Complexes of Silver(I) with Pyrazole, a Potentiometric Study

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The complex formation of silver(I) with pyrazole has been studied potentiometrically. The shift in potential values of a series of 20% ethanolic solutions of AgNO₃ in the absence as well as in the presence of varying amounts of the ligand and at µ = 0·1M (KNO₃) shows the formation of two complex species, Ag(Pz)⁺ and Ag(Pz)²⁺. log β₁ and log β₂ values of the complexes at 25°, 30° and 35°C are 2·04, 4·45; 1·90, 4·30; and 1·79, 4·23 respectively. Different thermodynamic functions have also been determined.

A n early observation of Schmidt¹ revealed that pyrazole produces colourations with certain transition metal ions. The first quantitative information regarding the complexation of pyrazole with Cd²⁺ was given by Andrews and Romary² and later by Crow³ using the polarographic methods. Crow and Westwood⁴ subsequently reported the polarographic results of their study on the complex formation of pyrazole with some other transition metal ions. Though pyrazole is a weakly base, the behaviour of these metal ions, in the presence and the absence of ligand as outlined in the above studies strongly supports the complexation of ligand with the metal ions. A survey of literature does not reveal any report on the study of silver-pyrazole complexes. Thus, it was thought of interest to study the behaviour of silver ions in the presence of pyrazole as the ligand potentiometrically with a view to making quantitative assessment of the composition and the stability constants of the complexes formed.

Materials and Methods
Pyrazole (Koch Light, London) was purified by repeated crystallization from absolute ethanol. Silver nitrate solution used was standardized against standard KCl. AR grade KNO₃ was used. All the solutions were prepared in doubly distilled air-free conductivity water. A solution of KNO₃ (1·0M) was used to maintain the ionic strength of the solutions. All the solutions used in potentiometric measurements, contained in addition to pyrazole, 0·5 M silver ions and 0·1M KNO₃ in 20% ethanol. The [pyrazole] was varied from 0·01 to 0·1M. Silver nitrate solution was standardized against standard KCl. AR grade KNO₃ was used. All the solutions were prepared in doubly distilled air-free conductivity water. A solution of KNO₃ (1·0M) was used to maintain the ionic strength of the solutions. All the solutions used in potentiometric measurements, contained in addition to pyrazole, 0·5 mM silver ions and 0·1M KNO₃ in 20% ethanol. The [pyrazole] was varied from 0·01 to 0·1M. The silver electrode used was cleaned with dil. HNO₃ and thoroughly washed with water. The cells of the types A and B were set up.

Cell 1— SCE 1 0·5 mM AgNO₃ in 20% ethanol |Ag⁺

Cell 2— SCE 0·5 mM AgNO₃ + x ml 0·5M pyrazole in |Ag⁺

E.m.f. measurements were made on a Leeds & Northrup type K₃ universal potentiometer bridge reading up to 0·5 mV. SCE connected through KNO₃-agar bridge was used as the reference electrode. Potentiometric studies were carried out at 25° ± 0·1°, 30° ± 0·1° and 35° ± 0·1° after the solutions had attained these temperatures. Each of the e.m.f. values was taken twice and the same was not recorded until the repeated value differed by not more than ±0·5 mV.

Method of calculation— The compositions and the stability constants of silver-pyrazole complexes have been determined using Leden's method⁶. The e.m.f. of the cell of the type A in the absence of ligand is given by Eq. (1).

E₁ = E' + RT \frac{\ln C_M}{nF} ...

where C_M is the [metal ion] and E' includes the potential of the calomel electrode, the liquid junction potential and the correction term for activity coefficients in mixed solvents.

In the presence of the ligand the e.m.f. of the cell of the type B is given by Eq. (2).

E₂ = E' + RT \frac{\ln [M]}{nF} ...

where [M] is the free [metal ion] left after the complex formation. Hence, the change in potential (ΔE) is given by Eq. (3).

ΔE = E₁ - E₂ = \frac{RT}{nF} \ln \frac{C_M}{[M]} ...

