Communications

de la faculté des sciences
de l'université d'ankara

Série B: Chimie

Tome 18 B
Année 1971

Complexes of Molybdenum with Sulphoxides

by

necla gündüz

6

Faculté des Sciences de l'Université d'Ankara
Ankara, Turquie
La Revue "Communications de la Faculté des Sciences de l'Université d'Ankara" est un organe de publication englobant toutes les disciplines scientifiques représentées à la Faculté: Mathématiques pures et appliquées, Astronomie, Physique et Chimie théorique, expérimentale et technique, Géologie, Botanique et Zoologie.

La Revue, à l'exception des tomes I, II, III, comprend trois séries

Série A: Mathématiques, Physique et Astronome.
Série B: Chimie.
Série C: Sciences naturelles.

En principe, la Revue est réservée aux mémoires originaux des membres de la Faculté. Elle accepte cependant, dans la mesure de la place disponible, les communications des auteurs étrangers. Les langues allemande, anglaise et française sont admises indifféremment. Les articles devront être accompagnés d'un bref sommaire en langue turque.

Complexes of Molybdenum with Sulphoxides

by

NECLĂ GÜNDÜZ

(Department of General Chemistry, Faculty of Science, Ankara University)

ABSTRACT

The coordination compounds have been prepared with molybdenum and sulphoxide and thiantrene-V-oxide. The subject has been chosen for two aspects. One is, molybdenum plays an important role in plant and animal bodies and acts as a catalyst. Also it is a fact that some bacteria such as azotobacter vinelandii and nitrogenase can not fix atmospheric nitrogen without molybdenum.

Secondly the diphenyl sulphoxide and thiantrene-V-oxide act as very good ligands for thorium and uranium which are transition elements.

Introduction

Since molybdenum plays an important role in plant and animal bodies it is worthwhile to investigate further the chemistry of it. In order to do this, the sound way, I think, is to prepare new molybdenum compounds, especially coordination compounds and study on them for several reasons. Under the influence of these points, some new complexes of molybdenum with diphenyl sulphoxide and thiantrene 5-oxide. Were prepared.

Diphenyl sulphoxide and thiantrene-5-oxide are fairly new and good ligands for transition elements. (1) (2) (3). They also form coordination compounds with uranium tetrachloride and thorium tetrachloride which have the same stoichiometry.(2)

MoCl₅ forms a complex with diphenyl sulphoxide in dry cyclohexane. As the molybdenum pentha chloride is very unstable in air reaction has been carried out under an inert atmosphere. Light green crystalline MoCl₅. Ph₂SO recrystallises from warm cyclohexane. In the same way only using the 1:3 molybdenum pentachloride and diphenyl sulphoxide, the light green crystal-
line compound MoCl$_5$.3Ph$_2$SO is obtained. But it readily decomposes on warming to give light green crystalline MoCl$_5$.Ph$_2$SO and Diphenyl sulfoxide is recovered from the filtrate.

Spectrophotometric investigations have shown that the $S = 0$ stretching band occurs at 1040 cm$^{-1}$ in diphenyl sulfoxide and shifts to lower frequencies on complex formation, indicating that bonding takes place through oxygen.

The magnetic susceptibility measurements have shown a magnetic moment of 1.68 B. M. which represents 1 free electron in the structure.

Molybdenum pentachloride do not form complexes with diphenyl sulphide, (diphenyl sulphone or thianntrene) under the above conditions. However Complex is formed with thianntrene V-Oxide (Thianox) of composition MoCl$_5$.1 thianox. Even in the presence of large amount of ligand, higher coordination compounds were not obtained. The $S = 0$ stretching band occurs at 1075 cm$^{-1}$ in thianox, shifts to lower frequencies on complex formation.

Solubilities of these complexes in appropriate solvents are too small for molecular weight determinations but from the analytical results it is likely that molybdenum exhibits the expected coordination number of 6. Though it was attempted to obtain the compounds with coordination number 8 but the addition compounds with coordination number 6 were formed.

**Experimental**

MoCl$_5$ was prepared in special apparatus from molybdenum and chlorine under dry atmosphere. Fig. 1.

Diphenyl sulfoxide, m.p 71°, and thianox m.p 143° were prepared by oxidation of the corresponding sulphides. Reactions
<table>
<thead>
<tr>
<th>Compound</th>
<th>Yield (%)</th>
<th>M.p. (°C)</th>
<th>Found (%)</th>
<th>Formula</th>
<th>Required (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoCl₂, Ph₂SO</td>
<td>% 70</td>
<td>161-166°</td>
<td>6.18</td>
<td>Cl₂H₂Cl₂OSMo</td>
<td>6.74</td>
</tr>
<tr>
<td>MoCl₂, l Thianox</td>
<td>% 65</td>
<td>189</td>
<td>13.21</td>
<td>Cl₂H₄Cl₂OS₂Mo</td>
<td>12.68</td>
</tr>
</tbody>
</table>

**Found (%)**

<table>
<thead>
<tr>
<th></th>
<th>S</th>
<th>Cl</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoCl₂, Ph₂SO</td>
<td>6.18</td>
<td>36.90</td>
<td>21.00</td>
</tr>
<tr>
<td>MoCl₂, l Thianox</td>
<td>13.21</td>
<td>35.40</td>
<td>18.60</td>
</tr>
</tbody>
</table>

**Required (%)**

<table>
<thead>
<tr>
<th></th>
<th>S</th>
<th>Cl</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoCl₂, Ph₂SO</td>
<td>6.74</td>
<td>37.28</td>
<td>20.18</td>
</tr>
<tr>
<td>MoCl₂, l Thianox</td>
<td>12.68</td>
<td>35.06</td>
<td>18.97</td>
</tr>
</tbody>
</table>
between the metal salts and the appropriate quantity of sulphoxides were carried out in anhydrous cyclohexane under an inert atmosphere. Yields, m.p and analytical results for the products are recorded in the table.

The magnetic susceptibility measurements, were made by the Gouy Balance.

ÖZET

Bu çalışmada molibdenin sulfoxit kompleksleri hazırlanıtı. Konu iki nokta göz önünde bulundurularak seçildi. Birincisi molibden gerek hayvan ve gerekse bitki bün-yesinde ceryan eden bazı reaksiyonlar için katalizőrdür ve nitrogenez, azota bakter gibi bakteriler molibden olmaksızın hava azotunu tesbit edemezler. İkincisi difenil sulfoxit ve thionax toryum ve uranyum gibi geçiş elementleri için iyi birer ligandlardır.

REFERENCES

Prix de l'abonnement annuel

Turquie : 15 TL ; Étranger : 30 TL.
Prix de ce numéro : 5 TL (pour la vente en Turquie).
Prière de s'adresser pour l'abonnement à : Fen Fakültesi Dekanlığı
Ankara, Turquie.