

# Pseudoaromaticity in Metal Chelates : Biguanides and N'-amidinoisourea Complexes

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Evidences for the sustenance of ring current in metal biguanides and metal N'-amidinoisoureas have been reviewed. Electrophilic substitution reactions i.e. halogenation, sulphonation, nitration, have been successfully performed on Cu(II), Ni(II), Cr(III) and Co(III) complexes. Diazotization reaction on acid stable complexes of Pt(II), Pd(II) and Au(I) has been reported. Preparation of robust water stable boron, carbon and silicon compounds with these ligands indicates electron delocalization in the ring system. The band ( $\approx 200$  nm) assigned to aromatic metal chelate ring systems has been red-shifted in their halogen derivatives. X-ray investigation on copper(II) and nickel(II) biguanides indicate shortening of C-N bond. Stabilities of halogeno-substituted compounds are less than the unsubstituted ones. For substituted and unsubstituted Cu(II) complexes,

lengthening of M-N bond nearer to halogen atom and shortening of  $\text{---}\overset{\text{---}}{\text{C}}\text{---NH}_2$  bond has

been attributed to drifting of delocalised electron cloud towards halogen. Nmr data on nickel(II) biguanide suggest sustenance of ring current. XPS data indicate absence of any quaternary nitrogen atom in metal biguanides. Pseudoaromatic behaviour as evidenced has been attributed to strong  $\pi$  electron delocalization over the entire complex molecule.

**M**ETAL chelates constitute a very large portion of inorganic ring systems. Stability and properties of these compounds are usually viewed from a consideration of the basicity of the donor atoms, chelate effect, stereochemistry of the complex molecule and overall electronic environment of the central metal atom. However, these considerations have not always been found to be adequate in explaining the characteristic properties of some metal chelates. Electron delocalisation over the whole metal ligand ring has been proposed in some cases as a probable stabilising factor. Several  $\pi$ -complexes and some metal chelate ring systems manifest chemical reactivity usually associated with aromatic substances. However, the concept of aromaticity is too broad for any unequivocal definition. 'An unsaturated cyclic or polycyclic molecule or ion may be classified as aromatic if all the annular atoms participate in a conjugate system such that, in the ground state, all the  $\pi$ -electrons (which are derived from atomic orbitals having axial orientation to the ring) are accommodated in bonding molecular orbitals in a closed (annular) shell'. Or more precisely, Elvidge and Jackman have defined an aromatic compound as a compound which will sustain an induced ring current. Whatever may be the correct definition, the compounds classified as aromatic display some characteristic properties. The sustenance of ring current in any compound can very well be detected by pmr spectroscopy. The pseudo-aromatic character discussed here is based on reactivity, particularly in electrophilic substitution reactions and on the criterion of anisotropic magnetic ring current in metal chelates studied through pmr spectroscopy.

Formation of inorganic heterocyclics through the alternation of two elements having different electronegativities and possible electron delocalization over the whole ring system is a subject of much discussion. Classical examples are the cyclotriborazine (borazine) ring and its oxygen analogues. Search for potential aromatic ring system made up of second-row elements capable of forming  $sp^2$  hybrid bonds which in turn can contribute  $\pi$ -electrons to form delocalised aromatic clouds of  $(4n+2)$   $\pi$ -electrons, has yielded quite a few system. A different situation, however, arises when third row elements, e.g. phosphorous, sulphur etc. capable of using d-orbitals in bonding are involved. Unlike aromatic rings where  $p\pi$ - $p\pi$  conjugation occurs by overlap of  $p\pi$ -orbitals in a plane perpendicular to the ring, overlap of  $d\pi$ -orbitals with  $p\pi$ -orbitals may occur either in a plane perpendicular to the ring or in the local plane of the ring involving  $d_{xy}$ ,  $d_{x^2-y^2}$  orbitals of one and  $sp$  hybrid orbitals of the other. An alternative interpretation was suggested by Dewar and coworkers<sup>3</sup> where non-interacting tricentric allylic  $\pi$ -bonds are formed. With alternating  $d\pi$ - $p\pi$  interacting orbitals, comparison has been made for both allylic and cyclic delocalization and the energies were calculated for six and eight coordination system<sup>3</sup>. However, with systems containing more than two alternating groups, the situation becomes more difficult for diagnosis, more so, when the system consists of  $p\pi$ - $p\pi$  and  $d\pi$ - $p\pi$  interacting species. This system, on the other hand, sometimes can offer more flexible situations for accommodation of  $\pi$ -electrons. Ligands having the possibility of  $p\pi$ - $p\pi$  or  $p\pi$ - $d\pi$  interaction can interact with metal ions to form cyclic delocalised

$\pi$ -electron system. By changing the metal ion the delocalisation can be varied from almost zero involvement to very high participation depending on the availability of d orbital with suitable symmetry. In mixed ligand complexes, electron density over the ring containing one ligand and the metal ion can be pushed or pulled depending on the electron attracting or electron repelling characteristic of the other ligand. Study of pseudo-aromatic characteristics in metal chelates has hence been considered a very worthwhile and interesting problem.

Much work on metal acetylacetonates as a probable system of this type has been reported<sup>4,5</sup>. The hydrogen at the central position in these chelate rings can be substituted by a variety of electrophilic reagents. However, nmr spectral studies with substituted and unsubstituted metal chelates do not unequivocally indicate sustenance of any ring current in these complexes. Electrophilic substitution reactions have also been carried out on metal thioacetylacetonates<sup>6</sup> with less success, but no pmr spectrum has been reported for them.