The ratio C_M/[M] is the inverse of the degree of formation so that

C_{M/[M]} = \text{antilog} \left( \frac{nF}{2·035 RT} \Delta E \right) \frac{1}{[M]}

Now a series of F₀[X] functions dependent on [free ligand] were derived from the shift of potentials (Eq. 4) of the metal ions over a wide range of ligand concentration, [X].

Antilog \left( \frac{nF}{2·035 RT} \Delta E \right) = F₀[X] = β₀ + β₁[X] + β₂[X]² + ... + βₙ[X]ⁿ ...

The initial term β₀ is the stability constant of the zero complex which by definition has the value unity, and βᵢ terms refer to the consecutive overall stability constant of the jth complex. The values

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of $\beta_j$ were determined by graphical extrapolation procedure of Leden using Eq. (5).

$$F_j(X) = \frac{F_{j-1}(X) - \beta_{j-1}}{\beta_j}/(X) \quad ... (5)$$

A series of $F_j[X]$ values corresponding to $F_i[X]$ values were obtained and plots of $F_j[X]$ vs $[X]$ (where $j = 1, 2, \text{etc.}$) were prepared until the final function $F_n[X]$ independent of $[X]$, i.e. $F_n[X] = \beta_n$, was obtained. The values of $\beta_j$ were the $F_j[X]$ values obtained from the graphs at $[X] = 0$. Different thermodynamic functions, viz. $\Delta F$, $\Delta H$, and $\Delta S$, on complex formation were determined at 30°C.

$$\Delta F = -RT \ln \beta \quad ... (6)$$

relating the stability constant ($\beta$) to the free energy change of the reaction was employed for evaluating $\Delta F$.

The value of $\Delta H$ was determined with the help of an isobar, Eq. (7).

$$\frac{d\ln \beta}{dT} = \frac{\Delta H}{RT^2}$$

or

$$\frac{d \log \beta}{d(1/T)} = \frac{\Delta H}{4.57} \quad ... (7)$$

The values of $\log \beta$ obtained at different temperatures were plotted as a function of $(1/T)$. The gradient of this plot at the point corresponding to 30°C was equated with $-\Delta H/4.57$. The entropy change ($\Delta S$) of the reaction was calculated from Eq. (8).

$$\Delta S = (\Delta H - \Delta F)/T \quad ... (8)$$

**Results and Discussion.**

The shift in potentials ($\Delta E$, Table 1) of the cells containing metal ions on increasing [pyrazole] strongly favours the complex formation. As the complexes formed are weak, the [free ligand] was justifiably assumed to be approximately equal to the total [ligand]. Fig. 1 shows the plots of $F_i[X]$ and $F_0[X]$ vs $[X]$. Extrapolation of these curves at $[X] = 0$ gives the values for $\beta_1$ and $\beta_2$. Plots of $F_n[X]$ were found to be horizontal linear curves indicating that two complexes are formed with silver and pyrazole.

For 1:1 and 1:2 (metal-ligand) complexes of silver(I)-pyrazole, the values of $\Delta F$, $\Delta H$ and $\Delta S$ at 30°C were found to be 2.64 and 5.96 kcal mole$^{-1}$, 10.85 and 9.03 kcal mole$^{-1}$, and 27.10 and 10.13 cal deg$^{-1}$ mole$^{-1}$ respectively. The values of $\log \beta$ for 1:1 and 1:2 complexes were 2.04, 1.90, 1.79 and 4.45, 4.30, 4.23 respectively at 25°, 30° and 35°C.

