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Synthesis and characterization of molybdenum complexes in low valent state

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Abstract : Several complexes of molybdenum in low valent state have been 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 of molybdenum complexes in low valent state stabilized by reductive nitrosylation in aqueous-aerobic medium.

(Keywords: molybdenum complexes, nitrosylation)

Introduction

This work comprises the synthesis and characterization of complex compounds of molybdenum (Mo) in low valent state. 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 of molybdenum complexes in low 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. Several complexes of molybdenum have been synthesized and these synthesized complexes have been characterised by different physico-chemical and spectroscopic methods[1-15].

Experimental

Following complexes have been prepared.

1. Synthesis of *Bis* (acetylacetonato) dinitrosylmolybdenum (0), $[Mo(NO)_2(acac)_2]$

Ammonium heptamolybdate (1.0g) and hydroxylamine hydrochloride (1.7g) were heated in 10ml dimethylformamide at 90^0C, sloly with constant stirring to get a green solution which was kept at 60^0C for about 15 minutes. A solution of acetylacetone (2ml) in 15 ml of methanolic-KOH (1.3g) was added and the resulting mixture was refluxed for an hour and poured into 250ml of boiling water. On keeping at ca. 90^0C for 30 minutes, the desired product started separting as a green solid. The mixture was allowed to cool and the precipitate was filtered, washed with water and dried. The crude product was purified by column chromatograph (silica gel, 60-120 mesh), using benzene as eluent. Yield, 600mg; m.p., 156^0 (lit. [141], 146-147^0C).

Anal. Calcd for $MoC_{10}H_{14}N_2O_6$; C, 33.89; H, 3.95; N, 7.90% Found: C, 34.75; H, 3.87; N, 8.00%.

2. Synthesis of Chlorobis (2,2'-bipyridyl) nitrosylmolybdenum (I) chloride, $[Mo(NO)(bipy)_2Cl]Cl$

$K_4[Mo(NO)(CN)_5].2H_2O$ (2.7g) was dissolved in 50 ml concentrated hydrochloric acid for 40 minutes under oxygen free atomosphere, 2,2'-bipyridyl (2.3g) was added to the clear wine red-green solution and refluxed for a while and cooled to room temperature. A light green compound that formed was filtered off and the filtrate was kept for crystallization in a closed container. The dark bluish green compound which crystallized on standing overnight was filtered,

washed with dilute hydrochloric acid and dried over KOH desiccator. Yield, 350 mg.
Anal. Calcd for $MoC_{20}H_{16}N_5Cl_2O$: C, 47.16; H, 3.14; N, 13.76; Cl, 13.93%. Found: C, 49.34; H, 2.85; N, 13.25; Cl, 13.68%.

3. Synthesis of Cesium Pentachloronitrosylmolybdenum (II), $Cs_2[Mo(NO)Cl_5]$

Ammonium heptamolybdate (1.0g) was dissolved in 20 ml water and 1.3g of hydroxylamine hydrocholoride was added to it and heated at 60-65^{0}C. The red organe precipitate initially formed slowly disappeared and the solution turned brown. Cesium chloride dissolved in concentrated hydrochloric acid (40ml) was added to it and the mixture was heated at boiling temperature and within 5 minutes, a bright, shining red brown crystals of $Cs_2[Mo(NO)Cl_5]$ started separating. After another 5 minutes of heating, the reaction mixture was allowed to cool to room temperature. The crystals thus formed were filtered, washed with methanol and ether and dried over KOH desiccator. Yield, 1.45 g.
Anal. Calcd for $Cs_2MoNOCl_5$: N, 2.46; Cl, 31.13%. Found: N, 2.52; Cl, 31.80%.

Results and Discussion

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 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 $\nu_{(Mo-N)}$ and $\delta_{(Mo-N-O)}$ is based on their low intensity. It is now established that the position of $\nu_{(N-O)}$ 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 $K_4[Mo(NO)(CN)_5]$.

An interesting 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 thiocyanato analog. 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.

In the electronic absorption spectra of $[Mo(NO)_2Cl_2(Py)_2]$ and other complexes, the electronic absorption maxima and the corresponding extinction co-efficients occurs around 463 n.m. and is assigned to a LMCT (ligand to metal change 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, $[Mo(NO)_2Cl_2(r\text{-}PiCl_2)]$ 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 bank around 377 n.m. 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 → , π→π* and * and n→σ*

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 π_v*→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 oxo analog and its intense nature suggests that the origin of this transitioin may be of the type $(\pi_{gh},d)/(\pi_{un},d) \rightarrow (d,\pi_{uh})/d\pi, gh)$.

As expected, complexes of the series containing $[Mo(NO)_2\}^6$ and $\{Mo(NO)\}^4$ moieties are diamagnetic in nature. Compounds containing $\{Mo(NO)\}^5$ configuration are paramagnetic with respect to one unpaired electron. The manetic moment values of the newly prepared complexes along with a few other reported compounds have been found in the range of 1.74 BM to 1.70 BM.

The spin orbit coupling constant (for Mo(I) is approximately 450 cm^{-1} for t_{2g}^5 configuration. The expected magnetic moment value for an octahedral complex would be of the order of 2.3 BM at 300^0K. From the magnetic moment data value it is apparent that all the complexes are having magnetic moment value less than that is expected. These low values imply a considerable distortion from the regular Octahedral structure for the nitrosyl complexes.

Conclusion

Nirosylation 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 depronated 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 comlicated 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 [140] 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 (140] 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 amidonitrosylmolybdenum 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 taks plac 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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