The other system under review in this paper e.g. the metal chelates with biguanide and N'-amido-nisouras have shown good evidences of  $\pi$ -electron delocalisation. The structure of these compounds had been suggested by various workers from time to time and the one suggested by Ray and Saha<sup>7</sup> was by far the most satisfactory one :

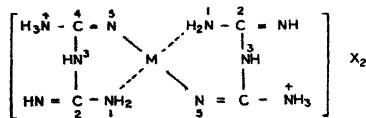
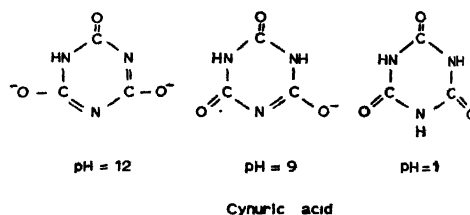


Figure-1

This explained most of the chemical behaviour of the metal biguanides except the observation of Slotta and Tschesche that the biguanide with substitution at position 3 is not capable of any complex formation. Also, normal salt of biguanide and biguanide base are capable of complex formation whereas the acid salt of the ligand needs sufficient alkali to form the complexes. The main criterion of complex compound formation has, therefore, been thought of as an appropriate ligand field formation around the central metal ion.

Let us consider symmetric triazines and other heterocyclics having similar ring systems as our model. Hirt and coworkers<sup>8,9</sup> correlated the u.v. absorption spectra and the structures of these oxygen containing triazines, their ions and their acyclic analogues. They assigned the weak transition occurring at 235 nm in melamine to a symmetry forbidden  $\pi$ -electron transition. The pH dependence of the u. v. absorption spectra of cyanuric acid and biguanide indicate the presence of three distinct forms.



Cyanuric acid

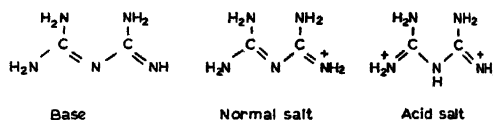


Figure 2. Biguanide

The addition of a single proton to biguanide does not shift the position of the absorption band (230 nm) while the addition of another proton makes the absorption band disappear indicating the formation of a nonconjugated structure. A simple LCAO-Huckel calculation on the skeleton :

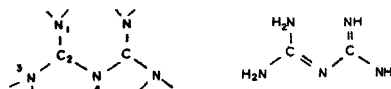


Figure-3

had been done to ascertain the nature of 230 nm transition in biguanide<sup>10</sup>. The total number of orbitals was taken as seven and the number of  $\pi$ -electrons as ten (seven from the constituting atoms and three from three  $\text{NH}_2$  groups). The coulomb integral parameters of N were varied. The following general conclusions were arrived at.

(a) The bond orders of various bonds are as follows :

$$\text{N}(1) - \text{C}(2) = 0.50$$

$$\text{C}(2) - \text{N}(3) = 0.69$$

$$\text{C}(2) - \text{N}(4) = 0.45$$

The corresponding calculated bond lengths are 1.37, 1.33 and 1.38.

(b) The lowest unfilled orbital is antisymmetric with respect to the reflection through a plane passing through N(4). The highest orbital is symmetric and there is one more antisymmetric and another symmetric level very close to it. The band at 230 nm may be ascribed to transition from the symmetric level to the antisymmetric one.

At this stage, it was thought interesting to study whether, in metal biguanides, similar consideration holds good or not and whether at least some metal

ion orbitals can help in  $\pi$ -electron delocalization over the whole chelate ring system. The u.v. spectral studies indicate that the band characteristics of biguanide base and monoprotonated biguanide in the complexes remain almost same with occasional spectral shifts.

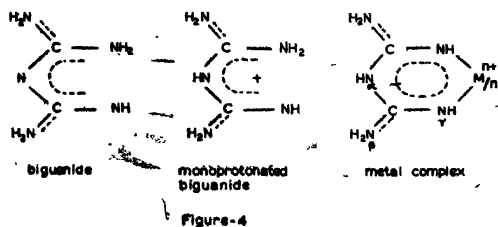
TABLE—1

| Compound   | Kk      | $\epsilon$ | $\epsilon$ per (bg) |
|--|---------|------------|---------------------|
| (bg)HCl  | 43.0    | 12,600     | 12,600              |
| (bg)2HCl   | No band | —          | —                   |
| Cu(bg) <sub>2</sub> Cl <sub>2</sub>                            | 38.4 sh | 1,300      | 10,400              |
|  | 43.0    | 19,500     |                     |
| Ni(bg) <sub>2</sub> Cl <sub>2</sub>                            | 43.0    | 27,500     | 13,750              |
| Pt(bg) <sub>2</sub> Cl <sub>2</sub>                            | 45.5    | 29,250     | 14,625              |
| Pd(bg) <sub>2</sub> Cl <sub>2</sub>                            | 33.4    | 395        |                     |
|  | 46.0    |            | 19,448              |
| Co(bg) <sub>2</sub> Cl <sub>2</sub>                            | 37.5 sh | 4,000      | 9,500               |
|  | 45.8 sh | 24,500     |                     |
| Cr(bg) <sub>2</sub> Cl <sub>2</sub>                            | 37.2 sh | 1,550      | 9,416               |
|  | 44.7    | 26,700     |                     |
| Ru(bg) <sub>2</sub> Cl <sub>2</sub>                            | 38.5    | 10,500     |                     |
|  | 48.0 sh |            | 13,666              |
| Rh(bg) <sub>2</sub> Cl <sub>2</sub>                            | 32.5    | 585        | 10,548              |
|  | 47.5 sh | 31,000     |                     |
| bg = C <sub>3</sub> N <sub>3</sub> H <sub>7</sub> <sup>+</sup> |         |            |                     |

Blue shifts have been observed for both square planar (Pt(II) and Pd(II)) and octahedral (Co(III), Cr(III), Ru(III), Rh(III)) complexes. One weak band also appears in this region for octahedral complexes.

