

Complex Compounds of Piperazine Dibiguanide with some Transition Metals

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Complex compounds of piperazine dibiguanide with chromium (III), cobalt (III), palladium (II), and osmium (VI) have been prepared and characterised.

Complex compounds of copper and nickel with piperazine dibiguanide have already been reported by Rây and Chowdhury¹. The present communication describes preparation and properties of the complex compounds of the above biguanide with chromium (III), cobalt (III), palladium (II) and osmium (VI).

With the exception of osmyl piperazine dibiguanide base, all the other complexes are insoluble or sparingly soluble in water. The complexes in general are insoluble in alcohol, acetone, chloroform and ether.

The palladium (II) and osmium (VI) compounds can be heated upto 110° without any appreciable change in composition while the chromium (III) and cobalt (III) complexes are unstable at this temperature. When heated to 90°, hydroxo aquo chromium/cobalt piperazine dibiguanide chloride $[\text{OH} \cdot \text{H}_2\text{O} \cdot \text{M Pipz (BigH)}_2] \text{Cl}_2 \cdot 0.5\text{H}_2\text{O}$ loses water giving rise to a dark red product which on analysis corresponded to the composition $(\text{OH} \cdot \text{Cl} \cdot \text{M Pipz (BigH)}_2) \text{Cl}$ where Pipz (BigH)_2 = a molecule of piperazine dibiguanide ($\text{C}_8\text{H}_{18}\text{N}_{10}$), and $\text{M} = \text{Cr}$ or Co . On exposure to moist air the dehydrated complexes regained their original rose red and orange red colours respectively, with the formation of the original ones. Loss of water from the palladium and osmyl complexes at a comparatively higher temperature than those of the corresponding cobaltic and chromium complexes is apparently due to the relatively higher stability of the former complexes.

Chromium (III) piperazine dibiguanide complexes are paramagnetic with a value for the magnetic moment corresponding to three unpaired electrons ($\mu_{\text{eff}} \sim 4.12$ B.M. at 31°). The cobalt (III) complexes are diamagnetic as expected. The magnetic moment values are in conformity with their octahedral configuration with $d^2 sp^3$ hybrid bonds. Palladium (II) complexes are also diamagnetic, suggesting a square planar structure.

The six oxidation states of osmium in the osmium complexes was confirmed by iodometric titration after extracting the liberated iodine with chloroform. All the

compounds yielded two equivalents of iodine per osmium atom. This indicates two electron reduction ($\text{OsVI} \rightarrow \text{OsIV}$). In sharp contrast to the paramagnetism expected for two $d\epsilon$ electrons, the room temperature magnetic susceptibility measurements show that the complexes are diamagnetic. This is probably due to the splitting of the t_{2g} orbitals to a lower singlet and an upper doublet, the separation between the two levels being sufficient for the two electrons of Os(VI) to pair in the singlet².

EXPERIMENTAL

Piperazine dibiguanide sulphate was prepared according to the method described by Rây and Chowdhury¹.

Hydroxo-aquo-chromium piperazine dibiguanide hydroxide: A solution of chrome alum (0.5 g in 25 ml. water) was added dropwise to a solution of piperazine dibiguanide sulphate (1 g.) in sodium hydroxide with occasional warming on water bath till a rose red precipitate was obtained. The precipitate was filtered and washed with cold water. It was dried in a desiccator containing fused calcium chloride and potassium hydroxide.

The substance is sparingly soluble in water and insoluble in alcohol, chloroform, acetone etc. It is readily decomposed by mineral acids. It suffers decomposition when heated above 100°.

Found: Cr 13.68, N 35.32, H_2O 12.07 (at 100°); $[\text{OH} \cdot \text{H}_2\text{O} \cdot \text{Cr Pipz}(\text{BigH})_2] (\text{OH})_2 \cdot 0.5\text{H}_2\text{O}$ requires Cr 13.47, N 36.26, H_2O 11.66%.

Hydroxo-aquo-chromium piperazine dibiguanide chloride: A suspension of the complex base in water was digested with a strong solution of ammonium chloride till evolution of ammonia ceased. A clear red solution was obtained. It was kept in a refrigerator overnight when a rose red mass separated out. It was separated, washed with cold water and dried in vacuum over fused calcium chloride.

The substance forms rose red powder, sparingly soluble in water, but insoluble in common organic solvents. It is decomposed when heated above 90°.

Found: Cr 12.24, N 32.10, Cl 16.66, H_2O 6.28;

$[\text{OH} \cdot \text{H}_2\text{O} \cdot \text{Cr Pipz}(\text{BigH})_2] \text{Cl}_2 \cdot 0.5 \text{H}_2\text{O}$ requires Cr 12.35, N 32.49, Cl 16.87, H_2O 6.41%.

