Reactions of Coordinated Ligands: Halogenation, Sulphonation & Nitration of Some Metal Complexes with N-Alkylbiguanide & O-Alkyl-N-amidinoisoureas*

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Compounds obtained by halogenation, sulphonation and nitration of some N-alkylbiguanide and O-alkyl-N'-amidinoisourea complexes of Cu(II), Ni(II), Co(III) and Cr(III) have been reported. Physicochemical studies on the complexes obtained indicate that substitution takes place at the coordinated nitrogen atoms. Thermal stabilities of $\text{N-X}$ ($X = \text{Cl/Br}$) bond depend mainly on the nature of metal atom. Halogenation of chelate ring increases $M-N$ bond lengths and interelectronic repulsion parameter ($H$) and decreases splitting energy parameter (10 $Dq$) and ring current density.

TABLE metal chelates of biguanides and N'-amidinoisoureas are believed to possess ring currents. This conclusion is supported by X-ray crystallographic and NMR spectral studies on some bis(biguanidinium) metal complexes as well as by their electrophilic substitution reactions. Similarly, the presence of strong ring currents in metal acetylacetonates has been supported by several workers on the basis of electrophilic substitution reactions and spectral studies. The present paper describes electrophilic substitution reactions of Cu(II), Ni(II), Co(II) and Cr(III) complexes with N-alkylbiguanides (I, $Z = \text{NH}$-alkyl) and O-alkyl-N'-amidinoisoureas (I, $Z = \text{O}$-alkyl).

The stabilities of these complexes are dependent on the $\pi$-electron delocalization in the chelate rings and unrelated to ligand basicities. The presence of alkyl groups in the ligand decreases the stability of (I with $Z = \text{NH}$-alkyl relative to metalbiguanides, but increases the same for (I with $Z = \text{O}$-alkyl relative to metal-amidinoisoureas.

Materials and Methods

Reagents used were of AR grade. The starting compounds were prepared by the known methods and purified by repeated recrystallizations from water. Analyses and oximetric titrations were carried out using conventional methods. The conductances and $p$H of the solutions were measured using Sytronics, type 302 conductivity bridge and Cambridge $p$H meter, respectively. IR spectra (4000 to 400 cm$^{-1}$) in nujol and KBr phases were recorded using Beckman IR-12 spectrophotometer. The magnetic susceptibilities were measured at two field strengths with Guoy-type balance using Hg[Co(CNS)$_4$]$_2$ as the calibrant. Electronic spectra (1000-350 nm) were recorded using Beckman DB-G spectrophotometer and thermal analyses (50 to 500$^{\circ}$) carried out using derivatograph (Pauik, Pauik and Erdey).

Chlorination — (i) For the preparation of compounds 1-5 (Table 1), a very fine suspension of the corresponding unsubstituted complex hydroxide in carbon tetrachloride (100 ml) was made. Chlorine gas ($\text{HCl + KMnO}_4$), was passed at the rate of 100 bubbles per min through the suspension at 10$^{\circ}$ for 30 min when colour of the mixture changed from rose-red to brown. Two drops of water were added to moisten the brown product and the passage of chlorine was continued for 4 hr more. The bluish-green mass was filtered, dried and crystallized from water. The compounds are moderately soluble in water and methanol; but insoluble in benzene, ether, chloroform, etc.

(ii) The complexes 6 and 7 (Table 1) were prepared by the above method but chlorine gas was passed through the suspension at 0$^{\circ}$ for 6 hr. The desired product was obtained by adding an excess of ethyl alcohol to highly concentrated aqueous solutions.
The compounds are highly hygroscopic and soluble in methanol.

(iii) The compounds 8-13 (Table 1) were prepared from the corresponding complex hydrides by passing a rapid stream of chlorine through their aqueous solutions (1%o). Initially brown foams formed which subsided within 1 hr leaving either precipitates or pasty masses. These were crystalized from methanol and dried over KOH.