**Table 1 — Effect of Varying [Pyrazole] on the Shift in Potentials ($\Delta E$) at Different Temperatures**

<table>
<thead>
<tr>
<th>Pyrazole ml</th>
<th>Ethanol ml</th>
<th>e.m.f. (V) at 25°C</th>
<th>e.m.f. (V) at 30°C</th>
<th>e.m.f. (V) at 35°C</th>
<th>$\Delta E$ (V) at 25°C</th>
<th>$\Delta E$ (V) at 30°C</th>
<th>$\Delta E$ (V) at 35°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-0</td>
<td>10-0</td>
<td>0.35675</td>
<td>0.35410</td>
<td>0.34905</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
</tr>
<tr>
<td>1-0</td>
<td>9-0</td>
<td>0.31725</td>
<td>0.31715</td>
<td>0.31505</td>
<td>0.03950</td>
<td>0.03695</td>
<td>0.03400</td>
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<tr>
<td>2-0</td>
<td>8-0</td>
<td>0.28960</td>
<td>0.29205</td>
<td>0.28955</td>
<td>0.06715</td>
<td>0.06205</td>
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</tr>
<tr>
<td>3-0</td>
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<td>0.27135</td>
<td>0.27400</td>
<td>0.27205</td>
<td>0.08540</td>
<td>0.08010</td>
<td>0.07700</td>
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<tr>
<td>4-0</td>
<td>6-0</td>
<td>0.25755</td>
<td>0.26120</td>
<td>0.25860</td>
<td>0.09920</td>
<td>0.09290</td>
<td>0.09045</td>
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<tr>
<td>5-0</td>
<td>5-0</td>
<td>0.24610</td>
<td>0.25045</td>
<td>0.24820</td>
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<td>0.23915</td>
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<tr>
<td>7-0</td>
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<td>0.12880</td>
<td>0.12100</td>
<td>0.11835</td>
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<tr>
<td>8-0</td>
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<td>0.22840</td>
<td>0.22530</td>
<td>0.14225</td>
<td>0.13570</td>
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</tr>
<tr>
<td>9-0</td>
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<td>0.14365</td>
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<tr>
<td>10-0</td>
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<td>0.21120</td>
<td>0.21535</td>
<td>0.21240</td>
<td>0.14555</td>
<td>0.13875</td>
<td>0.13665</td>
</tr>
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</table>
Since most stable silver complexes have linear structures and the present work provides two stability constants, we may correlate our observation assuming the formation of two complexes of the types Ag(Pz)$^+$ and Ag(Pz)$^-$ in solution. The stability constants for both the species decrease with the increase in temperature, suggesting that the degree of dissociation of the complexes formed in solution increases with the rise in temperature.

In view of the weakly basic nature of the pyrazole ($pK = 2.53$), strong complexes are not expected. It is possible, however, that during complexation with Ag$^+$ ion, metal-ligand $\pi$-bonding may occur to some extent as has been pointed out by Crow and Westwood. They reported that strong complexations are not expected of pyrazole with most of the transition metal ions. But with metals having a high proportion of filled $d$-shells it is possible for metal-ligand $\pi$-bonding to occur.

Acknowledgement

Our thanks are due to Shri D. Ghosh for assistance during this work.

References

Mixed Ligand Chelate of Mn(IV) with Triethylenetetramine & Acetylacetone

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A heterochelate of manganese(IV) containing triethylenetetramine co-ligated with acetylacetone is described. A probable structure (I) of the complex is suggested from the results of elemental analyses, electrical conductance, magnetic moment, molecular weight and visible and IR spectral data.

Well-characterized manganese(IV) complexes are relatively rare. The most important of them are the halogeno1, cyano2, iodato3, and oxalato4 complexes. Ray and Ray5 reported a series of Mn(IV) complexes with biguanide and ethylenedibiguanide. Nyholm and Turco6 reported the preparation of a binuclear dipyridyl complex containing manganese in two different oxidation states, viz. III and IV, and Poddar7 of a Mn(IV) chelate of piperazinedibiguanide.

The present paper reports a mixed ligand chelate of Mn(IV) with triethylenetetramine and acetylacetone. The characterization of the mixed ligand chelate has been made on the basis of magnetic, conductance, mol. wt and visible and IR data.

The reaction of Mn(III) acetylacetonate with triethylenetetramine in dry ethanol medium resulted in the formation of the mixed ligand chelate, triethylenetetramineacetylacetonatominanganese (IV) perchlorate, (Mn(trien)(acac)]ClO4, I, where trien is one molecule of triethylenetetramine and acac = acetylacetone.

