SECTION III:

STUDIES IN COPPER(II) CHELATES. 5-NITRO-O-PHENANTHROLINE MONO(SIGANIDE) COPPER(II) COMPLEXES.
ABSTRACT: SEVERAL mixed chelate complexes of copper(II) with 5-nitro-o-phenanthroline and biguanide, $N^1$-methylbiguanide or $N^1$-ethylbiguanide have been synthesised and characterised as $\text{[Cu(nitrophen)(BigH)]}_2X_2$ (where nitrophen = 5-nitro-o-phenanthroline, BigH = biguanide or substituted biguanide and $X = \text{chloride and bromide}$). The complexes are deep sky-blue in colour and behave as bi-univalent electrolytes in water. The magnetic moments ($\sim 1.80$ B.M.) and a single, somewhat broad and asymmetric absorption band around 15,400-16,700 cm$^{-1}$ (in water) have been interpreted as arising out of distorted octahedral structures of the complexes.

Spectral studies on the interaction of the bis(biguanide) copper(II) complexes with 5-nitro-o-phenanthroline reveal a 1:1 mixed chelate formation. The formation constants of several such mixed chelates have been evaluated and are of the order of $10^{2}$-10^{3}.

This study arose out of our desire to extend the synthesis of mixed chelate of copper(II) with o-phenanthroline and alkyl substituted biguanides. Whereas syntheses of complexes of the type $\alpha,\alpha'$-dipyridyl mono(methyl-ethylbiguanide) copper(II)$^1$ could be achieved, the same methods failed to provide the corresponding o-phenanthroline complexes as a pure crystalline state. This, we conjectured was due to the very small pH range where the mono(alkylbiguanide) copper(II) --- bis(alkylbiguanide) copper(II) equilibrium existed and also due to the high stability of the mono(o-phenanthroline) copper(II) complex compared to that of the mixed chelate. The situation was further aggravated by the lesser solubility of the mono(o-phenanthroline) copper(II) complex compound to the corresponding $\alpha,\alpha'$-dipyridyl compound.

We therefore looked for some other o-phenanthroline derivative where the sought-for syntheses might not be vitiated. It was finally possible to prepare
a series of mixed chelates of copper(II) with 5-nitro-o-phenanthroline on
the one hand and biguanide, \textit{N}^1\textit{N}-methylbiguanide or \textit{N}^1\textit{N}-ethylbiguanide on the other. The most important factor governing the syntheses of the mixed chelates was the pH of the solution containing the biguanide copper(II) system. We had to use a two moles proportion of the biguanide or substituted biguanide in order to keep the \textit{Cu}^{2+} in solution as the bis-complex and then the nitro-o-phenanthroline was added at around pH 6-7.

It is pertinent to mention here that even on setting the same conditions as we did for the 5-nitro-derivative, we failed to isolate any mixed copper(II) chelate with unsubstituted \textit{o}-phenanthroline and \textit{N}^1\textit{N}-methylbiguanide or \textit{N}^1\textit{N}-ethylbiguanide. The chloride and bromide salts have been obtained pure and the colours are deep to light sky-blue. All attempts to obtain the iodide salt in a pure state failed. All the complexes show usual molar conductance for bi-univalent electrolytes in water (200-250 mhos cm$^2$ mole$^{-1}$) (cf. Table-I).

Attempts to synthesise other salts of the mixed chelate cations led to the same results we had in the \textit{o}-phenanthroline or the \textit{\alpha,\alpha^{'}-dipyrilid}
series reported earlier in Section II. Addition of thiocyanate, (or aside/nitrite) to an aqueous solution of the complex chloride provided merely the precipitates of the highly insoluble diisothiocyanato/dinitro/diamidomono(5-nitro-o-phenanthroline) copper(II) complexes. These results pointed to a some slight dissociation in aqueous solution of the mixed chelates, such that on the addition of any of the above three ions, the insoluble 5-nitro-o-phenanthroline complexes result.