Bromination — (i) The compounds 14 and 15 (Table 1) were prepared by adding dropwise a slight excess of liquid bromine with constant stirring to a thick aqueous suspension of the corresponding complex hydrides at 0°. The light blue products obtained were filtered, washed with ice-cold water and dried over calcium chloride. The compounds are sparingly soluble in water and methanol.

(ii) Compounds 16, 17 and 18 (Table 1) were prepared similarly, using saturated aqueous solution of the complex hydrides.

Nitrination — For the preparation of the nitro compounds 19-22 (Table 1), nitrogen dioxide, prepared from Pb(NO₃)₄ and dried over H₂SO₄, was bubbled through a fine suspension of the corresponding complex hydrides at 0°. The rate was maintained at 70-80 bubbles/min. After 2 hr, the suspension was filtered and the residue washed with carbon tetrachloride and dried in vacuo over KOH.

Sulphonation — The compounds 23-26 (Table 1) were prepared by passing sulphur trioxide vapours (prepared from P₄O₁₀ and H₂SO₄) at the rate of 60-70 bubbles per min through the fine suspension of the corresponding complex hydrides in carbon tetrachloride at 10°. After 1 hr, the pasty mass was filtered, washed with carbon tetrachloride and dissolved in the minimum quantity of methyl alcohol. The solution was filtered and the filtrate was run into a large excess of (i) dimethylformamide for Co(III) complexes (ii) ether for Cr(III) complexes. The precipitate obtained in each case was dried in vacuo over KOH.

Preparation of sulphates from chlorides — The sulphate derivatives of the chloro-substituted complexes (compounds 27-33 in Table 1) were prepared by adding a saturated solution of sodium sulphate (30-40 ml) to an aqueous solution of the corresponding chloride at 20°. The resulting mixture was kept undisturbed overnight when beautiful crystals were obtained. These were filtered, washed with water and dried.

Preparation of nitrates from chlorides — The nitrates (compounds 34-38 in Table 1) were prepared by mixing a saturated solution of silver nitrate in methanol (200 ml) with the saturated methanolic solution (20 ml) of the corresponding chloride. The precipitate of AgCl was filtered off and the filtrate on slow evaporation, produced pinkish blue crystals which were washed with methanol and dried. The compounds are highly soluble in water, but less in methanol.

Preparation of HgCl derivatives — Compounds 39-44 (Table 1) were obtained by mixing 25 ml each of the saturated solutions of chlorosubstituted complex chloride and mercuric chloride at 10°. Voluminous crystalline precipitates, insoluble in common solvents, were obtained after 12 hr.

Satisfactory analyses (within ±1%) of these compounds for metals, halogens and nitrogen (Duma’s method) were obtained. Magnetic, spectral and conductance data indicate the metal atoms to be in their normal oxidation states (nickel and copper in +2 and cobalt and chromium in +3) and correspond to the respective molecular formula (Table 1).

The compounds explode on heating with or without conc.
Halogen estimation neutral with and acidic silver nitrate solution revealed the presence of both ionic and covalent halogens. They oxidize Fe$^{2+}$, Mn$^{2+}$, I$^{-}$ and SO$_4^{2-}$ ions to Fe$^{3+}$, MnO$_2$, I$_2$ and SO$_2^-$ and are reduced easily by boiling water, ethanol, dimethylformamide, ammonia or dilute alkali (NaOH/KOH) to the corresponding dehalogenated products.


**Results and Discussion**

The physical and chemical properties of the halogenated complexes indicate the presence of $\gg$N$-$X (X = Cl/Br) groups each of which acts as a 2-electron oxidizing agent by the following type of hydrolysis

$$\gg$N$-$X + H$_2$O $\rightarrow$ N$-$H$+$ HOX

... (I)

Oxidation values per mole indicate the presence of two $\gg$N$-$X groups per chelate ring in all the complexes except for Cu(II) (oxidn/mole toward FeSO$_4$ = 4) which contains one $\gg$N$-$X group per chelate ring$^4$. This may be due to the decreased electron density in monosubstituted ring. Jahn-Teller distortion or nonplanarity of the molecule$^6$. The formation of HgCl$_2$ derivatives$^{28}$ suggests the presence of free$-$NH$_3$ groups (I) and ring substitution.

