

COMMUNICATIONS

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

Série B: Chimie

TOME 19 B

ANNÉE 1972

Unusual Coordination Number of Molybdenum V.

by

NECLÂ GÜNDÜZ

5

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

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

Comité de Rédaction de la Série B

C. Tüzün S. Aybar M. Okay

Secrétaire de Publication

N. Gündüz

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 Astronomie.

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.

Adres: Fen Fakültesi Tebliğler Dergisi, Fen Fakültesi, Ankara, Turquie.

Unusual Coordination Number of Molybdenum V.

by

NECLÂ GÜNDÜZ

Department of Chemistry, Faculty of Science, University of Ankara.

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, $[\text{Mo}(\text{diars})_2\text{CO}]^+_2\text{I}^-$ and $[\text{Mo}(\text{diars})(\text{CO})_3\text{I}_2]$

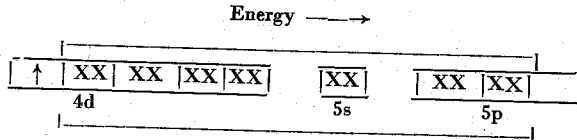
In the present work a complex of molybdenum V with coordination number of seven has been obtained in dry ethyl-acetate from the reaction of fused molybdenum pentachloride and hexamethylmelamine. Light green crystalline compound is rather stable in dry air. It has also been attempted to get higher coordination 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 $[\text{MoCl}_5(\text{HMM})_2]$ and bonding between hexamethylmelamine and molybdenum pentachloride takes place through nitrogen. H.M.M. stands for hexamethylmelamine which is very quire Lewis base with six amine grouping inside.

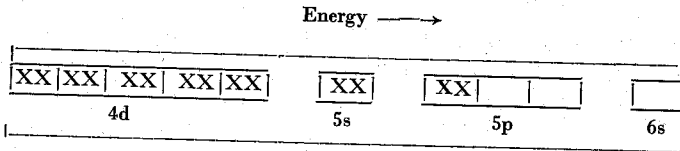
It should be noted that molybdenum pentachloride is a strong Lewis acid. So the reaction between them takes place readily.

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;



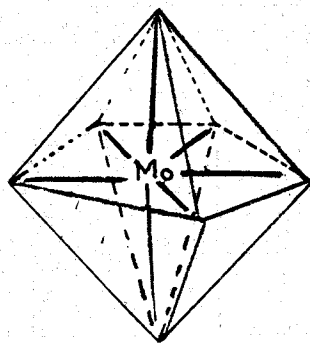
It indicates that a set of d^4sp^2 hybrid orbitals has been formed and that these are occupied by electron pairs (xx) donated by the seven ligands which two of them are H. M. M and five of them are chlorine electrons. It thus predicts that there will be paramagnetism due to one unpaired electron.

Or an outer complex type;



It indicates that a set of d^5sp 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 considerable, because the complex oxidizes slowly in air. As this hybridization is the same with seven coordinated zirconium^{1,3} and hafnium¹ it is possible to say, that complex has a geometry of pentagonal bipyramidal.



EXPERIMENTAL

Hexamethylmelamine has been prepared from syanuric chloride and dimethylamine in dry acetone⁴. Molybdenum pentachloride was prepared from molybdenum (B.D.H) and chlorine in a special apparatus⁵.

Preparation of complex: 0,546 g (2×10^{-3} M) MoCl_5 was dissolved in 25 ml ethyl-acetate, dried over calcium chloride. 0,840 g (4×10^{-3} M) hexamethylmelamine was dissolved in ethyl-acetate too, and was added drop by drop into the hexamethylmelamine 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

Compound	Found (%)			
	C	H	N	Cl
MoCl ₅ .2H.M.M	29.92	5.27	24.10	24.80
Formula	Required (%)			
	C	H	N	Cl
C ₁₈ N ₁₂ H ₃₆ Cl ₅ Mo	31.13	5.22	24.20	25.59
Yield : % 96				
M.P : 230°C (decomp)				

REFERENCES

- [1] F. Cotten and G. Wilkinson Advanced inorganic chemistry, interscience 1962.
- [2] H. L Nigam and R. S. Nyholm Proc. Chem. Soc 1957 321-2.
- [3] G. C. Hampson and L. Pauling. J. A. C. S. 1938, 60, 2702.
- [4] Turgut Gündüz Communications de la Faculte des Sciences de l'Universite D'Ankara Tome 15. B/6 Anneé 1968.
- [5] Neclâ Gündüz. Communications de La Faculte des Sciences de l'Universite D'Ankara Tome 18 B/6 Anneé 1971.
- [6] Selwood P. M. Magneto chemistry 2nd ed., Interscience, 1956.

Ö Z E T

Bu çalışmada molybden V ile hexamethyl melaminden yeni bir koordinasyon bileşiği hazırlandı ve bu bileşikte molibden pentaklorürün heksametilmelamine oranı 1:2 olarak bulundu. Bu ise molibden V için bilinmeyen yeni bir koordinasyon sayısıdır.

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.**