The aqueous solution absorption spectra reveal for all the complexes a somewhat broad and asymmetric peak. The frequency of absorption (15,400 cm$^{-1}$-16,700 cm$^{-1}$) is quite comparable to the biguanide-o-phenanthroline system
Table I

Conductance Measurements in Aqueous Solution and Magnetic Moment Values

<table>
<thead>
<tr>
<th>Complex</th>
<th>( \Lambda_M ) at ( ^\circ C )</th>
<th>Dia. Corr. ( \times 10^6 )</th>
<th>( \chi_M(\text{corr.}) ) ( \times 10^6 )</th>
<th>( \mu_{\text{eff.}} ) at ( ^\circ \text{abs.} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Cu(nitrophen)(BigH)} \text{Cl}_2 \cdot 0.5\text{H}_2\text{O} )</td>
<td>229.7 ( (24^\circ \text{C})^* )</td>
<td>212</td>
<td>1428</td>
<td>1.85 B.M. ( (297^\circ \text{abs.})^* )</td>
</tr>
<tr>
<td>( \text{Cu(nitrophen)(MeBigH)} \text{Cl}_2 \cdot 0.5\text{H}_2\text{O} )</td>
<td>202.7 ( (23^\circ \text{C}) )</td>
<td>230</td>
<td>1349</td>
<td>1.82 ( (307^\circ \text{abs.}) )</td>
</tr>
<tr>
<td>( \text{Cu(nitrophen)(EtBigH)} \text{Cl}_2 \cdot \text{H}_2\text{O} )</td>
<td>216.0 ( (23.5^\circ \text{C}) )</td>
<td>249</td>
<td>1363</td>
<td>1.85 ( (305^\circ \text{abs.}) )</td>
</tr>
</tbody>
</table>

\( \Lambda_M \) (Molar Conductance) = 2 \times \text{mean} \( \lambda_{\alpha} \), where \( \lambda_{\alpha} = \lambda_{\gamma} (1+0.692 \times n_1 \times n_2 \times v^{-1}) \) and \( n_1 \) and \( n_2 \) are the valencies of the ions.

\( \mu_{\text{eff.}} = 2.84 (\chi_M(\text{corr.}) \times T)^{\frac{1}{2}} \) B.M., where \( T \) = absolute temp.

*Figures in parentheses indicate temps. \( ^\circ \text{C} \) or absolute) at which measurements were made.

BigH = Biguanide, MeBigH = Methylbiguanide, EtBigH = Ethylbiguanide, nitrophen = 5-nitro-o-phenanthroline.
(15,600-17,000 cm\(^{-1}\)) and in keeping with our conclusions given in Section II, we believe the present complexes are also distorted octahedral\(^1,2,5\). A comparison of the spectra of the mixed chelates with that of the square planar bis(biguanide) copper(II) complex (~19,000 cm\(^{-1}\)) shows a significant shift of the absorption band to lower frequency. This is generally taken as an indication of stereochemical change from a four co-ordinated square planar state to a distorted octahedral structure\(^4,5\).

The mixed chelates were found to be soluble in several solvents namely water, ethyleneglycol and dimethylsulfoxide (DMSO). The absorption spectra run in these solvents of varying donor abilities reveal some variation in the frequency of absorption. This solvent dependence of the spectra only lend support to the proposed distorted octahedral structure of the chelates (cf. Table-II and Fig.-I)\(^2\). Further a prominent shoulder also appears in the DMSO spectra indicating further splitting of the original absorption band in aqueous solution.

The magnetic moments of these products are in the range ~1.80 B.M. However, this is to be appreciated that magnetic evidence over room temperature cannot be used readily to indicate the stereochemistry of copper(II) compounds\(^6,7\). Thus most copper(II) compounds have moments in the range 1.7-2.1 B.M. The "tetrahedral range" is expected ~ 2.0-2.2 B.M. and planar complexes are predicted to be having the spin moment of 1.75 B.M.

Besides the above synthetic studies extensive spectrophotometric measurements in aqueous solution have been undertaken and completed on the different mixed chelate systems. These studies have confirmed the formation of 1:1 biguanide/substituted biguanide : 5-nitro-o-phenanthroline complexes
Fig. Absorption spectra of 5-nitro-2-phenanthroline (L)-biguanide mixed chelates in different solvents at 0.004M concentration.

1. [Cu(L)(EtBigH)]Cl₂·H₂O, in aqueous medium; 2. [Cu(L)(MeBigH)]Cl₂·0.5H₂O in aqueous medium; 3. [Cu(L)(BigH)]Cl₂·0.5H₂O in aqueous medium; 4. [Cu(L)(MeBigH)]Cl₂·0.5H₂O in DMSO; 5. [Cu(L)(MeBigH)]Cl₂·0.5H₂O in ethylene glycol; 6. [Cu(L)(EtBigH)]Cl₂·H₂O in DMSO; 7. [Cu(BigH)]Cl₂·2H₂O, in aqueous medium.
Table-II