The crucial point in this calculation is the energy of the  $\pi$ -orbitals in relation to the metal orbitals. Considering the most probable sequence of level in order of increasing energy, the model predicts data consistent with the blue shift experimentally observed for square planar complexes. The blue shift in octahedral metal biguanides can also be explained by properly combining the symmetric and antisymmetric  $\pi$ -orbitals of the ligands to form orbitals belonging to a particular representation of D<sub>3</sub> group.

From these observations, it is concluded that the biguanide, monoprotonated biguanide and their metal chelates may contain delocalized  $\pi$ -electron system over the whole molecule.



The protons in metal chelate salts are very loosely bound as can be verified by the preparation of anhydrobases from metal biguanide hydroxides with the loss of water by heating at 100°C. X-ray investigation of ethylenedibiguanide copper(II) complex indicates

considerable shortening of C-N single bond lengths (1.29-1.43 Å)<sup>11</sup>. This may be attributed partly to the shortening of the atomic radii of the carbon and nitrogen atoms, owing to their state of hybridization and partly to the  $\pi$ -bond character of carbon nitrogen bond. The crystal structure determination of bis(biguanide)copper(II) chloride also indicates shortening of C-N single bond distances (1.28-1.36 Å)<sup>12</sup>. This may also be due to delocalization of  $\pi$ -electrons over the entire chelate ring. The M-N bond length in this case is found to be considerably shorter when compared to similar distances in complexes having little or no possibility of  $\pi$ -electron delocalization over the entire chelate ring.

With these observations it was first thought worthwhile to investigate chemically whether the  $\pi$ -electron delocalized system on biguanide can extend to available  $p\pi$  or  $d\pi$ -orbitals of nonmetallic ions. Attempts to prepare chelate compounds of boron, carbon and silicon have resulted in isolation of robust complexes.

N'-amidinoisoureas and biguanides react with trimethoxyborate and boric acid in methanol and water respectively giving rise to crystalline compounds<sup>13,14</sup>. These compounds are quite stable and hydrolyse very slowly in aqueous solution and rapidly in acid solution. They are stable upto 200°C and undergoes rapid decomposition at 250-300°C. They can be represented by the formula

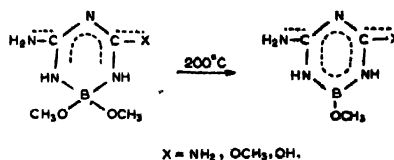


Figure - 5

The hydrolytic behaviour of these compounds in acid medium can be explained by considering the protonation of the nitrogen atom between the carbon atoms of the chelate ring disturbing the  $\pi$ -electron delocalization and consequent aromaticity. The  $\pi$ -bond between boron and nitrogen atom thus becomes prone to hydrolytic attack and eventual rupture.

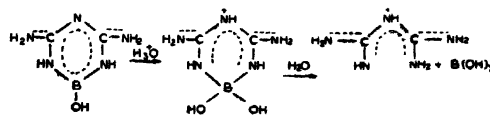


Figure-6

Cationic boron(III) chelates with these ligands having general composition  $BL_3^+X^-$  have also been synthesized by the transamination reaction between tris(diethylamino)borane and biguanides. The compounds have very stable B-N bonds and can be recrystallized from aqueous solutions.

It is interesting to note that the reaction between  $\text{Cl}_4/\text{CH}_2\text{I}_2$  with biguanide base in dry alcohol produces 2,4-diaminotriazine by simple mixing<sup>12</sup>. The ease with which the carbon atom is converted to  $\text{sp}^2$  from  $\text{sp}^3$  hybridised state indicates preference of delocalized  $\pi$ -electron system in biguanide to extend to the carbon atom producing an aromatic compound.

Reaction between an electrophilic silicon compound and ligand biguanide leads to the formation of a number of heterocyclics in which Si-N bonds have been found to be extremely stable towards hydrolysis<sup>13</sup>. However, it is well known from the study of the chemistry of silazanes and silezenes that Si-N bonds are highly susceptible to hydrolysis. It may, hence, be presumed that anhydro biguanide base in alcoholic solution possesses sufficient  $\pi$ -electrons to interact with some of the bonding  $\pi$ -orbitals of the silicon atom so that a stable silicon heterocyclic complex is formed. The compound, may

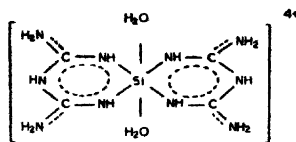


Figure - 7

be regarded as the only known water soluble cationic silicon (IV) complex having stable Si-N bonds.

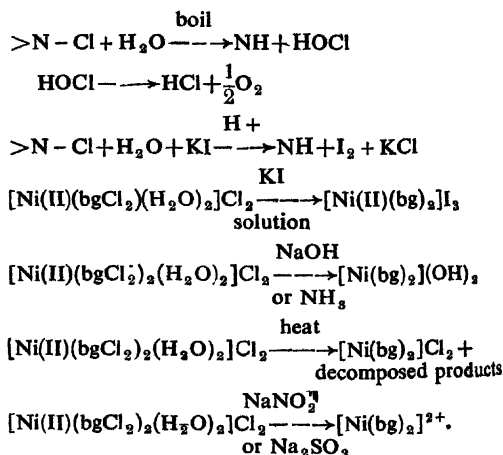
From these observations, it becomes apparent that biguanide and  $\text{N}'$ -amidinoisoureas are capable of extending the  $\pi$ -electron delocalisation in them to other ions having orbitals of suitable symmetry. The ligands form extremely stable robust complexes with many transition metal ions. Their behaviour sometimes can not be explained through consideration of usual parameters. Complete  $\pi$ -electron delocalization in these metal ligand rings and the consequent development of pseudoaromaticity in these systems have been considered a possibility. Electrophilic substitution reactions were performed on these complexes to test any aromatic behaviour. Some of the complexes are unstable to reagents commonly used for electrophilic substitution reactions for benzene.

