# SOME NEW ORGANIC COMPLEXES OF MOLYBDENUM

by

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## Özet

Molibden gerek hayvan ve gerekse bitki bünyesinde cereyan eden bazı reaksiyonlar için katalizör olduğundan büyük ehemmiyet arzeder. Bu reaksiyonların sonuçları bilinmekte ve fakat mekanizmaları halen bilinmemektedir.

Bundan başka, molibden azotobakter ve nitrogenaz gibi bakterilerin hava azotunu tesbitinde de pek mühim rol oynamaktadır. Bu hayati olayın da mekanizması bilinmemekle beraber molibdenin yardımı olmaksızın bu bakterilerin hava azotunu tesbit edemedikleri gösterilmiştir. Azot hayati olayların dayandığı bir kaç temel taşdan birisi olduğundan, bu sihirli ameliyenin esasının aydınlatılması ve hızla artan dünya nüfusuna bu sayede bol ve ucuz azot bileşikleri temini hususu, bugün için ilmin başlıca konularından birisidir. Çünkü halen bilinen metodlarla elde edilen azot bileşikleri oldukça pahalıdır.

Azot tesbitinin aydınlatılması hususunda yapılan bütün çalışmalar bir netice vermediğinden, ilim adamları bilhassa yeni molibden kompleksleri yapılması ve bunların muhtelif şartlar altında azot tesbiti için denenmesinde büyük faydalar mülâhaza etmektedirler. Zira bu suretle yapılan komplekslerden birisi bu sahada iyi bir netice verebilir.

Nitekim bağ energisi hayli büyük olan hidrojende böyle denemek suretile kinolinli Cu-II tuzu çözeltisinde tesbit edilmiştir.

Bundan dolayı bu çalışmada yeni molibden kompleksleri hazırlandı, koordinasyon kimyaları incelendi ve fakat iyi bir çözücü bulunamadığından azot tesbiti bakımından muhtelif şartlarda denenemedi.

## Abstract

Molydenum plays a very important role in plant and animal bodies. In both cases it functions as a catalyst. Although the result of the catalytic reactions of it are known, the mechanism of the reactions are still open to debate.

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Moreover molybdenum takes a great part in the fixation of atmospheric nitrogen by some species of bacteria, such as azotobacter vinelandii and nitrogenase, In the absence of molybdenum, these bacteria cannot show any activity in connection with nitrogen fixation. At present time nothing is knocwn about the mechanism of the fixation. Since nitrogen is one of the few foundation stones of life the magic mystery of this process should be understood and be imitated in industry, because of the great demand for nitrogenous compounds of the rapidlty increasing population of the world. Although some methods have been devised so far, in order to fix nitrogen and get nitrogenous compounds, they want very large quantities of energy, (heat and pressure).

As an organic approache to this goal, many scientists agree on making new complexes of molibdenum and trying them under different conditions for nitrogen fixation. Perhaps one structure can do this vital transformation man-made conditions. The fixation of gaseous hydrogen which has a rather large bonding energy, in the quinolinic solution of copper-II, was discovered by a similar method.

Hence, in this study some new complexes of molybdenum have been prepared and investigated in terms of coordination chemistry. Since an appropriate solvent could not be found, they have not been tried for the fixation of nitrogen in possible conditions.

## Introduction

Transition elements with unfilled d-electron subshell are of great interest in connection with catalysis. They play a very important role in the sequence of reactions, irrespective of, whether they are inorganic, organic or biological. Most enzymes contain one or two transition elements. Among these elements molybdenum holds a unique place because it functions as catalyst either in animal or plant bodies. It promotes and controls some complex reactions that go on in the living cells [1]. the distribution of molybdenum in the different parts of animal and vegetable bodies changes widely. It tends to concentrate in the seeds of plants, especially in peas and beans [2].

Moreover, there are certain signs that molybdenum plays a very important part in the fixation of atmospheric nitrogen. Bortels showed that several species of azotobacter, a powerful nitrogen fixing microorganism, are unable to fix gaseous nitrogen in the absence of molybdenum [3], [4].