This is an example where partial ligand exchange is accompanied by the oxidation of the central metal ion. The oxidation may be aerial, since the reaction does not involve the use of any oxidizing agent. It is relatively easier to oxidize [Mn(III)] to Mn(IV) than to Mn(II)]. However, we believe that it is a case of disproportionation [2Mn(III) → Mn(II) + Mn(IV)]. The brown product which was obtained as an initial precipitate during the isolation of the Mn(IV) chelate (vide experimental) is probably a Mn(II) compound which, however, could not be isolated in the pure state.

The mixed ligand chelate is a dark purple, almost black, crystalline solid fairly soluble in water but very sparingly soluble in ethanol and methanol. The compound is surprisingly stable towards hydrolysis unlike other Mn(IV) compounds. A deep violet aqueous solution is stable for a few hours after which hydrated Mn(II) oxide separates out. A molar conductance value of 130 mhos cm⁻¹ for a 10⁻²Μ aq. solution is indicative of an uni-univalent balance calibrated with CuSO₄·5H₂O. Diamagnetic corrections are according to Selwood6. The IR spectra were recorded in nujol on a Perkin-Elmer model 21 IR spectrophotometer. Visible and near UV spectrum of aq. solution was recorded on a Hilger Uvispek spectrophotometer.
electrolytic nature of the complex. Cryoscopic measurements in aq. solution gave a mol. wt value of 410 which is in fair agreement with the monomeric formula.

The oxidation state of manganese in the complex has been determined iodometrically by reacting the compound with acidified potassium iodide and estimating the liberated iodine with standard thiosulphate solution. In a typical titration 0·01063 g of the chelate consumed 1·15 ml of a 0·0488N thiosulphate (theoretically expected value 1·1 ml). The method gave a value of ~4 for the oxidation state of the metal ion and is in accordance with the formulation (I). IR spectrum of the chelate shows two bands at 3287 and 1587 cm\(^{-1}\) due to the stretching and deformation of NH\(_2\) groups\(^{10,11}\). This indicates that deprotonation presumably occurred at the imine nitrogens rather than at the amine nitrogens. Absence of any strong absorption around 1650 cm\(^{-1}\) is indicative of the absence of Schiff base type of linkages in the complex\(^{10,12}\).

The effective magnetic moment of the complex at 29°C has been found to be 2·71 BM which is considerably lower than the expected spin-only value of 3·87 BM corresponding to three unpaired electrons (\(\Delta E\)). A similar observation was made by Ray and Ray who obtained much lower values of magnetic moments (2·05-2·49 BM) for a series of Mn(IV) biguanide complexes\(^*\). MnO\(_2\) is known\(^{18}\) to have a quartet cubic level 4T\(_{2g}\) splits into two tetragonal components 4B\(_2\) and 4E. The present complex, owing to cis-geometry of the acetylacetonate ligand, belongs to the C\(_{2v}\) point group and the two strong bands at 21180 and 19230 cm\(^{-1}\) may be assigned to 4B\(_2\)->4B\(_2\) and 4B\(_2\)->4E transitions respectively, giving the \(D_J\) value as 2118 cm\(^{-1}\). The corresponding values for [Mn(H\(_2\))\(_2\)]\(^+\) (ref. 18) and [Mn(BigH\(_2\))(OH)]\(^+\) (ref. 16) are 2175 and 1592 cm\(^{-1}\) respectively. The higher energy shoulder at 26300 cm\(^{-1}\) is due to charge transfer in the metal-p-diketone system\(^{18}\), which probably obscures the close-by second ligand field band in the higher energy region.

References
Reactions of Cu(II), Ni(II), Pd(II), Co(III) & Cr(III) with Some Heterocyclic Biguanides

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A LARGE number of aliphatic and aromatic biguanides have been synthesized and their metal chelates studied. However, except some metal chelates of piperazine biguanide, no such compounds of other heterocyclic biguanides are described in literature. The present investigation was undertaken to study the chelating behaviour of morpholine- and piperidine-biguanides towards Cu(II), Ni(II), Pd(II), Cr(III) and Co(III), in order to ascertain the influence of the heterocyclic moieties on the basicity and complex-forming capability of the biguanide molecule as well as on metallic chelates they form. The pH titration technique and an application of Bjerrum's method was resorted to for the determination of stability constants of the complexes.