Even with this limitation, a number of stable complexes has undergone electrophilic substitution reactions. Halogenation reactions are possible only with chlorine and bromine. Chlorine, one of the strongest electrophilic reagents, reacts most.

When chlorine was passed through the suspension of  $[\text{Ni}(\text{II})(\text{bg})_2]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$  in carbontetrachloride, a maroon red compound  $[\text{Ni}(\text{III})(\text{bg})_2\text{Cl}_2]\text{Cl}$  which remain unchanged towards excess chlorine gas was formed<sup>14</sup>. On adding one or two drops of water to this maroon red suspension in presence of chlorine, a greenish blue compound was formed in moderate yields together with some amount of nickel chloride and biguanide acid chloride<sup>12</sup>. The greenish blue product was purified by repeated crystallization from water or

methanol at room temperature. It is resistant to hydrolysis or alcoholysis below  $60^\circ\text{C}$  and is soluble in polar solvents. The paramagnetism of this compound ( $\mu_{\text{eff}} = 2.89 \text{ B.M.}$ ) and the presence of three absorption peaks in the visible region indicate the octahedral coordination of nickel(II).

Chloride estimations in neutral, aqueous or methanolic medium with silver nitrate, conductometric titration with aqueous silver nitrate solution and conductance measurements in these solvents suggested the presence of two chloride ions per molecule. The compound was found to be an eight electron oxidizing agent towards acidified potassium iodide or ferrous sulphate solution. Total chloride estimations confirmed the presence of six chlorine atoms per molecule of the compound. The compound reacts with neutral potassium iodide solution to produce the green polyhalide<sup>15</sup>. The physical and chemical properties of this complex suggest the presence of four chlorine atoms in the rings bound to nitrogen atoms. The compound decomposes with explosion when heated alone or with concentrated sulphuric acid. It is stable in air and decomposes with evolution of oxygen only when the aqueous solution of the compound is heated on a water bath. The aqueous solution of the compound can very easily be reduced to  $[\text{Ni}(\text{II})(\text{bg})_2]^{2+}$  by alkali, ammonia or mild reducing agents like sodium nitrite, sodium sulphite, sulphur dioxide and hydrazine. The anion of the halosubstituted compound can be replaced by sulphate, nitrate or bicarbonate ion. Thermal analysis of this complex indicated an exothermic decomposition peak at nearly  $150^\circ\text{C}$  with the loss of four chlorine atoms and the formation of  $[\text{Ni}(\text{II})(\text{bg})_2]\text{Cl}_2$  together with some decomposed products. All these properties of this compound can best be described considering the presence of four  $>\text{N}-\text{Cl}$  bonds per molecule.



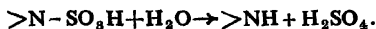
Following the same method of preparation, chloro-substituted trisbiguanide complexes of  $\text{Co}(\text{III})$  and  $\text{Cr}(\text{III})$  were obtained. The final products were always the hexachlorosubstituted products. They are identical in all physical and chemical properties with the corresponding halogeno-substituted nickel(II) complex,

showing oxidation values of 13 and 12 respectively. The former one is diamagnetic and the latter one paramagnetic with  $\mu_{eff}$  value of 4.05 B.M. indicating the presence of Cr(III) species. The anions in these cases can also be replaced by sulphate, nitrate or bicarbonate. The action of chlorine on  $[\text{Co(III)(bg)}_2(\text{H}_2\text{O})(\text{OH})]\text{Cl}_2$  produces always the tetrachloro-substituted products. The maximum number of chlorine atoms that can be introduced per metal biguanide ring is always two indicating the substitution at two equivalent nitrogen atoms in each ring.

Similarly, the action of liquid bromine on  $[\text{Co(III)(bg)}_2]\text{Br}_3$  in carbon tetrachloride suspension produced hexabromo-substituted products in the presence of slight moisture. It is much less soluble in water or methanol than the corresponding chloro-substituted products and is prone to slow hydrolysis in aqueous solution. The action of chlorine or bromine on Cu(II) biguanide compounds, on the other hand, always produced monohalogen substitution per ring. The physical and chemical properties of the copper(II) compounds are almost the same as its nickel(II) analogue.

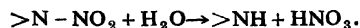
Attempted chlorination on Pt(II), Pd(II), Mn(III), Ag(I) and Au(I) biguanides in carbon tetrachloride suspension resulted in the isolation of higher valent metal complexes<sup>17,18,19,20,21</sup>. These complexes showed no sign of decomposition in presence of water. The action of chlorine on biguanide normal salt or base in carbon tetrachloride suspension in presence of slight moisture produced the acid salt of the ligand without any chlorosubstitution or decomposition of the ligand. It may be noted that the hydrogen atom attached to central carbon atom of acetylacetone can be replaced by the electrophilic reagents even when it is not attached to any metal ion<sup>22</sup>.

An effort was made to sulphonate the metal biguanide complexes. Sulphur trioxide vapour, prepared by the action of concentrated sulphuric acid on phosphorous pentoxide, was passed through the suspension of metal chelate for about 2 to 3 hours. Only Cr(III) and Co(III) biguanides underwent sulphonation, while others were decomposed under such conditions. Hexa-sulphonated compounds were isolated in cases of Co(III) and Cr(III) while trissulphonated products were obtained in case of Cr(III) complexes as intermediate one. This indicates that all the chelate rings in any complex molecule first undergo monosubstitution and then disubstitution with excess reagent. The sulphonated compounds are hydrolysed readily in water producing acidic solutions. This can be explained in the following way



The hexanitrosubstituted product of Co(III) biguanide was obtained by the interaction of  $\text{N}_2\text{O}_4$  with  $[\text{Co(III)(bg)}_2](\text{NO}_3)_3$  in dry carbon tetrachloride suspension, while tetrasubstituted product was obtained with  $[\text{Co(III)(bg)}_2(\text{H}_2\text{O})(\text{OH})](\text{NO}_3)_2$ . These compounds are diamagnetic and undergo rapid hydrolysis in aqueous solution producing acidic reaction, perhaps due to

following type of hydrolysis.