Absorption Spectral Data of the Mixed Chelates

<table>
<thead>
<tr>
<th>Complex</th>
<th>State</th>
<th>Colour</th>
<th>Absorption Spectral Band (cm⁻¹)</th>
<th>ε&lt;sub&gt;max&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Cu(BigH)₂Cl₂</td>
<td>Aq.Soln.</td>
<td>Rose-red</td>
<td>19.230-18.670</td>
<td>41.25&lt;sup&gt;**&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>Ethyleneglycol</td>
<td>Light green</td>
<td>14.290-13.330</td>
<td>69.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Deep sky-blue</td>
<td>16.130-14.930</td>
<td>62.00</td>
</tr>
<tr>
<td></td>
<td>Ethyleneglycol</td>
<td>Yellowish green (i)</td>
<td>13.830-13.160</td>
<td>65.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Light sky-blue</td>
<td>20.830-20.410(sh)</td>
<td>45.50</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>14.930-14.080</td>
<td>65.00</td>
</tr>
<tr>
<td></td>
<td>Ethyleneglycol</td>
<td>Yellowish green (i)</td>
<td>13.830-13.160</td>
<td>63.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Light sky-blue</td>
<td>20.410-20.000(sh)</td>
<td>45.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>14.930-14.080</td>
<td>63.00</td>
</tr>
<tr>
<td>5. Cu(L)(BigH)Cl₂</td>
<td>Cu(BigH)₂Cl₂ in aq.soln. and nitrophen in 1:1 ratio at pH 7 in aq.alc.soln.</td>
<td>Deep sky-blue</td>
<td>16.670-15.380</td>
<td>62.50&lt;sup&gt;*&lt;/sup&gt;</td>
</tr>
<tr>
<td>7. Cu(L)(EtBigH)Cl₂</td>
<td>Cu(EtBigH)₂Cl₂ in aq. soln. and nitrophen in 1:1 ratio at pH 7 in aq.alc.soln.</td>
<td>Deep sky-blue</td>
<td>16.670-15.620</td>
<td>67.50</td>
</tr>
</tbody>
</table>

<sup>*</sup>Some variations in molar extinction co-efficients of the complexes are inevitably observed in changing the solvent from 100% water to 1:1 aqueous-alcohol.

<sup>**</sup>Extinction co-efficient value reported by Ray and Ray<sup>12</sup> is 58.50 (at 19.230 cm⁻¹).

Sh = Shoulder, DMSO = Dimethylsulfoxide, L = 5-nitro-o-phenanthroline.
in solution (cf. Figs. -II and III). The optimum pH range of formation and stability of the complexes has also been determined and finally the formation constants evaluated following the same technique and assumptions as in Section II. The formation constant values are of the order of $10^8-10^9$ (cf. Table-III) and compare favourably with the values obtained for the biguanide-$\kappa^1,\kappa^2$-dipyridyl system and the biguanide-$\kappa^1$-phenanthroline system. During all the solution studies no attempt was made to maintain ionic strength constant by the addition of an electrolyte such as KCl or KNO$_3$ etc. in view of our apprehensions expressed earlier in Section II.

**EXPERIMENTAL**

Biguanide acid sulfate and substituted (methyl- and ethyl-)biguanide acid sulfate were synthesised by following published procedures$^8,9$ and were recrystallised from hot water. Copper(II) chloride dihydrate was B.D.H.L.R. sample.

(1) 5-Nitro-$\kappa^1$-phenanthroline-Biguanide Copper(II) Chloride:

Biguanide acid sulfate (0.9 g) was dissolved in hot water (10 ml.) and was treated with an aqueous solution of barium chloride (1.2 g in 5 ml.). The mixture was digested on a steam bath for 50 mins, and was filtered. The filtrate was then treated with an aqueous solution of CuCl$_2$ (0.54 g in 2 ml.). The pH of the solution was raised to 7 by dil. (2N)$\text{NH}_4\text{OH}$ when a red-violet solution formed. This was then treated with an alcoholic solution of 5-nitro-$\kappa^1$-phenanthroline (0.25 g in ~5 ml.) with constant stirring to give a sky-blue solution. Immediately bright sky-blue crystals separated out.
TABLE XIII (mM)

EFFECT OF pH ON THE ABSORPTION SPECTRA OF THE SYSTEM:

\[ \text{Fe}^{2+} + \text{OX} \rightarrow \text{Fe}^{3+} + \text{OX}^{-} \]

\( \lambda \text{(mm)} \)

1. At pH 3;
2. At pH 6;
3. At pH 7;
4. At pH 9;
5. At pH 10.
Figure 1: Solution composition study on the mixed chelate formation.

