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Complexes of Molybdenum in Zero Valent State

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Abstract : Several complexes of molybdenum in zero valent state were synthesized and characterized on the basis of physico-chemical analysis and spectroscopic methods. Molybdenum can exist in different oxidation states such as -2, 0, +1, +2, +3, +4, +5 and +6. In this paper authors wish to report the synthesis and characterization of molybdenum complexes in zero valent state stabilized by reductive nitrosylation in aqueous-aerobic medium. In these synthesis, higher valence state of molybdenum have been reduced to lower valence state by nitrosylation.

(Keywords : molybdenum complexes, nitrosylation).

Introduction

Molybdenum, the 34th most abundant element was discovered by Hjelm in 1790 from mineral molybdenite, MoS_2, the principal ore of molybdenum. Besides its extensive use to improve the strength, corrosion resistance and thermal stability of ferrous alloys, chemical uses of molybdenum are limited, but are constantly expanding because molybdenum unlike other transition metals is classified as relatively harmless to the environment[1]. Several works on zero valent chemistry of metals like chromium molybdenum and tungsten are reported in the literature.[2-3] Molybdenum can exist in different oxidation states such as –2, 0, +1, +2, +3, +4, +5 and +6. The activity of molybdenum in the natural system is comprised of different oxidation states. The origin of the molybdenum activity involved in such reactions, essentially rests on the key role of MoO_4^{2-} (VI). Probably the stability of this anion in a wider pH range (suitable for biological activities of molybdenum in metalloproteins) alongwith its readiness to enhance the coordination number and its ready reducibility accounts for its biological role as a sole representative of heavier transition metals. Amongst all the molybdoproteins known till date, the nitrogenase is the most difficult one to prepare. It is because if one believes that molecular nitrogen is going to attach with the molybdenum centres in nitrogenase using back bonding scheme, molybdenum should be in lower oxidation state. Unfortunately our present chemical knowledge about the aqueous chemistry of the lower oxidation states of molybdenum is very meagre. In view of this it would be highly interesting to explore the possibilities of reducing hexavalent molybdenum to lower ones in aqueous media. In this paper authors wish to report the synthesis and characterization of molybdenum complexes in zero valent state. In these syntheses, higher valence states of molybdenum have been reduced to lower valence state by nitrosylation[4-15].

Experimental

Several complexes of molybdenum in zero valent state were synthesized. These synthesized complexes were characterized by physico-chemical analysis and spectroscopic studies. Analytical data of these complexes are given in table-1.