Attempted halogenation, sulphonation and nitration of the free ligands failed in aqueous or non-aqueous media. A mixture of ligand and metal salts, subjected to chlorination, bromination, nitration and sulphonation reactions under identical conditions, produced no substituted products indicating complex formation as the main criteria for success of these reactions.

Among the higher valent metal complexes with these ligands$^{24-30}$, only hydrolytically unstable and metastable ones are substituted by chlorine in the presence of moisture. On this basis, the following mechanism (Scheme 1) for halo-substitution has been suggested.

During reduction step (Scheme 1), high electron densities are produced momentarily at the two coordinated nitrogen atoms (shown by arrow) making them susceptible to electrophilic attack.

The halogenated complexes are always less stable than the corresponding simple ones both thermally and chemically. The stabilities of the halogenated complexes (from pH measurements) are of the same order as those of the corresponding dehalogenated ones with respect to the nature of ligands and the metal atoms$^{38-40}$ except for Cu(II) complexes which are comparatively more stable probably due to monosubstitution per chelate ring. Highly stable complexes ($92 \times 10^{12}$ for bis and $9.7 \times 10^{10}$ for tris complexes) were successfully halogenated. Less stable complexes undergo complete rupture under these electrophilic conditions.

Sulphonation and nitration were possible with a few complexes (Table 1). They are instantaneously hydrolysed according to Eq. 1 (X = NO$_2$ or SO$_4^-$).

**IR spectra** — Assignments of some bands of these complexes have been made elsewhere$^{6,32,33}$. A band around 3300 cm$^{-1}$ present only in simple and monohalogenated complexes is assigned to $\nu$N$_2$-H (I). The highest and lowest frequency bands between 1700 and 1500 cm$^{-1}$ are assigned to asymmetric and symmetric $\nu$N$-$C$-$N (ring) respectively. Splitting of the former and broadening of the latter bands were observed in the monohalo-substituted complexes. Bands at 1430 (ring vibration)$^{34}$ and 1250 cm$^{-1}$ (C$-$NH$_3$) undergo red- and blue-shifts after halogenation. The shifting of these bands can be explained if the presence of a strong chelate ring current is taken into account.

**Thermal analysis** — Interpretation of TGA curves (Fig. 1) was made on the basis of weight loss and product analyses.

Endothermic step-I indicates loss of lattice-held or coordinated water molecules. Higher temperatures for Ni(II) complexes indicate the presence of coordinated water (curve 6, Fig. 1). The dehydrated complexes are transformed into the original complexes in the presence of moisture. Highly exothermic step-II corresponds to loss of halogens due to $\gg$N$-$X bond cleavage. $\gg$N$-$Cl bond is thermally stabler than $\gg$N$-$Br (curves 4, 5, Fig. 1). Products left are mainly dehalogenated complexes (80%) together with some decomposed products. Step-III probably involves fusion and decomposition and leaves a polymeric residue. Products left after step-IV were metal oxides or sulphates.

**Electronic spectra** — The splitting energy (10 $Dq$) and interelectronic repulsion ($B$) parameters for simple and halogenated complexes were calculated. For octahedral Ni(II) complexes, parameters were determined from the ratio $\nu_4/\nu_2$ and the relation $\nu_4 + \nu_2 - 30 Dq = 15 B$ (Table 2). For Cr(III) complexes, $B$ was calculated from the relation $B = (2\nu_4^2 + \nu_2^2 - 30 \nu_4 \nu_2)/(15 \nu_2 - 27 \nu_4)$. For Co(III) complexes, the relation $C = 4B$ was used to evaluate the parameters (Table 3).

