Unusual Coordination Number of Molybdenum V,

by

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ABSTRACT

In the present work a new coordination compound of molybdenum V with hexamethyl melamine has been obtained and found that the ratio of molybdenum pentachloride to hexamethylmelamine is 1: 2. This is an unknown coordination number of molybdenum V.

INTRODUCTION

Molybdenum is found in the various oxidation states, which exhibit several coordination numbers such as molybdenum 0; exhibits 6, molybdenum II; 4, 5, 7, 8, 9, molybdenum III; 6, 8, molybdenum IV; 4, 5, 6, 8, molybdenum V; 5, 6, 8 and molybdenum VI exhibits 4, 6.

The coordination number 7 was reported only in the following complexes\(^1,2\) in which the oxidation state of molybdenum is II, \([\text{Mo(diars)}_2\text{CO}]^{+2}\text{I}^-\) and \([\text{Mo(diars)(CO)}_3\text{I}_2]\)

In the present work a complex of molybdenum V with coordination number of seven has been obtained in dry ethyl-acetate from the reaction of fused molybdenum pentachloride and hexamethylmelamine. Light green crystalline compound is rather stable in dry air. It has also been attempted to get higher coordination number of molybdenum V with hexamethylmelamine, but all experiments were unsuccessful. In every case coordination numbers of seven was found.

The analytical data which obtained from the elemental analysis, magnetic susceptibility measurements and infrared spectrum
have indicated that complex should be in the following composition \([\text{MoCl}_6(\text{HMM})_2]\) and bonding between hexamethylenamine and molybdenum pentachloride takes place through nitrogen. H.M.M. stands for hexamethylenamine which is very quire Lewis base with six amine grouping inside.

It should be noted that molybdenum pentachloride is a strong Lewis acid. So the reaction between them takes place readily.

Since complex shows a magnetic susceptibility of 1, 7 B. M. which means one free electron in the structure, the orbital diagram of it, is likely to be either an inner complex type;

\[
\begin{array}{c}
\text{Energy} \rightarrow \\
\begin{array}{c|c|c|c|c}
\uparrow & \text{XX} & \text{XX} & \text{XX} & \text{XX} \\
\downarrow & \text{4d} & & & \\
\end{array}
\begin{array}{c|c|c}
\text{XX} & \text{XX} & \text{XX} \\
\downarrow & \text{5s} & \text{5p} \\
\end{array}
\end{array}
\]

It indicates that a set of \(d^4p^2\) hybrid orbitals has been formed and that these are occupied by electron pairs (xx) donated by the seven ligands which two of them are H. M. M and five of them are chlorine electrons. It thus predicts that there will be paramagnetism due to one unpaired electron.

Or an outer complex type;

\[
\begin{array}{c}
\text{Energy} \rightarrow \\
\begin{array}{c|c|c|c|c|c}
\text{XX} & \text{XX} & \text{XX} & \text{XX} & \text{XX} \\
\downarrow & \text{4d} & & & & \\
\end{array}
\begin{array}{c|c|c|c}
\text{XX} & \text{XX} & \text{XX} & \text{XX} \\
\downarrow & \text{5s} & \text{5p} & \text{6s} \\
\end{array}
\end{array}
\]

It indicates that a set of \(d^5p\) hybrid orbitals has been formed and occupied by electron pairs (xx) donated by seven ligands and it shows that 6s orbital has been occupied by the one of the 4d electrons.

Now, second diagram could be more considarable, because the complex oxidizes slowly in air. As this hybridization is the same with seven coordinated zirconium\(^1\,^3\) and hafnium\(^1\) it is possible to say, that complex has a geometry of pentagonal bipyramidal.
EXPERIMENTAL

Hexamethylen melamine has been prepared from syanuric chloride and dimethylamine in dry acetone. Molybdenum pentachloride was prepared from molybdenum (B.D.H) and chlorine in a special apparatus.

Preparation of complex: 0.546 g (2 x 10^{-3} M) MoCl_5 was dissolved in 25 ml ethyl-acetate, dried over calcium chloride. 0.840 g (4 x 10^{-3} M) hexamethylen melamine was dissolved in ethyl-acetate too, and was added drop by drop into the hexamethylen melamine solution. Light green compound formed in each drop of molybdenum pentachloride. After addition was completed the precipitate was allowed to stand for three hours. The crystals was filtered by a buchner funnel and washed with ethylacetate. As the appropriate solvent could not be found recrystallizations could not be made. Instead the precipitation was made slowly in dilute solutions and the precipitate washed with its solvent several times. Compound was dried in a vacuum dessicator over calcium chloride.

In the same way two other compounds in compositions 1:1 and 1:3 was attempted to prepare but analytical result have indicated that both of these are the same with the compound in compositions 1:2 described above.

Yield, melting point and analytical data for the product are recorded in the table below.
Magnetic measurements was made on a Gouy type magnetic balance and corrections was made by Pascal constants 6.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Found (%)</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>H</td>
<td>N</td>
<td>Cl</td>
</tr>
<tr>
<td>MoCl₂.2H₂O.M.</td>
<td>29.92</td>
<td>5.27</td>
<td>24.10</td>
<td>24.80</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Formula</th>
<th>Required (%)</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>H</td>
<td>N</td>
<td>Cl</td>
</tr>
<tr>
<td>C₁₂N₃H₃₂Cl₅Mo</td>
<td>31.13</td>
<td>5.22</td>
<td>24.20</td>
<td>25.59</td>
</tr>
</tbody>
</table>

Yield : % 96  
M.P : 230°C (decomp)

REFERENCES


ÖZET

Bu çalışmada molybden V ile hexamethyl melaminden yeni bir koordinasyon bileşği hazırlanı ve bu bileşikte molybden pentaklorürün hekzametilmelamine oranı 1:2 olarak bulundu. Bu ise moliibden V için bilinmiyen yeni bir koordinasyon sayısıdır.
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