Since molybdenum is essentially concerned with the fixation of atmospheric nitrogen [5],[6], the chemistry of it bears an extra-ordinary importance because of the great demand for nitrogenous compounds by the rapidly increasing population of the world. It can be safely said that nitrogen one of the few foundation stones of life. Although the results of these vital reactions are known, the mechanisms of them are still open to debate[7],[8]. Once it was also thought that certain plant and animal bodies were able to fix atmospheric nitrogen, şubsequently, it was shown the nitrogen fixation of these bodies was due to the existence of micro-organisms which fixed and lived in symbiosm in these living-beings [9]. Today there are good grounds that gaseous nitrogen can only be fixed by certain micro-organisms and lower sea plants, such as spirilla and blue-green algae [10].

If we knew something about the structures of certain molybdenum –containing enzymes and the mechanisms of the natural nitrogen fixation, we could possibly imitate the structure and the mechanisms of the reactions in industry in order to manufacture ample, cheap nitrogen compounds to meet the great nitrogen requirement of the world. Although, 100.000,000 tons of nitrogen compounds formed annually by lightining and tons of man-made nitrogenous compounds are given to the soil in order to compensate the nitrogen loss of the soil they still fall short.

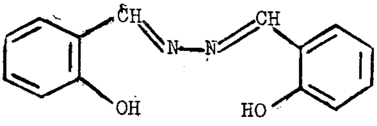
Because of the importance of this subject, scientists agreed that, it is worthwhile in every way to augment the number of complexes of transition elements, namely the complexes of molybodenum, iron, cobalt and tungsten and try them for nitrogen fixation under different conditions. Even as, the fixation of hydrogen in quinoline solution of copper-II, has been found by trying different possibilities [11], [12], [13], [14].

A group of leading scientists of nitrogen fixation are especially in favour of preparing and examining molybdenum compounds in connection with nitrogen fixation [15], [16], [17]. Also some scientists are in favour of trying dinuclear complexes of molybdenum or other promising transition elements for nitrogen fixation. Certainly they do not ignore mononuclear complexes as well, [16], [17], [18], [19].

Under the influence of these views, I made some new complex organic compounds, cotaining oxygen and nitrogen ligands, of molybdenum and examined the coordination properties of them. Since a good solvent has not been found they have not been tried for nitrogen fixation impressirely. Up to now, not only molybdenum complexes but also the complexes of other transition metals have been prepared and tried for nitrogen fixation but no positive result has been obtained [1], [16], [20].

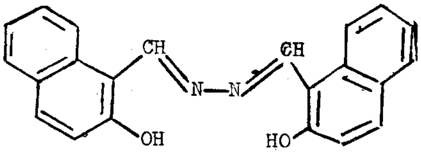
## Mo Complexes

In this study some quinque valent and one quadri valent complexes of molybdenum have been prepared with compounds containing oxygen and nitrogen ligands I, II.



I

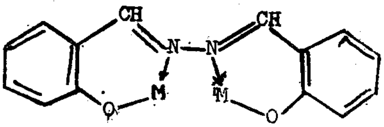
Salicylaldazine



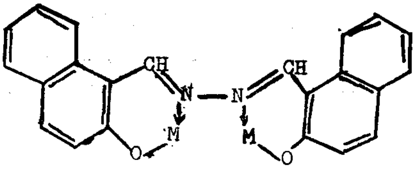
II

β-Hydroxy-α-Napfthaldazine

All attempts made to prepare dinuclear complexes from these failed, III, IV.



III

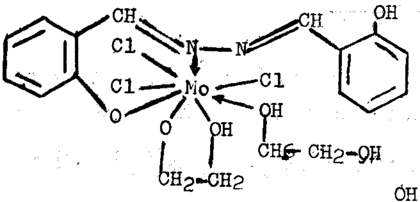


IV

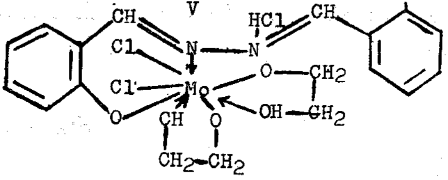
Instead of these, mononuclear compounds of the azines have been obtained.

## Trichloro–Molybdenum–V–Salicylaldazine–bis–Ethanediol

Complex V or VI was prepared from salicylaldazine and $MoCl_5$ in dry dioxane. Ethanediol which appears in the structure comes from the decomposition of dioxane, because there is not any other possibility.



V



VI

Pale green crystals

M.P. 152° C (decomp.)