Table- 1
Analytical composition of complexes

Sl. No.	Name of the compound	Formula	M.P./Decomp. temp. (^{0}C)	% composition calculated (found)			
				C	H	N	Cl/S
1	Dichlorodinitrosylbis (pyridine) molybdenum (0), $[Mo(NO)_2Cl_2(Py)_2]$	$MoC_{10}H_{10}N_4O_2Cl_2$	>180 D	31.16 (31.27)	2.59 (2.85)	21.80 (21.88)	18.44 (18.24)
2	Dichlorodinitrosylbis (γ-picoline) molybdenum (0), $[Mo(NO)_2Cl_2(\gamma$-pic$)_2]$	$MoC_{12}H_{14}N_4O_2Cl_2$	>150 D	34.85 (34.14)	3.40 (3.69)	13.56 (13.10)	17.17 (16.90)
3	Dichlorodinitrosylbis (β-picoline) molybdenum (0), $[Mo(NO)_2Cl_2(\beta$-pic$)_2]$	$MoC_{12}H_{14}N_4O_2Cl_2$	>150 D	34.85 (35.06)	3.40 (2.81)	13.56 (13.30)	17.17 (16.85)
4	Bis-(dimethyldithiocarbamato) dinitrosylmolybdenum (0), $[Mo(NO)_2(Me_2$dtc$)_2]$	$MoC_6H_{12}N_4S_4O_4$	>275 D	18.35 (18.16)	3.75 (3.03)	13.85 (14.14)	32.85 (32.32)
5	Bis(cysteine) dinitrosylmolybdenum (0), $[Mo(NO)_2($cysteine$)_2]$	$MoC_6H_{12}N_4O_6S_2$	>150 D	18.18 (18.02)	3.00 (2.67)	15.16 (14.75)	16.17 (15.85)
6	Bis (acetylacetonato) dinitrosylmolybdenum (0), $[Mo(NO)_2(acac)_2]$	$MoC_{10}H_{14}N_2O_6$	156	33.89 (34.75)	3.95 (3.87)	7.90 (8.00)	-
7	Dichloro (o-phenanthroline) dinitrosylmolybdenum (0), $[Mo(NO)_2Cl_2($o-Phen$)]$	$MoC_{12}H_8N_4O_2Cl_2$	>180 D	35.40 (36.02)	1.96 (2.30)	13.76 (13.50)	17.43 (16.80)
8	(2,2'-Bipyridyl) dichlorodinitrosylmolybdenum (0), $[Mo(NO)_2($biphy$)Cl_2]$	$MoC_{10}H_8N_4O_2Cl_2$	>180 D	31.34 (30.85)	2.09 (2.65)	14.64 (14.68)	18.51 (17.90)
9	Caesiumtetrachlorodinitrosylmolybdenum (0), $Cs_2[Mo(NO)_2Cl_4]$	$Cs_2MoN_2O_2Cl_4$	>200 D	-	-	5.00 (5.20)	25.15 (25.36)
10	Di- (tetraethylammonium) tetracyanodinitrosylmolybdenum (0), $[(C_2H_5)_4N]_2[Mo(NO)_2(CN)_4]$	$MoC_{20}H_{40}N_8O_2$	>150 D	46.17 (46.48)	7.60 (6.42)	21.05 (20.40)	-
11	Tetraethylammoniumbis-(oxalato) dinitrosylmolybdenum (0), $[(C_2H_5)_4N]_2[Mo(NO)_2(C_2O_4)_2]$	$MoC_{20}H_{40}N_4O_{10}$	>200 D	40.54 (40.42)	3.38 (4.50)	9.45 (10.25)	-

Results and Discussion

IR Spectra: IR spectra in the range 4000 - 200 cm^{-1} and 4000 - 400 cm^{-1} were recorded on Perkin Elmer model 580 and 377 Infrared Grating Spectrometers respectively. Samples were prepared as KBr or CsI pellets. Far IR spectra were recorded with polytech FIR-30 Fourier IR and Hitachi FIS-1 Spectrometers in the range 600-100 cm^{-1} and 400-30 cm^{-1} respectively. The IR data is tabulated in Table- 2.

Table- 2

Sl. No.	Compound	ϑ NO s'(cm^{-1})	ϑ(Mo-N)/δ(Mo-N-O) (cm^{-1})	Other important vibrations
1	$[Mo(NO)_2Cl_2(Py)_2]$	1780(vs), 1670(vs)	580(w), 555(m), 575(w)	312, 280 ν(Mo-Cl)
2	$[Mo(NO)_2Cl_2(\gamma\text{-pic})_2]$	1780(vs), 1670(vs)	580(m), 555(m),475(w)	310, 280 ν(Mo-Cl)
3	$[Mo(NO)_2Cl_2(\beta\text{-pic})_2]$	1775(vs), 1670(vs)	570(w), 545(w),485(w)	310, 285ν(Mo-Cl)
4	$[Mo(NO)_2(Me_2dtc)_2]$	1760(vs), 1655(vs)	572(m), 530(m), 480(w)	370, 350 ν(Mo-S)
5	$[Mo(NO)_2(cysteine)_2]$	1795(vs), 1650(vs)	-	-
6	$[Mo(NO)_2(acac)_2]$	1770(vs), 1655(vs)	562(w), 545(m), 475(m)	440, 415 ν(Mo-O)
7	$[Mo(NO)_2Cl_2(o\text{-Phen})]$	1790(vs), 1680(vs)	570(w), 545(m), 485(w)	318, 285 νMo-Cl)
8	$[Mo(NO)_2(bipy)Cl_2]$	1785(vs), 1675(vs)	565(w), 545(m), 485(w)	320, 295 ν(Mo-Cl)
9	$Cs_2[Mo(NO)_2Cl_4]$	1765(vs), 1620(vs)	560(m), 545(m), 472(w)	295, 280 ν(Mo-Cl)
10	$[Et_4N]_2[Mo(NO)_2(CN)_4]$	1785(vs), 1775(vs)	550(m), 470(w), -	2140 ν(C≡N)
11	$[Et_4N]_2[Mo(NO)_2(C_2O_4)_2]$	1785(vs), 1630(vs)	565(m), 552(m), -	465, 438 ν(Mo-O)

vs- very sharp, m- medium, w- weak.