Usually biguanides and substituted biguanides behave as ampholytes. Depending on the pH they behave as monocydic and diacydic bases. The diprotonated biguanidium ion \( LH^+ \) (where \( LH \) stands for morpholine and piperidine biguanides) are formed at high acid concentrations. The acid dissociation constants \( \Delta K_1 \) and \( \Delta K_2 \) of the heterocyclic biguanide bases have been determined at 25° and 35° and \( \mu = 0-5 M \) (KCl) and the data have been employed in calculating the values of the stability constants of the metallic complexes. From the \( \Delta K \) values, it was possible to work out a correlation between the basicity of the ligands and the stability of the metal chelates. In addition solid complexes have also been isolated and their magnetic moments determined (Table I).

Materials and Methods

Preparation of the biguanides — Morpholine and piperidine biguanide hydrochlorides, melting points 189-90° and 206-7° respectively, were obtained by fusing an intimate mixture of equimolar proportions of hydrochlorides of morpholine and piperidine with dicyandiamide at 165°.

Copper(II) monobiguanide complexes — The Cu(II) monobiguanide chlorides have been isolated by mixing the alcoholic solutions of CuCl₂ and the corresponding biguanide hydrochloride in 1:1 molar ratio and adjusting the pH of the mixture to 5-5 to 4-0 with dil. HCl.

Bis-biguanide complexes — Cu(II), Ni(II) and Pd(II) bis-biguanide hydroxides were prepared by mixing aqueous solutions of the metal chloride and biguanide hydrochloride in 1:2 molar ratio and adjusting the pH to 8-0-10-0 with dil. KOH solution; however, at pH 6-9-7-0 (NH₄OH), the corresponding chlorides were formed. The chloride salts could also be obtained by digesting the complex hydroxides with concentrated aqueous solution of ammonium chloride and concentrating the resulting solutions on a water-bath.

Cu(II) and Ni(II) bis-morpholine biguanide hydroxides dissolve completely in excess caustic alkali (pH > 10-5) forming clear solutions. On standing overnight in a desiccator over fused CaCl₂ and KOH, well-defined beautiful crystals of the corresponding anhydrobases separated out. The complex anhydrobases of piperidine biguanide precipitated out immediately on adding metal chlorides in strongly alkaline solution of the biguanide.

When an ammoniacal solution of NiCl₂ was added to the solution of morpholine biguanide in the presence of excess caustic potash, another yellow crystalline double compound, \([\text{Ni(morph. Big)}]_2\cdot \text{Ni(OH)}_2\cdot \text{H₂O}\) was obtained.

Tris-biguanide complexes — Complex Cr(III) hydroxide of morpholine biguanide was obtained by warming a mixture of aqueous solution of chromium and strongly alkaline solution of the biguanide hydrochloride in 1:3 molar ratio. Complex Co(III) hydroxide, however, was obtained on passing a current of air for several hours through a strongly alkaline mixture of cobalt(II) chloride and the ligand in 1:3 ratio. The complex chlorides were then prepared by digesting the complex chloride with NH₄Cl. With piperidine biguanide two anhydrobases only of Cr(III) and Co(III) were obtained.
Attempts for the preparation of complex chlorides and complex hydroxides of Cr(III) and Co(III) with piperidine biguanide and complex anhydrobases of Pd(II), Cr(III) and Co(III) with morpholine biguanide were unsuccessful.