Moreover, if we add a small amount of ethanediol in the medium the reaction proceeds very readily and clearly with good yields. One can think that in the second case another compound is obtained. By thinking about this possibility the compound was prepared in two ways and all the physical and chemical properties were found to be the same.

Although numbers V and VI are possible, it is most likely that the real structure is number V because of the stability of $MoCl_3^{+2}$ ion. Neverthless number VI and the like are not far remote possibilities.

The structures, throughout of this study have been estabished by the microanalytical results, coordination rules and magnetic sus, ceptibility measurements. Magnetic susceptibilities calculated by the following equations.

$$Xg = \frac{2.gl.pull}{H^2\ W}$$

$$Xm = Xg.\ m$$

$$Xa = Xmok$$

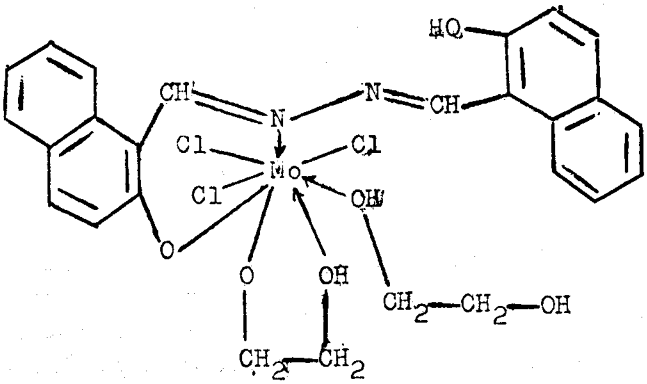
$$\mu = 2.84 \sqrt{Xa.\ T}$$

$$\mu = \sqrt{n\ (n-2)}$$

The magnetic susceptibility was found to be 1.68 B. M. This amount represents 1 free electron in the structure.

## Trichloro-Molybdenum-V-β-Hydroxy-α-Naphthaldazine-bis-Ethanediol

Complex was obtained by the same method from the compounds in dry dioxane.



VII

Red crystals

M.P. 164-5 °C

There ars still other possibilities for the structure as is the case with number V. A magnetic susceptibility was found to be 1.70 M. B.

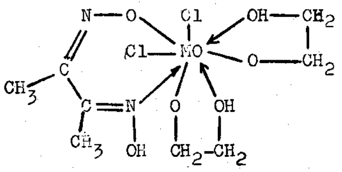
In both complexes magnetic susceptibility measurements were made on a gouy type magnetic balance and structural corrections were made according to Selwood [21], [22]. In dry state complexes are fairly stable but in water they readily decompose. If they are left to the exposure of air for a long period of time they gradually oxidize and magnetic susceptibilities fall to zero, due to the formation of molybdenum- VI. The electronic configuration of both complexes can be shown as below, with the d4 sp3 hybrid configuration

|  |  | 4s |  |  | 5s |  | 5p |  |
|---|---|---|---|---|---|---|---|---|
| ↓ | x | x | x | x | x | x | x | x |
|  | x | x | x | x | x | x | x | x |

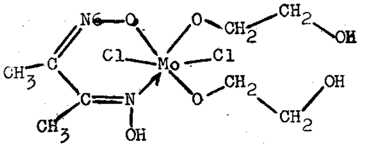
Very slightly coloured solutions of both complexes in benzene have been tried for nitrogen fixation in a pressure bo, which was specially designed, but no positive result has been observed.

**Dichloro–Molybdenum V–Dimethylglyoxime–bis –Ethanediol.**

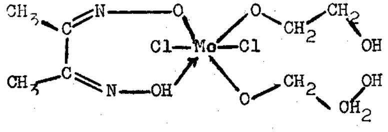
A complex was prepared by heating $MoCl_5$ and dimethylglyoxime in dry dioxane. The complex is highly hygroscopic and decomposes easily in the presence of moisture. From the analytical results, magnetic susceptibility measurements, it was concluded that the complex had the structure number VIII, IX or X. Since the formation of seven-membered rings are highly difficult, the existence of X is unlikely. But on the other hand it is a well known fact that Mo-O bonding is stronger than Mo—N. So electronic configuration of the compound can be given either by $d^4sp^3$ or $d^4sp$ hybrids. A magnetic susceptibility was found to be 1.48 B. M. This result is somehow lower than to be expected.



