COMMUNICATIONS

DE LA FACUTÉ DES SCIENCES
DE L'UNIVERSITÉ D'ANKARA

Série B: Chimie

TOME 18 B ANNÉE 1971

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Faculté des Sciences de l'Université d'Ankara
Ankara, Turquie

Communications de la Faculté des Sciences de l'Université d'Ankara

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Complexes of Molybdenum with Sulphoxides

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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 thoruim and uranimu 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 stoicheiometry.(2)

$MoCl_5$ 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 $MoCl_5$. Ph_2SO recrystallises from warm cylohexane. In the same way only using the 1:3 molybdenum penthachloride and diphenyl sulphoxide, the light green crystal-

line compound $MoCl_5.3Ph_2SO$ is obtained. But it readily decomposes on warming to give light green crystalline $MoCl_5.Ph_2SO$ 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 sulphoxide and shifts to lower frequencies on complex formation, indicating that bonding takes place through oxygen.

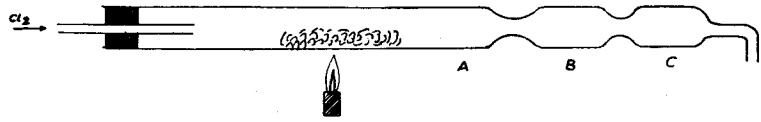
The magnetic susceptibility measurements have shown a magnetic moment of 1,68 B. M. which represents 1 free electron in the structure.

Molybdenum pentachloride do not form complexes with diphenyl sulphide, (diphenyl sulphone or thiantrene) under the above conditions. Hovewer Complex is formed with thiantrene 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 af 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 sulphoxide, m.p 71°, and thianox m.p 143° were prepared by oxidation of the corresponding sulphides. Reactions

TABLE

Compound	Yield (%)	M.p (°C)	Found (%)			Formula	Required (%)		
			S	Cl	Mo		S	Cl	Mo
$MoCl_5.Ph_2SO$	% 70	161–166°	6,18	36,90	21,00	$C_{12}H_{10}Cl_5OSMo$	6,74	37,28	20,18
$MoCl_5$.1 Thianox	% 65	180	13,21	35,40	18,60	$C_{12}H_8Cl_5OS_2Mo$	12,68	35,06	18,97

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 sulfoksit kompleksleri hazırlandı. Konu iki nokta göz önünde bulundurularak seçildi. Birincisi molibden gerek hayvan ve gerekse bitki bünyesinde cereyan eden bazı reaksiyonlar için katalizördür ve nitrogenez, azota bakter gibi bakteriler molibden olmaksızın hava azotunu tesbit edemezler. İkincisi difenil sulfoksit ve thionax toryum ve uranyum gibi geçiş elementleri için iyi birer liganddırlar.

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Prix de l'abonnement annuel

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Prix de ce numéro : 5 TL (pour la vente en Turquie).

Prière de s'adresser pour l'abonnement à : Fen Fakültesi Dekanlığı
Ankara, Turquie.

Ankara Üniversitesi Basımevi - 1972