Hydroxo-aquo-cobaltic piperazine dibiguanide hydroxide: A solution of cobalt chloride (0.7 g. in 50 ml. water) was added to a solution of piperazine dibiguanide sulphate (2.2 g.) in strong alkali when a red solution was obtained. A vigorous current of air was passed through the solution for about 6 hrs.. A rose red solution was obtained. It was warmed on water bath and then cooled in a refrigerator. A rose

2. K. A. K. Lott and M. C. R. Symons, *Jour. Chem. Soc.*, 1960, 973.

red precipitate was obtained. The precipitate was washed with cold water and alcohol. It was then dried in a desiccator over fused calcium chloride and potassium hydroxide.

The substance forms rose red powder insoluble in water, alcohol, chloroform and acetone. It undergoes decomposition when heated above 100°.

Found : Co 15. 98, N 36. 19, H₂O 9. 38 (at 100°) ;

[OH.H₂O.Co Pipz (BigH)₂] (OH)₂, requires Co 15. 45, N 36. 64, H₂O 9. 42%.

Hydroxo-aquo-cobaltic piperazine dibiguanide chloride : This compound was prepared by the action of ammonium chloride on a suspension of the complex base in water. An orange red precipitate was obtained. It was filtered, washed with cold water and dried in a vacuum desiccator over fused calcium chloride.

The substance forms orange red powder insoluble in water and common organic solvents. It is decomposed by dilute mineral acids. It can be heated upto 90° without any decomposition.

Found : Co 13.86, N 33. 20, Cl 16. 25, H₂O 6. 45 (at 90°) ;

[OH.H₂O. Co Pipz (BigH)₂] Cl₂, 0.5H₂O requires Co 13. 79, N 32. 72, Cl 16.59, H₂O 6. 31%.

Palladium piperazine dibiguanide hydroxide : 50 ml. of '001 M solution of palladium chloride in dilute hydrochloric acid was added to 0.6 g. of piperazine dibiguanide sulphate dissolved in sodium hydroxide solution. The resultant solution was alkaline. It was warmed on water bath for some time when a light yellow mass separated out. It was filtered and washed first with cold water and then with alcohol. It was dried in a desiccator over fused calcium chloride and potassium hydroxide.

The compound forms light yellow powder, insoluble in water, alcohol, chloroform and acetone. It liberates ammonia when treated with ammonium salts.

Found : Pd 21. 78, N 28. 54, H₂O 25. 52 (at 110°) ;

[Pd Pipz (BigH)₂] (OH)₂, 5 H₂O requires Pd 22. 03, N 28. 80, H₂O 26. 02%.

Palladium piperazine dibiguanide chloride : This compound was obtained as a light yellow residue when the complex base was digested with a solution of ammonium chloride till the evolution of ammonia ceased. The product was washed with cold water and alcohol. It was dried in air.

The substance forms light yellow powder sparingly soluble in hot water, insoluble in alcohol, chloroform and benzene. It is decomposed by concentrated hydrochloric acid but is unaffected by dilute mineral acids.

Found : Pd 21. 93, N 28. 69, Cl 14. 70, H₂O 11. 71 (at 110°) ;

[Pd Pipz (BigH)₂] Cl₂, 3 H₂O requires Pd 21. 98, N 28. 82, Cl 14. 62, H₂O 11. 12%.

Osmyl piperazine dibiguanide hydroxide : This was obtained as a yellow precipitate when a solution of 70 ml. sodium osmate containing 0.19 g. of osmium was added to a solution of .5 g. piperazine dibiguanide in alkali. The precipitate was washed with cold water and dried in a desiccator over fused calcium chloride and potassium hydroxide.

The compound is fairly soluble in water but insoluble in alcohol, chloroform and acetone.

Found : Os 35.35, N 27.00, H₂O 10.35 (at 110°) ;

[OsO₂ Pipz (BigH)₂] (OH)₂, H₂O requires Os 35.38, N 26.07, H₂O 10.23%.

Osmyl piperazine dibiguanide chloride : Brown crystals of the complex chloride were obtained by treating the complex base with concentrated hydrochloric acid, These were washed with ether and dried in air.

The compound is sparingly soluble in water, insoluble in alcohol, chloroform, acetone and ether. When treated with dilute hydrochloric acid, it dissolves giving rise to a green solution.

Found : Os 31.00, N 22.40, Cl 11.61, H₂O 14.55 (at 110°) ;

[OsO₂ Pipz (BigH)₂] Cl₂, 5 H₂O requires Os 29.86, N 21.98, Cl 11.15, H₂O 14.11%.

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