VIII



IX



X

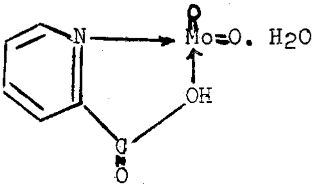
Pale green crystals

M.P. 150°C (Decomp.)

### Molybdenum–IV–α–Picolinicacid$_1$

This complex was prepared in dry dioxane from $MoCl_5$ and α-picolinic acid. Under the light of analytical results and magnetic susceptibilities the structure was concluded to be XI. This result is seemingly strange because I started with Mo-V. This unexpected result is probably due to disproportionation of Mo-V.

$$2MoCl_5 \longrightarrow Mo^{+4} + Mo^{+6}$$



XI

Pale yellow crystals

Decomp. above 200°C

## EXPERIMENTAL

### Trichloro-Molybdenum V- Salicyladazine-bis-Ethanediol

1.4 g. fused MoCl5 ($\frac{1}{200}$ M ) is introduced into a reaction flask and washed with 3-4 ml. of anhydrous dioxane (Analar) and decanted. Since $MoCl_5$ is very hygroscopic this procedure is carried out as quiskly as possible.

Then 10 ml of dioxane (Analar) and subsequent to this 1.2 g. salicylaldazine are added onto $MoCl_5$. This mixture is heated under a short reflexer up to 60-70 °C and shaken constantly. While the mixture is shaken 0.6 g. ethanediol mixed with 1 ml of dioxane is added dropwise. With the addition of every drop the dark colour of the solution gradually turns to light green. Near the end of the addition, pale green crystals begin to accumulate in the reaction vessel and at the same time HCl gas evolves. All of this is completed in half an hour.

The content of the vessel is left for a while to settle down and then is filtered by sucking through a Buchner funnel. The crystals are washed twice by 5 ml of hot dioxane and filtered again properly. Then the crystals together with the filter paper are put into a dessicator and dried overnight.

The complex, in the dry state, is highly stable in air but it slowly oxidizes within a long period of time. The yield is 40-50 % in respect to $MoCl_5$. It decomposes at 152 °C. It decomposes in water, acetone or alcohol and does not dissolve in benzene or chloroform in appreciable amount.

After making all the structural corrections and calculations 1.70 B. M. has been found.

Calculated : C 38.29; H 3.90; 0 17.02; N 4.96; Mo 17.02

Found : C 37.78; H 3.62; O 17.13; N 4.78; Mo 17.46

$C_{18} H_{22} 0_6 N_2 Cl_3 Mo$. M = 564 g.

### Trichloro–Molybdenum V–β–Hydroxy–α–Naphthaldazine–bis–Ethanediol.

1.4 g fused $MoCl_5$ $(\frac{1}{200} M)$ is introduced into a reaction vessel and washed out with 3-4 ml of dry (analar) dioxane as quickly as possible and then the dioxane is decanted. 1.78 g $(\frac{1}{200} M)$ β–hydroxy –α– Naphthaldazine and 10 ml dry dioxane (analar) are added into the reaction as well.

While heating and stirring the mixture, a solution of 0.6 g ethanediol 1 ml of dioxane is added dropwise. The solution becomes gradually red the reaction continues. At the end of the reaction a red crystallin compound settles down to the bottom of the reaction cessel. During the reaction HCl gas evolves slowly.

The reaction is completed in about one hour. The red crystals are sucked by a Buchner funnel and washed clean twice with 5 ml of hot dioxane and dried one night in a dessicator. M. P. 164–165 °C (decom), yield 90 %. The complex does not dissolve in chloroform, carbontetrachloride but is very slightly soluble in dioxane and readily decomposes in alchocol and acetone, giving a green solution.

(M = 662 g), ($C_{26}$ $H_{26}$ $O_6$ $N_2$ $Cl_2$ Mo).

Calculated : C 46.99; H 3.92; O 14.46; N 4.20; Mo 14.46

Found : C 47.29; H. 4.07; O 14.66; N 3.63; Mo 14.78

A magnetic moment of 1.68 B. M. has been found.