Conditions: \( \text{La}(\text{II})_2 \text{Cl}_2 \cdot 2\text{H}_2\text{O}, 0.004M \) and 5-nitro-8-phenanthroline, 0.004M at pH 7.

- 1: 520 \( \mu \)
- 2: 750 \( \mu \)
- 3: 520 \( \mu \)
### Table-III

**Formation Constant Values of the Heterochelate Complexes**

Initial concn. of bis(biguanide or subst. biguanide) complex = 0.004 M.  
Initial concn. of 5-nitro-o-phenanthroline (nitrophene) = 0.004 M.  
Wavelength of measurements = 620 mµ.

Initial concn. of nitrophene = 0.004 M.

\[
\begin{align*}
\epsilon_{\text{Cu(nitrophene)(BigH)Cl}_2} &= 62.50 \\
\epsilon_{\text{Cu(nitrophene)(MeBigH)Cl}_2} &= 58.75 \\
\epsilon_{\text{Cu(nitrophene)}^{2+}} &= 11.50
\end{align*}
\]

<table>
<thead>
<tr>
<th>System</th>
<th>( \left[ \text{Cu(BigH)} \right] \times 10^{-3} )</th>
<th>( \left[ \text{Cu(nitrophene)} \right] \times 10^{-3} )</th>
<th>( \left[ \text{Mixed complex} \right] \times 10^{-3} )</th>
<th>( \left[ \text{BigH} \right] ) or ( \left[ \text{Subst. BigH} \right] )</th>
<th>( K )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. ( \left[ \text{Cu(BigH)} \right] \times 10^{-3} ) and nitrophene</td>
<td>4.5</td>
<td>0.173</td>
<td>1.510 M</td>
<td>2.490 M</td>
<td>5.510 \times 10^{-10} M</td>
</tr>
<tr>
<td>2. ( \left[ \text{Cu(MeBigH)} \right] \times 10^{-3} ) and nitrophene</td>
<td>4.5</td>
<td>0.115</td>
<td>2.540</td>
<td>1.460</td>
<td>7.296 \times 10^{-10}</td>
</tr>
<tr>
<td>3. ( \left[ \text{Cu(StBigH)} \right] \times 10^{-3} ) and nitrophene</td>
<td>4.5</td>
<td>0.108</td>
<td>2.893</td>
<td>1.107</td>
<td>7.120 \times 10^{-10}</td>
</tr>
<tr>
<td>5.5</td>
<td>0.212</td>
<td>1.035</td>
<td>2.965</td>
<td>5.580 \times 10^{-9}</td>
<td>5.52 \times 10^8</td>
</tr>
</tbody>
</table>
After half an hour, the crystals were filtered, and recrystallised from warm water, filtered, washed with alcohol and dried in air.

(Found: Cu, 13.51; N, 23.65; Cl, 15.08; H₂O, 2.10.

\[ \text{Cu(nitrophen)(MeHg)}_2 \text{Cl}_2 \cdot 0.5\text{H}_2\text{O} \text{ requires Cu, 15.58; N, 23.56; Cl, 15.15; } \text{H}_2\text{O, 1.62%.} \]

(2) 5-Nitro-o-phenanthroline-Biguamide Copper(II) Bromide:

The pure 5-nitro-o-phenanthroline-biguamide copper(II) chloride was dissolved in minimum volume of warm water and was treated with a dilute solution of KBr. Light sky-blue crystals separated, were filtered after half an hour and recrystallised from hot water, filtered, washed with alcohol and dried in air.

(Found: Cu, 11.55; N, 20.44; Br, 29.22.

\[ \text{Cu(nitrophen)(MeHg)}_2 \text{Br}_2 \text{ requires Cu, 11.58; N, 20.40; Br, 29.17%.} \]

(3) 5-Nitro-o-phenanthroline-Methylbiguanide Copper(II) Chloride:

It was prepared by following the procedures similar to 5-nitro-o-phenanthroline-biguamide copper(II) chloride with little modifications. The pH of the solution was raised to 7-7.5. The bright sky-blue solution formed on the addition of the heterocyclic ligand was allowed to stand for several hours. Dirty sky-blue crystals formed, filtered and recrystallised from warm water (pH 7-7.5), washed with alcohol and air dried.

