text{p}K_1\) versus \(\beta\text{p}K_a\) of the ligand (Fig. 1) characterizes qualitatively the bonding capacity of the ligands for lead(II) ions. The increase in basicity of the ligands results in the increase of their donor strength. But lead(II) is a weak acceptor of electrons. In the case of pyridine, \(\pi\)-bonding from the metal to the ligand \(\pi^*\)-orbital is prominent. The ligand-metal \(\sigma\)-bonding, though weaker than that in the corresponding proton complexes, is assumed to change in the same way as proton-ligand bonding. Substituents which increase the charge density of the nitrogen atom in the pyridine ring are bound to the metal ion. Such substituents will, therefore, have opposite effects on the strength of \(L\rightarrow M\) \(\sigma\)-bonding as well as on the pyridine moiety as a whole results

### Table 1 — Acid Dissociation Constants of Pyridine and Methyl Substituted Pyridines

<table>
<thead>
<tr>
<th>Method</th>
<th>Medium and temp.</th>
<th>(\text{p}K_a)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>H, Ag-AgCl</td>
<td>C(_2)H(_2)OH (20°)</td>
<td>5.17</td>
<td>7</td>
</tr>
<tr>
<td>Glass-electrode</td>
<td>(\mu=0.61(\text{M})) KNO(_3) (25°)</td>
<td>5.44</td>
<td>8</td>
</tr>
<tr>
<td>pH-metric</td>
<td>50% C(_2)H(_2)OH (25°)</td>
<td>4.34</td>
<td>9</td>
</tr>
<tr>
<td>(n=0)</td>
<td>(\mu=0.5(\text{M})) KNO(_3)</td>
<td>4.28</td>
<td>This work</td>
</tr>
<tr>
<td>(\alpha)-Picoline</td>
<td>H, Ag-AgCl</td>
<td>C(_2)H(_2)OH (20°)</td>
<td>5.97</td>
</tr>
<tr>
<td>Glass-electrode</td>
<td>(\mu=0.61(\text{M})) KNO(_3) (25°)</td>
<td>6.21</td>
<td>8</td>
</tr>
<tr>
<td>pH-metric</td>
<td>50% C(_2)H(_2)OH (25°)</td>
<td>4.93</td>
<td>This work</td>
</tr>
<tr>
<td>(\beta)-Picoline</td>
<td>H, Ag-AgCl</td>
<td>C(_2)H(_2)OH (20°)</td>
<td>5.68</td>
</tr>
<tr>
<td>Glass-electrode</td>
<td>(\mu=0.61(\text{M})) KNO(_3) (25°)</td>
<td>5.88</td>
<td>8</td>
</tr>
<tr>
<td>pH-metric</td>
<td>50% C(_2)H(_2)OH (25°)</td>
<td>4.64</td>
<td>This work</td>
</tr>
<tr>
<td>(\gamma)-Picoline</td>
<td>H, Ag-AgCl</td>
<td>C(_2)H(_2)OH (20°)</td>
<td>6.02</td>
</tr>
<tr>
<td>Glass-electrode</td>
<td>(\mu=0.61(\text{M})) KNO(_3) (25°)</td>
<td>6.24</td>
<td>8</td>
</tr>
<tr>
<td>pH-metric</td>
<td>50% C(_2)H(_2)OH (25°)</td>
<td>4.96</td>
<td>This work</td>
</tr>
</tbody>
</table>

![Fig. 1 — Plot of log \(K_1\) versus \(\text{p}K_a\) of the ligands](image)
in a decrease of π-acceptor characteristics of the ligand which precludes the possibility of back-donation. In the case of 2-methyl- and 4-methylpyridines (both having resonance), π-contributions are almost the same and the σ-bonding is greater for 4-methylpyridine; as in case of 2-methylpyridine steric factor may come into play. So the stability constant values for lead (II) complexes with pyridine and methyl-substituted pyridines should follow the order viz. 3-methylpyridine < 2-methylpyridine < 4-methylpyridine < pyridine, same as observed in this investigation.