### Dichloro–Molybdenum V–Dimethylglyoime–Ethanediol[1]

2.8 g ( $\frac{1}{100}$ M ) fused $MoCl_5$ is introduced into a reaction vessel and washed out with 6 ml of dry dioxane. Onto the compound 10 ml. of dry dioxane and 2.4 g dimethyglyoxine are introduced as well. By heating and stirring the mixture a solution of 1 g dry ethonediol in 1 ml of dry dioxane is added dropwise. A slight HCl evolution occurs during the reaction. The reaction is complete in about half an hour. The content of the reaction vessel is left overnight in a dry box and then filtered strongly by a Buchner funnel and the crystals are washed clean twice by 3 ml of dioxane as quickly as possible. (The compound is hygroscopic). It is put into a dessicator and dried over night . The compound is not soluble in benzene, carben tetrachloride or toluene but is very slightly soluble in dioxane and readily decomposes in alcohol and acetone. The complex decomposes above 150°C (yield 20-25 %).

Analysis :

Calculated : C 23.76; H. 4.10; 0 23.76; N 6.93; Mo 23.76; Cl 17.58

Found : C 23.67, H. 4.07; 0 24.07; N 6.93; Mo 24.01; Cl 17.25

Magnetic Moment 1,43 B. M.

### Molydenum IV –α– Picolinic acid[1]

0.28 g fused $MoCl_5$ is weighed into a reaction vessel 0.22 g of α– picolinic acid and 10 ml of dioxane are added onto the compound. Since the reaction is sluggish, it is heated and strirred vigorously. It is advisable to keep everything scrupulously clean and dry. If the reaction vessel is not dry enough a violet coloration is observed. The reaction is complete in half an hour. The pale yellow crystals are sucked and washed with 3 ml of dioxane and dried in a dessicator. It dissolves in benzene, toluene and water giving a violet coloration. It decomposes above 200°C. (Yield 20 %).

Analysis :

Calculated : C, 26.77; H 2.60; O 29.73; N 5.20; Mo 35.82

Found : C 27.24; H 2.67; O 29.70; N 4.89; Mo 35.99

Magnetic susceptibility measurements showed the complex to be diamagnetic.

**Acknowledgement**

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## References

[1] *Kıliffer and Linz Molybdenum Compounds*, Interscience, 952
[2] **Drea W. F.** *J. Nutrition* (934), 8, 229. (935), 10, 351
[3] **Bortels H.** *Archive für Mikrobiologie* (930), 1 333
[4] **Anderson A. T.** *Aust.* Inst. Agri. Sci. (942), 8, 73
[5] **Anderson A. T.** *Inorg. Nitrogen Metabolism*, John Hopkins, 956
[6] **Roberts E. R.** *Proc.* Fertilizer Soc. (959), 54
[7] **Blake T.** *Ph. D. Thesis*, Imperial College, London, 960
[8] **Wursteman F.** *Ph. D. Thesis*, Imperial College, London, 962
[9] *Comp.* Biochem. Physiolo Vol. 4, pp 353-61, 962
[10] **Calvin M.** and **Wilmarth W. K,** *J. Am. Chem.* Soc. (956), 78, 1301
[11] **Winfield M. E.** *Royal.* Soc. Aust. (955), 5, 217
[12] **Halpern J.** *Quarterly Reviews*, (956), 10, 463
[13] **Wilmarth W. K.** *J. Am. Chem. Soc.* (956), 78, 1308
[14] **Singleton J. H.** and **Roberts E. R.** *Trans.* Far. Soc. (951), 41, 1318
[15] **Winfield M. E.** *Pure Appl. Cçhem. Aust.* (955), 5, 217
[16] **Malatesta L.** *Chem.* Abs. (940), 34, 82
[17] **Pauling L.** *Chem.* Eng. News (947), 25, 2970
[18] **Malatesta L.** *Chem.* Abds. (940), 34, 5366
[19] **Bailar J. C.** *Chemistry of the Coordination Comp.* Chapman and Hall London, 956
[20] **Nicholas D. J. D.** and **Stevens H. M.** *Refractories*, 4, 178
[21] **Selwood P. M.** *Magnetochemistry*, Interscience, 956
[22] **Lewis** and **Wilkins**, *Modern Coordination Chemistry*, Interscience, 956.
[23] **Gilbert T. W.** *J. Am. Chem. Soc.* (960), 82, 1087.

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