(Found: Cu, 15.12; N, 23.20; Cl, 14.75; H₂O, 1.90.

\[ \text{Cu(nitrophen)(MeHg)}_2 \text{Cl}_2 \cdot 0.5\text{H}_2\text{O} \text{ requires Cu, 15.17; N, 23.18; Cl, 14.71; } \text{H}_2\text{O, 1.86%.} \]
(4) 5-Nitro-o-phenanthroline-Methylbiguanide Copper(II) Bromide:

It was prepared like the corresponding bromide salt of biguanide copper(II) complex. The dirty sky-blue with violet tinge crystals appear after several hours on keeping it at room temperature, recrystallised from hot water, filtered, washed with alcohol and air dried.

(Found: Cu, 12.90; N, 18.18; Br, 25.92; H₂O, 8.68.
\[ \text{Cu(nitrophen)(MeBigH)Br₂·3H₂O} \] requires Cu, 12.95; N, 18.15; Br, 25.89; H₂O, 8.78%)

(5) 5-Nitro-o-phenanthroline-Ethylbiguanide Copper(II) Chloride:

This was prepared by following the procedure similar to the corresponding 5-nitro-o-phenanthroline methylbiguanide copper(II) chloride. Here the blue solution was allowed to stand for 20-24 hrs. when dark sky-blue crystals formed; recrystallised from minimum volume of warm water (at pH 7-7.5). filtered, washed with alcohol and air dried.

(Found: Cu, 12.52; N, 22.15; Cl, 14.10; H₂O, 5.61.
\[ \text{Cu(nitrophen)(EtBigH)Cl₂·H₂O} \] requires Cu, 12.54; N, 22.11; Cl, 14.02; H₂O, 5.55%)

Bis(biguanide or subst.biguanide) copper(II) chlorides were synthesized by following published procedures⁹,¹⁰. Partial analyses are given below:

(6) Bis(biguanide) Copper(II) Chloride:

(Found: Cu, 17.00; H₂O, 9.78.
\[ \text{Cu(BigH)₂·Cl₂·2H₂O} \] Calcd.: Cu, 17.05; H₂O, 9.66%).
(7) Bis(methylbiguanide) Copper(II) Chloride:

(Found: Cu, 15.45; H₂O, 11.07.
\[ \text{Cu(MeBigH)}_2\text{Cl}_2 \cdot 2.5\text{H}_2\text{O} \text{ Calcd.: Cu, 15.51; H}_2\text{O, 10.99%} \].

(8) Bis(ethylbiguanide) Copper(II) Chloride:

(Found: Cu, 14.48; H₂O, 10.20.
\[ \text{Cu(EtBigH)}_2\text{Cl}_2 \cdot 2.5\text{H}_2\text{O} \text{ Calcd.: Cu, 14.52; H}_2\text{O, 10.28%} \].

Analytical Procedures:

Water of hydration was determined by loss at 110-115°C for one hour.

Nitrogen was estimated by combustion technique (Dumas' method).

Halogens were estimated as silver halides.

These complexes decomposed only incompletely with H₂S. These were ultimately fused with KHSO₄ (10-15 times by weight). The cooled fused mass was then moistened with concentrated H₂SO₄ and heated to dense white fumes. This process was repeated for 3-4 times and finally heated strongly for half an hour. The cooled mass was then dissolved in hot acidified (H₂SO₄) water and copper content was estimated iodometrically.

The magnetic susceptibility measurements of the complexes at room temperature were made by a Gouy's Balance with field strength 8.566X10⁵ gauss using G.R. grade CuSO₄·5H₂O as a standard. Diamagnetic corrections were taken from Selwood¹¹.

Conductivities in water were measured by Philips conductivity bridge type PR9500.
The absorption spectra of the isolated complexes in water, dimethylsulfoxide and ethyleneglycol were measured at 0.004M concentrations in a Hilger & Watts UVISPEK spectrophotometer using 1 cm. cells over the range of 370-900 m.µ.

Solution spectral studies on the composition and formation pH ranges were run at 0.004M bis(biguanide or subst.biguanide) copper(II) chloride level. The weighed 5-nitro-o-phenanthroline was dissolved in 10 ml. of hot spirit, then weighed amount of complex dissolved in about 8 ml. water was added, pH adjusted to the desired value using a Beckman Zeromatic pH meter and finally volume made upto 25 ml with water. The spectra were run over the range 400 m.µ—750 m.µ. pH variations were made with 0.004M copper(II) bis(biguanide or subst.biguanide) chloride, and 0.004M 5-nitro-o-phenanthroline within the range pH 4.5-9.0. Molar ratio variations were done at constant (0.004M) copper(II) bis(biguanide or subst.biguanide) chloride, varying 5-nitro-o-phenanthroline (0.002M-0.014M) at a fixed pH 7.
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