From the similarities in the behaviour of metal biguanides and metal N'-amidinoisoureas, the presence of pseudoaromatic ring currents in metal N'-amidinoisoureas was predicted and on this basis similar electrophilic substitution reactions were performed on these complexes. The action of chlorine and bromine on nickel(II) and copper(II) complexes under similar conditions as those of biguanides led to the isolation of chloro- and bromo-substituted complexes of nickel(II) and copper(II). In case of nickel(II), dihalosubstituted (per ring) products were obtained in all cases, while the monosubstituted (per ring) complexes were isolated in case of copper compounds. The physical and chemical properties of these halogenosubstituted complexes were found to be comparable to those of biguanides.

In these electrophilic substituted ligand complexes of metals, the position of substitution have been predicted to be at the nitrogen atoms of the chelate ring, coordinated to the metal ion and not at the side chain  $-\text{NH}_2$  groups. It has been observed that each metal chelate ring can take up at least two halogen atoms or two electrophilic groups and in no case, compounds having more than two electrophilic groups per ring have been isolated. Cu(II) complexes however, have always one halogen atom per metal-ligand ring. The preparation of -HgCl derivative of these halogenosubstituted complexes confirms the presence of substituted group at the two coordinated nitrogen atoms and not at the side chain<sup>23</sup>. The -HgCl derivatives, in the present case, can only be formed if there are free  $-\text{NH}_2$  groups at the side chain. The treatment of the  $\text{HgCl}_2$  solution with the solution of nonsubstituted complexes produced the insoluble -HgCl derivative. Similarly, the addition of  $\text{HgCl}_2$  solution to the aqueous solutions of halogenosubstituted products produced similar -HgCl derivatives having almost identical properties. All these -HgCl derivatives are insoluble in water. Again the side chain  $>\text{N}-\text{Cl}$  groups should behave like  $\text{NH}_2\text{Cl}$  and are expected to be more sensitive to hydrolytic attack. The present chlorosubstituted products show no sign of hydrolysis in aqueous solution below  $40^\circ\text{C}$  and can be recrystallized from water.

During electrophilic substitution reactions, decomposition or substitution products of biguanide have never been produced, showing the stability of the coordinated ligands towards these reagents. The stability of these complexes with substituted ligands may be due to presence of pseudoaromaticity in these compounds.

Another test for the presence of delocalized ring current is positive diazotization reaction on some metal chelates of this group. In case of free ligands (biguanide and N'-amidinoisourea) no diazotized product has been isolated so far. The presence of delocalized ring current in these metal chelates will make each of the chelate ring behave like an aromatic amine. Only few acid stable metal biguanides i. e. Pt(II), Pd(II) and

Au(I) biguanides respond to this reaction. Brilliant red diazo-compounds are obtained from each of these white compounds. Their physico-chemical properties and infrared spectral studies confirm the presence of diazo-group in these complexes.

The mechanism of these electrophilic substitution reactions can be visualized from the physical and chemical nature of the intermediate and final products. It has been observed that during halogenation, higher valent metal complexes are formed in many cases. Of these few complexes of the ions i.e. Ni(III), Pd(IV), Pt(IV), Ag(III) and Au(III) have been isolated. The complexes, which are resistant to hydrolysis, do not undergo electrophilic substitution reactions. In case of Cu(II), Co(III) and Cr(III) complexes, intermediate compounds having intense colouration are formed, which however, could not be isolated in the pure state. Physico-chemical properties indicate the presence of higher valent metal species in these intermediate products. These findings strongly suggest halogenation to be preceded by complex formation with higher valent metal ions and subsequent hydrolytic decomposition to give halogeno-substituted products of the metal ion in its usual oxidation state. In this process electron density momentarily increases at sites nearest to the metal ion i.e. coordinated nitrogen atoms then become the positions of attack by the electrophile. Where the higher valent complexes are reasonably stable to hydrolytic decomposition process, there is no possibility of the above mechanism to operate and as such no substituted product with electrophile is obtained. It has been observed that Pd(IV), Pt(IV), Ag(III) and Au(III) complexes with these ligands are not easily hydrolysable.

On the basis of the above observations, the following probable mechanism for chloro-substitution is suggested.

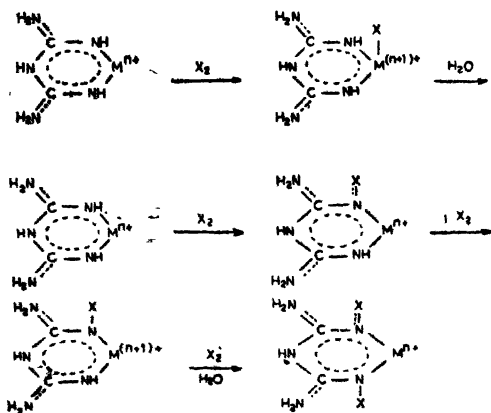


Figure - 8

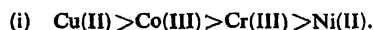
#### Stabilities of the complexes :

The stability constants of the halogeno-substituted complexes could not be determined due to their slow

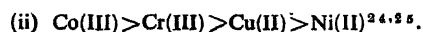
decomposition in aqueous or nonaqueous medium resulting in N-hal bond cleavage. These complexes are far less stable than their parent compounds towards various chemical reagents. In most cases,  $>N-X$  bond undergoes rupture and the halogeno-substituted complexes revert back to the original ones. Hence, variation of stabilities of these halogeno-substituted complexes towards different chemical agents is due mainly to difference of the  $>N-X$  bond strength. However, their stabilities are found to depend on the nature of the ligand, the halogen and the metal atom i.e. the overall electronic environment on the metal chelate ring.