The appearance of two very strong bands in the range 1785-1740 and 1670-1620 cm^{-1} suggests that the two nitrosyl groups are attached to the metal in cis-fashion. This is in accordance to the expectation of Feltham and Enemark based on molecular orbital energy level diagram. The characterization of $\nu_{(Mo\text{-}N)}$ and $\delta_{(Mo\text{-}N\text{-}O)}$ is based on their low intensity. It is now established that the position of $\nu_{(N\text{-}O)}$ in no way reflects the mode of attachment of the nitrosyl group to the metal. Interestingly, even with a linear mode of attachment M-N-O as observed in X-ray structural investigations, the highest ν_{NO} is observed for $Na_2[Fe(NO)(CN)_5]$ at 1944 cm^{-1} and the lowest has been recorded at 1455 cm^{-1} for $K_4[Mo(NO)(CN)_5]$.

Correlation may be obtained from this series $[Mo(NO)_2X_4]^{2-}$(X= NCS^-, Cl^-, CN^-) regarding the low frequency vibrations responsible for ν(Mo-N) and δ(Mo-N-O). Taking the corresponding chloro complex as a reference compound, Mo-Cl vibrations of which do not appear in this region, we find a trend in two weak absorption bands in the region 570-550 cm^{-1} and 475-470 cm^{-1}. The respective position of these bands are : 550, 470 cm^{-1} for the cyano complex, 560, 472 cm^{-1} for the chloro and 570, 475 cm^{-1} for the thiocyanatoanalog. If we assign tentatively these sets of vibrations originating from Mo-N

stretching vibrations, the competitive bonding ability of these three co-ligands can be clearly seen. The order thus emerging is CN >Cl^-> – NCS^-. With the series of neutral complexes, there is no appreciable change in the appearance of the ν_{NO} band at the higher frequency.

Electronic spectra : The electronic spectral data is given in Table- 3.

Table- 3
The electronic spectral data of the complexes

Sl.No.	Compound	Solvent	λ_{max} (nm)
1	$[Mo(NO)_2Cl_2(Py)_2]$	CH_3 CN	463 (2.0 x 10^3) 377(sh) 305 (10.6 x 10^3)
2	$[Mo(NO)_2Cl_2(\gamma\text{-pic})_2]$	CH_3 CN	500 (2.3 x 10^3), 380 (sh) 260 (41.3 x 10^3)
3	$[Mo(NO)_2Cl_2(\beta\text{-pic})_2]$	CH_3 CN	448 (11.6 x 10^3)
4	$[Mo(NO)_2(Me_2dtc)_2]$	-	-
5	$[Mo(NO)_2(cysteine)_2]$		
6	$[Mo(NO)_2(acac)_2]$	DMF	550 (5.8 x 10^3) 412 (9.4 x 10^3) 336 (10.6 x 10^3
7	$[Mo(NO)_2Cl_2(o\text{-Phen})]$	-	-
8	$[Mo(NO)_2(bipy)Cl_2]$	-	-
9	$Cs_2[Mo(NO)_2Cl_4]$	-	-
10	$[Et_4N]_2[Mo(NO)_2(CN)_4]$	DMF	382 (11.5 x 10^3) 316 (31.8 x 10^3
11	$[Et_4N]_2[Mo(NO)_2(C_2O_4)_2]$	DMF	620 (6.1 x 10^3) 498 (sh) 325 (46 x 10^3

In the electronic absorption spectra of $[Mo(NO)_2Cl_2(Py)_2]$ and other complexes[1], the electronic absorption maxima and the corresponding extinction co-efficients occurs around 463 n.m. and is assigned to a LMCT (ligand to metal charge trnasfer) of the type $\pi v^* \rightarrow$ d (Mo).The position of these bands is affected by several factors for example, the oxidation state of the metal, the presence of other ligands.

