Complexes of Al(III) and Be(II) with Biguanide

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Biguanide, IR spectra

Three complexes of biguanide (C₅N₅H₇) having the compositions [Be(C₅N₅H₆)OH • H₂O], [Be(C₅N₅H₇)₂(OH)]₂, and [(C₅N₅H₇)₂Al(OC₂H₅)Cl] have been synthesised and characterized by elemental analysis and IR spectra.

Introduction

Biguanide can function as a bidentate ligand with a replaceable hydrogen atom in a potentially acidic imino group and a coordinating amino group for chelation with metal ions. Structurally, it can be represented as

\[
\text{H}_2\text{N} - \text{C} = \text{N} - \text{C} = \text{NH}_2
\]

\[
\text{NH} \quad \text{NH}
\]

Although plenty of informations have so far been gathered regarding the preparation and properties of biguanide and substituted biguanides of transition metals², very few refer to those of non-transition elements². With the development of crystal and ligand field theory, it has been postulated that orbital perturbation takes place due to metal-ligand electrostatic interaction for which the metal outer orbitals undergo hybridisation, using the vacant d, s and p orbitals into a symmetric form. These hybridised orbitals directed in space overlap with the filled ligand orbitals to form metal ligand coordinated bonds. This idea led to the exploration and study of the possibility of metallic and overlapping and thus the formation of coordination compounds of non-transitional elements. The stability of these complexes will, however, depend on the donor acceptor property of the ligand and the central ion.

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Experimental

Materials: Biguanide base¹, and beryllium(II)-acetylacetonate³ were prepared as described in the literature. Anhydrous aluminium(III) chloride used was reagent quality (E. Merck).

Method of preparation of the complexes

Monochloro-bis(biguanidino)-ethoxy-aluminium-(III)-chloride: \([\text{Be(C}_5\text{N}_5\text{H}_7\text{)}\text{Al(OC}_2\text{H}_5\text{)Cl}] (1)\)

10 g of biguanide base were dissolved in 100 ml ethanol and to the solution 20.7 g of beryllium(II)-acetylacetonate in 100 ml ethanol were added drop wise with constant stirring when a white precipitate appeared. The precipitate was washed with alcohol and dried over fused calcium chloride in a desiccator. The compound is stable in the dry state. It reacts alkaline to litmus.

Bis(biguanidino)beryllium(II)-hydroxide: \([\text{Be(C}_5\text{N}_5\text{H}_7\text{)}\text{OH} • \text{H}_2\text{O}] (2)\)

10 g of biguanide base were dissolved in 100 ml ethanol and to the solution 20.7 g of beryllium(II)-acetylacetonate in 100 ml methanol were added dropwise with constant stirring when a white precipitate appeared. The precipitate was washed with alcohol and dried over fused calcium chloride in a desiccator. The compound is stable in the dry state. It reacts alkaline to litmus.

Bis(biguanidino)beryllium(II)-hydroxide: \([\text{Be(C}_5\text{N}_5\text{H}_7\text{)}\text{OH}] (3)\)

5 g of biguanide base were dissolved in 100 ml methyl alcohol and to the solution 5.2 g of beryllium acetylacetonate in 100 ml methanol were added dropwise with constant stirring. The solution was then refluxed for about six hours. It was then cooled overnight when a white crystalline precipitate

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Table I. Analytical data of Be(II) and Al(III) complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>C [%]</th>
<th>H [%]</th>
<th>N [%]</th>
<th>OC2H5 [%]</th>
<th>Cl [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 [Al(C2N5H7)2 • (OC2H5)Cl]Cl</td>
<td>Found: 20.58</td>
<td>5.30</td>
<td>40.25</td>
<td>12.88</td>
<td>20.20</td>
</tr>
<tr>
<td></td>
<td>Caled: 20.86</td>
<td>5.51</td>
<td>40.58</td>
<td>13.04</td>
<td>20.58</td>
</tr>
<tr>
<td>2 Be(C2N5H6)OH • H2O</td>
<td>Found: 16.40</td>
<td>6.76</td>
<td>47.92</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>Caled: 16.66</td>
<td>6.25</td>
<td>48.61</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>3 Be(C2N5H7)2 (OH)2</td>
<td>Found: 19.35</td>
<td>6.40</td>
<td>56.85</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>Caled: 19.59</td>
<td>6.53</td>
<td>57.14</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

Discussion

The biguanide molecule should have the following fundamental infrared absorption frequencies: The N—H stretching absorption, the N—H deformation, the −NH3⁺ symmetrical bending and the amide (1). All these bands were observed in the complexes of Be(II) and Al(III) (see Table II). The strong bands in the region ~1350–1500 cm⁻¹ have been attributed to the B—N stretching vibration by earlier workers. In the present series of compounds, ν(Be—N) or ν(Al—N) appear at lower frequencies (~750 cm⁻¹) due to the highly electropositive character of Be or Al in comparison to B. The strong bands at ~1370 cm⁻¹ and at ~1500 cm⁻¹ are assigned to be C—N stretching vibration and −NH3⁺ symmetrical bend respectively. Due to the electron releasing character of the −OC₂H₅ group, a new band (~1100 cm⁻¹) is observed in compound (1). This is assigned to be C—OR stretching vibration.

Thermal analysis of the complexes shows a pronounced two step decomposition. The first step generally leads to the formation of an anhydrobase of the metal biguanide and the final step indicated the overall decomposition of the compound to the corresponding metal oxide.

1 P. Ráy, Chem. Revs. 61, 313 [1961].
2 D. Sen and A. Moitra, J. inorg. nuclear Chem. 34, 3643 [1972].