The halogeno-substituted biguanide complexes are found to be more stable than the corresponding halogeno-substituted N'-amidinoisourea complexes. The same trend is also observed for their corresponding nonsubstituted complexes. The extent of electron delocalisation in biguanide complexes should be more than the corresponding N'-amidinoisourea complexes, since in the latter case, more electronegative atom, oxygen, is attached to the ring in place of nitrogen in biguanides.

In halogeno-substituted complexes, the metal ions may be arranged as follows :



For nonsubstituted complexes the order is :



Decreased stability of halo-substituted complexes can be attributed to withdrawal of electron density from the chelate ring towards the electronegative halogen atom. The decrease of stability should, therefore, be proportional to the number of halogen atoms attached per ring. The highest stability of Cu(II) chelates in (i) may be due to monosubstitution per ring. The difference in stabilities of these halogeno-substituted complexes towards different chemical agents is reflected in the variation of  $>N-X$  bond strengths in these complexes and vice versa. The  $>N-X$  bond strength is certainly influenced by the extent of electron delocalization in the ring as it will extend to X through interaction of  $X-pz$  orbital with the ring  $\pi$ -system. The experimentally observed variation for  $>N-X$  bond strength for disubstituted complexes are  $Co(III) > Cr(III) > Ni(II)$  which is same as those for the unsubstituted complexes. In case of sulphonated complexes, trisubstituted Cr(III) biguanides have been found to be more stable to hydrolytic attack than hexasubstituted products as suggested from conductance data.

#### Infrared spectral studies :

The infra-red spectra of the halogeno-substituted and simple complexes were taken in the range  $4000\text{ cm}^{-1}$  to  $400\text{ cm}^{-1}$ . Significant differences were observed between the spectra of these two series of complexes for Co(III), Cr(III), Cu(II) and Ni(II). Among the several bands observed for simple complexes in the region from  $3200\text{ cm}^{-1}$  to  $3450\text{ cm}^{-1}$ , the lowest

one ( $\approx 3270 \text{ cm}^{-1}$ ) is found to be absent in the halogeno-substituted complexes and may therefore be due to  $\nu \text{ N-H}$  (nitrogen coordinated to the metal). The asymmetric and symmetric band for  $\nu \text{ N-C-N}$  (ring) group (at  $\approx 1670 \text{ cm}^{-1}$  and  $\approx 1520 \text{ cm}^{-1}$ ) in unsubstituted complexes show considerable red shift in the corresponding halogeno-substituted complexes ( $\approx 1630 \text{ cm}^{-1}$  and  $\approx 1450 \text{ cm}^{-1}$ ). This may be due to flow of electron density from the ring towards the halogen atom. The band at  $\approx 760 \text{ cm}^{-1}$  (N-H bending) present in the simple complexes is found to be absent in the corresponding halogeno-substituted complexes indicating the halo substitution at the ring nitrogen atoms.

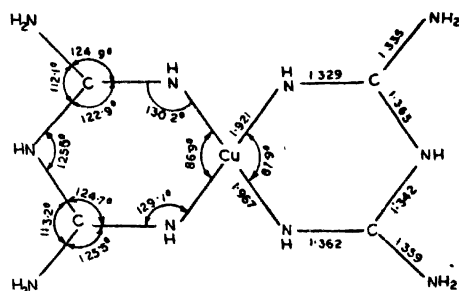
### Electronic spectra :

The electronic spectra of these complexes were taken in the range 170 nm to 1000 nm. In case of free ligand only one absorption band at  $\approx 230 \text{ nm}$  was observed for biguanide and biguanide normal salts. In case of metal biguanides, the position of  $\approx 230 \text{ nm}$  peak remains almost unaltered, but another new peak in the range 190 nm to 204 nm appears in all complexes. This new peak may be due to the formation of a heterocyclic pseudoaromatic ring with the metal atom. In the halogeno-substituted complexes, the new peak shows a red shift probably due to extension of  $\pi$ -electron delocalization through the halogen atom.

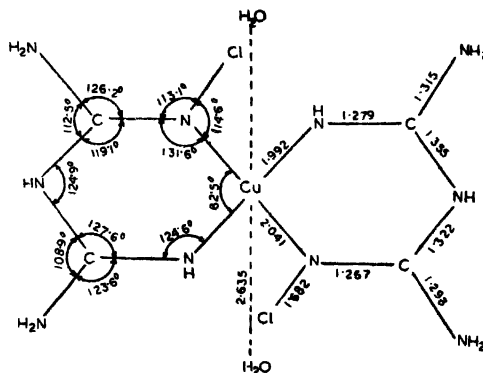
For Cr(III) complexes, Racah parameter was evaluated from the equation  $B = (2\nu_1^2 + \nu_2^2 - 3\nu_1\nu_2) / (15\nu_2 - 2\nu_1)$ . In case of Co(III) complexes, no spin forbidden transition was observed and the parameters were evaluated with the aid of relations  $C=4B$ . The accuracy of the result is limited but sufficient for comparative study.

A decrease of  $10 Dq$  and an increase of  $B$  values are generally observed in the halogeno-substituted complexes compared to simple ones. The presence of halogen atom in the ligand weakens  $\sigma$  and  $\pi$ -donor capacities of the nitrogen atoms. The weaker  $\sigma$ -bonds give rise to increase of M-N bond distances and which in turn decreases the  $\pi$ -overlap between the ligand and the metal orbitals. This observation has been amply substantiated by comparison of X-ray structural data of halogeno substituted and unsubstituted bis(biguanide) copper(II) chloride dihydrate<sup>26</sup>. A comparison of bond distances indicate bond lengthening of M-N bond in halogenated complexes (Fig. 9).