A decrease in 10 $Dq$ and increase in $B$ values was observed for the halogeno-substituted complexes.
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Fig. 1 — TGA and DTG curves for Cu(II), Ni(II) and Cu(III) complexes

(1) Ni(HMIm)2Cl2-H2O
(2) Cu(HMIm)2Cl2-H2O
(3) Cu(ClO4)2-6H2O
(4) Cu(NH3)4Cl2-6H2O
(5) Cu(NH3)2Cl2-6H2O
(6) Ni(NH3)2Cl2-2H2O

Temperature, °C

Weight Loss

500 500
Table 2 — Electronic Spectral Data* of Cu(II) Complexes in Water or Methanol

<table>
<thead>
<tr>
<th>Compound</th>
<th>ν (cm⁻¹)</th>
<th>10 Dq (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(Hbgl)₂Cl₂</td>
<td>1887</td>
<td>18800</td>
</tr>
<tr>
<td>Cu(mHbgl)₂Cl₂</td>
<td>18796</td>
<td>18800</td>
</tr>
<tr>
<td>Cu(aiul)₂</td>
<td>19525</td>
<td>19500</td>
</tr>
<tr>
<td>Cu(mHbgl)₂Cl₂</td>
<td>18181</td>
<td>18180</td>
</tr>
<tr>
<td>Cu(cmHbgl)₂Cl₂</td>
<td>16129</td>
<td>16130</td>
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<tr>
<td>Cu(mHbgl)₂Cl₂</td>
<td>16000</td>
<td>16000</td>
</tr>
<tr>
<td>Cu(aiul)₂</td>
<td>14084</td>
<td>14080</td>
</tr>
<tr>
<td>Cu(cmHbgl)₂Cl₂</td>
<td>14818</td>
<td>14810</td>
</tr>
</tbody>
</table>

* Molar absorption values in parentheses.

Table 3 — Electronic Spectral Data* of Ni(II), Co(II) and Cr(III) Complexes in Water or Methanol

<table>
<thead>
<tr>
<th>Compound</th>
<th>Transitions (cm⁻¹)</th>
<th>10 Dq (cm⁻¹)</th>
<th>B (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ni(dcHbgl)₂(H₂O)₄]Cl₂</td>
<td>ν₁ = 15700</td>
<td>25590</td>
<td>9700</td>
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<tr>
<td>[Ni(mHbgl)₂(H₂O)₂]</td>
<td>ν₁ = 15137</td>
<td>26750</td>
<td>9200</td>
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<tr>
<td>[Ni(aiul)₂(H₂O)₄]</td>
<td>ν₁ = 15267</td>
<td>26880</td>
<td>9300</td>
</tr>
<tr>
<td>Co(Hbgl)₃(OH)</td>
<td>ν₁ = 20746</td>
<td>17932</td>
<td>22500</td>
</tr>
<tr>
<td>Co(mHbgl)₃(OH)</td>
<td>ν₁ = 20661</td>
<td>17577</td>
<td>22400</td>
</tr>
<tr>
<td>Co(mHbgl)₃(OH)</td>
<td>ν₁ = 20500</td>
<td>17350</td>
<td>22200</td>
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<tr>
<td>Co(dcHbgl)₃Cl</td>
<td>ν₁ = 18020</td>
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<td>22020</td>
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<tr>
<td>Co(cmHbgl)₃Cl</td>
<td>ν₁ = 17980</td>
<td>26310</td>
<td>20060</td>
</tr>
<tr>
<td>Co(dcHbgl)₃Cl</td>
<td>ν₁ = 18030</td>
<td>25860</td>
<td>19980</td>
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</tbody>
</table>

*Figures in parentheses indicate molar absorbance.

The 10 Dq value decreases due to halosubstitution, but this reduces the ligand field strength as well as the covalency resulting in the decrease in the 10 Dq and B values respectively.

References