Physical data — The elemental analyses were done by conventional chemical methods. The percentage of water was calculated from the loss in weight on heating the sample up to 130°C. Magnetic susceptibilities were measured in a Gouy balance using Hg[Co(SCN)₄] as calibrant.
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The study of the metal chelates of the present two ligands was of special interest due to the fact that they are similar in structure except that the 

The usual methods for the preparation of the biguanide-metal hydroxides and chlorides failed with piperidine biguanide. The product in each case was the complex anhydrobase. Even the product obtained by refluxing CuCl₃, piperidine HCl and dicyandiamide was also the complex anhydrobase of the metal ion. The complex metal chlorides and hydroxides of the piperidine biguanide reported in the present study were therefore, prepared by strict control of the pH of the systems concerned. For Cu(II) and Ni(II) complexes, the idea of the optimum pH for formation of complex hydroxides or chlorides was obtained directly from the formation curves. In the case of Pd(II) complexes, the pH value was adjusted by the method of trial and error.

One more peculiar aspect is that the Cu(II) mono-biguanide chloride salts reported here are the first examples of these type of complexes which have been prepared directly. The other Cu(II) mono-biguanide complexes reported earlier were prepared by restricting the decomposition of the copper bis-biguanide complexes up to the mono complex stage.

Proton-ligand stability constants (pfK values)—The titration data are in support of the formation of the diprotonated species LH₂⁺ at high acid concentration while LH³⁺ predominate at low acid concentration. The pfK values of the ligands were determined using Bjerrum's method. The value of α, i.e. the average number of protons attached per ligand ion at various pH values has been calculated from the ligand titration curve. The formation curves of the proton-ligand system have been found to be between 0 and 2 in α scale denoting that two dissociations are possible. The pfK values were directly read from the curves and are given in Table 2.

Metal-ligand stability constants (log K values)—Bjerrum's method has also been applied to calculate the metal-ligand stability constants from potentiometric titration data. Formation curves are shown in Fig. 1 and the values of log K are given in Table 3.

Since formation of Ni(II) bis-biguanide complex is a single step process, the average decomposition constant (k̂av) of the complexes has been calculated from the relation,

$$ k_{av} = [LH] $$ at $\bar{n} = 1$
**Table 2**—Acid Dissociation Constants of the Ligands

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Temp. °C</th>
<th>( pK_1 )</th>
<th>( pK_2 )</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Morpholine</td>
<td>25</td>
<td>8-70</td>
<td>2-70</td>
<td>4</td>
</tr>
<tr>
<td>Morpholine</td>
<td>25</td>
<td>11-95</td>
<td>1-95</td>
<td></td>
</tr>
<tr>
<td>biguanide</td>
<td>35</td>
<td>11-40</td>
<td>1-40</td>
<td>Present investigation</td>
</tr>
<tr>
<td>Piperidine</td>
<td>35</td>
<td>11-42</td>
<td>1-42</td>
<td>5</td>
</tr>
<tr>
<td>biguanide</td>
<td>35</td>
<td>11-60</td>
<td>1-60</td>
<td></td>
</tr>
</tbody>
</table>

**Table 3**—Stability Constants of Metal Chelates of the Biguanides

\[ \log K_x \] \( \log K_2 \) \( \log K_3 \) \( \log \beta \) 

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
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</thead>
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<td>6-60</td>
<td>14-99</td>
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</tr>
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</table>

As biguanides generally behave as monoacidic bases, their basic strengths are compared in terms of their first acid dissociation constant. Table 4 gives the \( pK_1 \) values of the present ligands and some related compounds along with the log \( \beta \) values of their metal chelates at 35°C. It is evident from Table 2 that the tendency of the ligands to accept the second proton is about \( 10^{-7} \) to \( 10^{-8} \) times that of the first.

Introduction of the heterocyclic ring no doubt increased the basicity of the biguanide molecules under study (Tables 2 and 4) in the same expected order as the corresponding heterocyclic amines but to a lesser degree. The greater basicity of pipéridine biguanide over morpholine biguanide is also reflected in the greater values of metal-ligand stability constants (log \( \beta \)) of this ligand than those of the other (Table 3).

The decrease in \( pK \) values as well as the log \( K \) values with increase in temperature may be due to the fact that higher the temperature, greater is the dissociation. The values of \( K_1 > K_2 > K_3 \) and this is due to steric effects.

**References**