It is of interest to note that the two water molecules in the halogeno-substituted Cu(II) complexes are situated in *trans* positions at distances 2.635 from the  $\text{Cu}^{2+}$  ion, while in unsubstituted Cu(II) complexes their positions could not be ascertained near the complex molecule.  $\pi$ -electron cloud in unsubstituted complex seems to prevent the water molecules to approach the metal ion in the complex. But in halogeno-substituted compounds the electron cloud may to some extent be localised towards electronegative chlorine making room for the approaching water molecules.



Bis(biguanide)Copper(II) Chloride dihydrate



Bis(Chlorobiguanide) Copper(II) Chloride dihydrate

Fig 9

It has been observed that nickel(II) always form square planar complexes with biguanides and  $\text{N}^+$ -amidinoisoureas, but it forms octahedral complexes with halogeno-substituted ligands, the *trans* positions being

TABLE 2—ELECTRONIC SPECTRAL DATA OF METAL COMPLEXES AND THEIR CHLORODERIVATIVES.

| Compound                                    | $\nu_1(\text{cm}^{-1})$ | 10 Dq (cm <sup>-1</sup> ) |  |
|---|-------------------------|---------------------------|--|
| 1. [Cu(bg) <sub>2</sub> ]Cl <sub>2</sub>    | 18867 (42.0)            | 18867                     |  |
| 2. [Cu(aiu) <sub>2</sub> ]Cl <sub>2</sub>   | 19525 (43.2)            | 19525                     |  |
| 3. [Cu(bgCl) <sub>2</sub> ]Cl <sub>2</sub>  | 16129 (47.5)            | 16129                     |  |
| 4. [Cu(aiuCl) <sub>2</sub> ]Cl <sub>2</sub> | 14084 (38.6)            | 14084                     |  |

| Compound                                     | $\nu_1(\text{cm}^{-1})$<br>${}^1A_{1g} \rightarrow {}^1T_{1g}$ | $\nu_2(\text{cm}^{-1})$<br>${}^1A_{1g} \rightarrow {}^1T_{2g}$ | 10 Dq (cm <sup>-1</sup> ) | B(cm <sup>-1</sup> ) |
|--|--|--|---------------------------|----------------------|
| 1. [Co(bg) <sub>2</sub> ]Cl <sub>2</sub>     | 20746(143.2)   | 27932(152.1)   | 22500                     | 450                  |
| 2. [Co(maiu) <sub>2</sub> ]Cl <sub>2</sub>   | 20500(175.6)   | 27350(192.7)   | 22200                     | 428                  |
| 3. [Co(bgCl) <sub>2</sub> ]Cl <sub>2</sub>   | 18020(256)   | 25900(665)   | 20020                     | 520                  |
| 4. [Co(maiuCl) <sub>2</sub> ]Cl <sub>2</sub> | 18050(285)   | 25860(760)   | 19980                     | 490                  |

| Compound                                   | $\nu_1(\text{cm}^{-1})$<br>${}^4A_{2g} \rightarrow {}^4T_{2g}$ | $\nu_2(\text{cm}^{-1})$<br>${}^4A_{2g} \rightarrow {}^4T_{1g}$<br>(F) | 10 Dq (cm <sup>-1</sup> ) | B(cm <sup>-1</sup> ) |
|--|--|---|---------------------------|----------------------|
| 1. [Cr(bg) <sub>3</sub> ]Cl <sub>3</sub>   | 19841  | 26178   | 14840                     | 605                  |
| 2. [Cr(bgCl) <sub>3</sub> ]Cl <sub>3</sub> | 18160  | 25350   | 18160                     | 750                  |

occupied by water molecules. It can be argued that the presence of strong  $\pi$ -bond between ligand  $\pi$  and metal  $\pi$  orbitals in the unsubstituted complexes prevents the formation of octahedral compounds. In the halogeno-substituted complexes, the decrease of  $\pi$ -bonding character between the ligand and the metal favours the formation of octahedral complexes.

#### Thermal analysis :

The thermal analysis of the ligands, their unsubstituted and halogeno-substituted complexes were performed in the temperature range 30°C to 500°C. In case of halogeno-substituted complexes, one extra highly exothermic peak is observed in the temperature range 140°C – 180°C. It is found that N'-amidinoisourea complexes decompose always at lower temperatures than the corresponding biguanide complexes. This step is attributed to cleavage of >N-X bond as verified from mass loss. Thermal stabilities of the >N-X bond for metal biguanides and metal N'-amidinoisourea complexes can be arranged in the following order : Co(III) > Cr(III) > Ni(II), which corresponds to the general stability of unsubstituted complexes. Thus the thermal stabilities of the >N-X bond depend on the nature of the metal atom for the similarly substituted complexes. As mentioned earlier, the >N-X bond strength depends on the extent of  $\pi$  electron delocalization in the metal chelate ring in substituted and unsubstituted complexes. This variation in >N-X bond strength reflects the variation of the pseudoaromatic character of the different chelate ring with same ligand and different metal ion. The >N-Br bond was always found to be thermally less stable than corresponding >N-Cl bond which is attributed to decreased  $\sigma$  bond strength as >N-Br bond distance must be greater than the corresponding >N-Cl bond distances.

Creitz *et al.*<sup>27</sup> have made X-ray studies and nmr spectral studies on bis(biguanide) nickel(II) chloride. C-N bond distance is in the range 1.28-1.35 Å consistent with our suggestion of  $\pi$ -electron delocalisation. Hnmr studies indicate  $\tau$  values 0.12 for N( $\alpha$ ), 3.4 for N( $\beta$ ) and 5.35 for N( $\gamma$ ) (Fig 4). The downfield chemical shift of 0.12 for N( $\alpha$ ) has been attributed to ring current effect arising from the  $\pi$  cloud by  $p\pi$  ligand orbital and  $d\pi$  metal orbital. The chemical shift of 3.40 for N( $\beta$ ) has been ascribed to electron attracting >C=NH group which withdraws electron density from aminonitrogen and in turn from the protons. The high field position of the N( $\gamma$ ) in respect to other two peaks may be attributed to shielding by the  $d_{xy}$  orbital of the diamagnetic  $d^8$  metal ion. The model emerging out of this study indicates clearly the sustenance of ring current over the metal biguanide ring.