References


Stability Constants of Mn(II), Fe(II), Co(II), Ni(II), Cu(II) & Zn(II) with 1-(2-Quinolyazo)-2-acenaphthylene & 1-(2-Lepidylazo)-2-acenaphthylene

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Received 8 February 1978; accepted 19 June 1978

Dissociation constants of the two heterocyclic azo dyes, 1-(2-quinolyazo)-2-acenaphthylene and 1-(2-lepidylazo)-2-acenaphthylene, and the stability constants of their complexes with bivalent metal ions have been determined pH-metrically, at 30 ± 1°C in 75% dioxan medium and at different ionic strengths of NaClO4. Thermodynamic stabilization energies (∆H) of the complexes have been calculated using the method of George and McClure.

For the spectrophotometric determination of many metal ions, 1-(2-quinolyazo)-2-acenaphthylene (QAAC) and 1-(2-lepidylazo)-2-acenaphthylene (LAAc) have been used. The present note deals with the determination of dissociation constants of these dyes and formation constants of their complexes with bivalent transition metal ions. The studies have been carried out in 75% dioxan medium at 30 ± 1°C. The formation constants of the metal-QAAC complexes have been studied at different ionic strengths of sodium perchlorate and have been compared with the results obtained at ionic strength μ = 0.2 for metal-LAAc complexes. The thermodynamic stabilization energy (∆H) values have been calculated from log K∞ values according to the method described by George and McClure.

A Beckman, pH-meter (expansomatic, SS-2 model) in conjunction with a glass electrode (0-14 pH range) and calomel electrode assembly, was used for pH-measurements. The pH meter was standardized with potassium hydrogen phthalate and phosphate buffers. The calibration of pH meter reading was corrected in 3:1 dioxan/water by titrating 50 ml of 3:1 dioxan/water at ionic strength (μ) = 0.1 with standard perchloric acid.

QAAC and LAAc were synthesized by methods described earlier. Solutions of these dyes were prepared in freshly distilled dioxan. All the metal ion solutions were prepared by dissolving the corresponding (AR quality) sulphates or nitrates and were standardized by well known methods. Sodium perchlorate (Riedel) was used to keep ionic strength constant. A 0.05 M solution of tetramethylammonium hydroxide (TMAH) (E. Merck, A.G., Darmstadt) in 75% dioxan (aqueous) was used as the titrant and this solution was standardized with a standard solution of oxalic acid. The dioxan used was purified by refluxing with sodium metal for 24 hr and was freshly distilled over sodium before use. All the other chemicals used were of reagent grade.

All the measurements were carried out at 30 ± 1°C. Pre-saturated nitrogen (with 75% dioxan) was used during the course of titrations.

pH-titration procedure the experimental method of Bjerrum and Calvin, as modified by Irving and Rossotti, was used to determine the values of ∆H and pL. The following solutions (set I) were titrated against M/20 TMAH solution in 75% dioxan for determination of stability constants of metal complexes at different ionic strengths.

(i) 1.0 ml HClO4 (0.01M) + 2.0 ml NaClO4 (2.0M) + 1.0 ml KNO3 or K2SO4 (0.01M) + 1.0 ml H2O + 15.0 ml dioxan.

(ii) 1.0 ml HClO4 (0.01M) + 2.0 ml NaClO4 (2.0M) + 1.0 ml KNO3 or K2SO4 (0.01M) + 1.0 ml H2O + 15.0 ml QAAC or LAAc (3.33×10-3M) in dioxan.

(iii) 1.0 ml HClO4 (0.01M) + 2.0 ml NaClO4 (2.0M) + 0.01 ml metal nitrate or sulphate (0.01M) + 1.0 ml H2O + 15 ml QAAC (3.33×10-3M) in dioxan.

In other sets, II, III and IV (studied only with QAAC) required amount of NaClO4 was added to maintain ionic strength at 0.01 and 0.005 M. In all the cases, corrections for change in volume on mixing dioxan and aqueous solution (total volume = 19.67 ml due to contraction on mixing dioxan and water) as well as changes in volume which take place during the course of titrations, were made.

From the titration curves of acid alone and those obtained in the presence of ligand at a particular constant ionic strength, ∆H values of the ligand (QAAC or LAAc) at various pH values were calculated and the pKOH and pKn values of the ligands were found by plotting log [qH(-1)]/(2-qH) versus pH and log [qH/(1-qH)] versus pH respectively.