For the complex, $[Mo(NO)_2Cl_2(\gamma\text{-Picl}_2)]$ the assignments of absorption bands are according to the discussion mentioned above. Thus, the lowest energy band around 460 nm is assigned to $\pi v^* \rightarrow$d(Mo) (LMCT) and a relatively weak band around 377 nm has been assigned to $\sigma \rightarrow \sigma^*$ charge transfer.

In case of the complexes of the type $[Mo(NO)_2(S_2CNEt_2)_2]$ the considering the

presence of the co-ligand, dithiocarbamate. The lowest engery band at 518 nm. The electronic spectrum of free dithiocarbamate exhibits three bands in the u.v.region and on complexation, the shift in these bands are not significant.The nature of these transitions is intra ligand: $n \rightarrow \pi\pi^*$ and $n \rightarrow \sigma^*$

For the compounds of the type $[(PPh_4)_2[Mo(NO)_2(NCS)_4]$ the highest energy band around 430 and 440 n.m. is due to intra ligand charge transfer transition of dithiocarbamate ligand. The lowest energy band is then assigned to $\pi v^* \rightarrow d(MO)$ transition. However, the middle band at 380 nm has a very high extinction coefficient. The corresponding oxo analogue shows a band at 400 nm with low extinction coefficient. The position of this band at 380 nm compared to 400 nm for the oxoanalog and its intense nature suggests that the origin of this transitioin may be of the type $(\pi_{gh},d)/(\pi_{un},d)$ (d, π_{uh})/d, πgh). As expected, complexes of the series containing $[Mo(NO)_2\}_6$ and $\{Mo(NO)\}^4$ moieties are diamagnetic in nature. The expected magnetic moment value 4 an octahedral complex[2] would be of the order of 2.3 BM act 3000K. From the magentic moment data value it is apparent that all the complexes are having magnetic moment value less that is expected. These low values imply a considerable distortion from the regular octahedral structure for the nitrosyl complexes.

Conclusion

Nitrosylation reaction of a transition metal compound with hydroxylamine is generally believed to take place in strong alkaline medium whereby hydroxylamine disproportionates to give an unstable 'NOH' which is believed to be deprotonated to generate NO-. Strong alkali is needed for the deprotonation step. However, the recent findings on nitrosylation of molybdenum as molybdate with hydroxylamine in acidic medium definitely suggests a complicated mechanism. The concurrent coprotonaton of hydroxylamine occurs along with the intramolecular electron transfer process as:

$$Mo^{VI} + H_2NOH \rightarrow Mo\text{-}NO + 3H^+$$

However, the formation of a yellow colour by the reaction of MoO_4^{2-} and NH_2OH suggests the formation of $\{Mo(NO)\}^4$ moiety instantaneously. The relationship between electron transfer and deprotonation processes is not clear. However, this can be viewed as follows. It has been observed that the same group of workers that when hydroxylamine is used in many fold excess compared to the molybdate, complexes containing $\{Mo(NO)(NH_2O)\}^4$ configuartion are formed instead of simple $\{Mo(NO)\}^4$ moiety.

When hydroxylamine in the reaction mixture is not in sufficient excess $\{Mo(NO)\}^4$ group is only formed without the coordinated hydroxylamido (-1) moiety. However, we have observed that when the ratio of molybdate to hydroxylamine is 1:3, hydroxyl- amidonitro-sylmolybdenum moiety is generated. Wieghardt and coworkers have shown that the coordinated NH_2O(-1) group can be further deprotonated to yield NHO(-2) type of bidentate ligands. Thus two successive deprotonation of hydroxylamine with a $\{Mo(NO)\}_4$ group takes place as given below:

$$\{Mo(NO)\}^4 + NH_2OH \rightarrow \{Mo(NO)(NH_2O)\}_4$$
$$\{Mo(NO)(NH_2O)\}^4 \rightarrow \{Mo(NO)(HNO)\}^4$$

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