Another proof of the  $\pi$  electron delocalisation in this series of compounds comes from a study of N( $1s$ ) photoelectron spectra of transition metal biguanides by Swartz and Alfonso<sup>28</sup>. Siegbahn *et al.*<sup>29</sup> have shown that XPS can differentiate between nitrogen atoms in -NH<sub>2</sub> and -NH<sub>3</sub><sup>+</sup> groups. Cox *et al.*<sup>30</sup> reported N( $1s$ ) chemical shift ranging from 1.6 to 2.2 eV between protonated and unprotonated (-NH<sub>2</sub>) nitrogen atom in

a series of nitrogen bases. Studies on [Cr(bg)<sub>3</sub>]<sup>+</sup>Cl<sub>3</sub><sup>-</sup> indicated a rather broad spectrum which on Gaussian analysis can be split into two lines with FWHM of 1.9 eV separated by 1.5 eV with a relative intensity of 2:3. The early structure (Ray and Saha) has a total cationic

TABLE 3—N(1s) BINDING ENERGIES FOR METAL BIGUANIDE COMPLEXES<sup>28</sup>.

| Compound  | Nitrogen (1s) binding energy (eV) | FWHM (eV) |
|---|-----------------------------------|-----------|
| Metal biguanide complexes <sup>a</sup>  |                                   |           |
| [Cr(C <sub>2</sub> N <sub>3</sub> H <sub>7</sub> ) <sub>3</sub> ] <sup>+</sup> Cl <sub>3</sub> <sup>-</sup>                     | 399.4                             | 2.8       |
| [Cr(C <sub>2</sub> N <sub>3</sub> H <sub>7</sub> ) <sub>3</sub> ] <sup>+</sup> H <sub>3</sub> O <sup>+</sup>                    | 399.2                             | 3.0       |
| [Ag(II)(C <sub>2</sub> N <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> ] <sup>+</sup> (SO <sub>4</sub> ) <sub>2</sub> <sup>-</sup> | 400.0                             | 2.4       |
| Cu(C <sub>2</sub> N <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> -p-C <sub>6</sub> H <sub>4</sub> SO <sub>3</sub> ) <sub>2</sub>  | 400.0                             | 2.7       |
| [Co(C <sub>2</sub> N <sub>3</sub> H <sub>7</sub> ) <sub>3</sub> ] <sup>+</sup> Cl <sub>3</sub> <sup>-</sup>                     | 399.2                             | 2.7       |
| [Co(C <sub>2</sub> N <sub>3</sub> H <sub>7</sub> ) <sub>3</sub> ] <sup>+</sup> H <sub>3</sub> O <sup>+</sup>                    | 398.9                             | 2.9       |
| Ni(C <sub>2</sub> N <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> -p-C <sub>6</sub> H <sub>4</sub> SO <sub>3</sub> ) <sub>2</sub>  | 400.2                             | 2.        |
| [Ni(C <sub>2</sub> N <sub>3</sub> H <sub>7</sub> ) <sub>3</sub> ] <sup>+</sup> H <sub>3</sub> O <sup>+</sup>                    | 398.9                             | 2.7       |
| [Cu(C <sub>2</sub> N <sub>3</sub> H <sub>7</sub> ) <sub>3</sub> ] <sup>+</sup> H <sub>3</sub> O <sup>+</sup>                    | 399.5                             | 2.9       |
| [Cu(C <sub>2</sub> N <sub>3</sub> H <sub>7</sub> ) <sub>3</sub> ] <sup>+</sup> Cl <sub>3</sub> <sup>-</sup>                     | 399.5                             | 2.5       |

charge of +1. But with the XPS data it should be at least +2. With the lowest value of the chemical shift between NH<sub>2</sub> and NH<sub>3</sub><sup>+</sup> i.e., 1.6 eV<sup>30</sup> and with the separation of 1.5 eV as obtained from the spectrum of tris(biguanide) chromium(III) complex, one would expect a spectrum with a FWHM of 3.8 eV which is broader at least by 0.9 eV from any spectra obtained for biguanide complexes. It rules out the possibility of the presence of a quarternary nitrogen atom in the complex molecule. Alternatively, the metal biguanide structure can only be viewed as having extensive  $\pi$ -electron delocalisation over the whole molecule.

It can, hence, be concluded that the metal biguanides and metal N'-amidinoisoureas are having extensive  $\pi$ -electron delocalisation over the whole molecule as evidenced through various chemical and physical properties of these compounds. This has given rise to pseudoaromatic behaviour in these metal chelates.

#### Experimental

Stability of >N-X bonds in these halogeno-substituted complexes towards hydrolysis at different temperatures (from 50°C to 90°C) was studied by recording the pH change of aqueous or methanolic solutions of these compounds. The change of pH with time at different temperatures was measured by "Cambridge pH meter".

Electronic spectra were recorded in "Beckmann DB-G" spectrophotometer in aqueous solutions at ambient temperatures.

Thermal analysis of these halogeno-substituted and unsubstituted complexes of Cu(II), Ni(II), Co(III) and Cr(III) was performed in "Derivatograph" system Paulik Paulik and Erdely with a temperature rise of 5°C/minute.



I. r. spectra were taken in "Beckmann, IR-12" spectrophotometer in nujol mull and in KBr phase.

### Acknowledgement

We pay our respect to Prof. P. Rây whose monumental work in the field of metal biguanides inspired us all through our investigation.

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