# Spectral and Thermal Studies of Some Binuclear Dimeric Mo-*O*-Mo Bridged Oxomolybdenum(V) Complexes with Bis(carboxamides) Derived from 4,4'-Diaminobiphenyl, 1,4-diaminobenzene with Anhydrides

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**Abstract:** A study of doubly bidentate ligands like 4,4'-bis-(phthalamidyl)biphenyl Bd(PAH)$_2$, 4,4'-bis-(Succinamidyl)biphenyl Bd(SAH)$_2$, 1,4-bis-(phthalamidyl)monophenyl PPD(PAH)$_2$ and 1,4-bis-(succinamidyl)monophenyl PPD(SAH)$_2$ with oxomolybdenum(V) is described. The complexes were prepared by reaction with the precursor (PyH)$_2$[MoOCl$_5$]. The coordination behavior of the complexes have been determined with the help of elemental composition, infrared and electronic spectroscopy, cyclicvoltammetric and thermal studies.

## Introduction

The oxomolybdenum(V) complexes is dominated by both terminal oxo and bridged Oxo binuclear species. Infact, the chemistry and structure of binuclear bridged molybdenum(V) complexes has been much interest, because redox centers of molybdenum containing enzymes. In general molybdenum is a necessary cofactor for a number of redox enzymes[1-4]. The ligands containing carboxyamide chain having O$_4$ donor atoms and their complexes have pharmacological activities[5-8]. A number of reports on binucleating carboxyamide ligands with first row transition metals are available[9-12], no study on the oxomolybdenum(V) complexes of such ligands has been reported. In this paper, we report the synthesis and spectral properties of oxomolybdenum(V) complexes of bis-(carboxyamide) ligands derived from 4,4' - diaminodiphenyl and 1,4-diaminobenzene reacted with Phthalic and Succinic anhydrides. The Structures of the ligands is depicted in the Figure 1.

## Experimental

All chemicals were of analytical grade and were used without further purification. (PyH)$_2$ [MoOCl$_5$] was prepared by the literature method[13]. The bis-(Carboxyamides) were synthesized by substantially modifying a published method[11]. All the Complexes were prepared in nitrogen atmosphere.
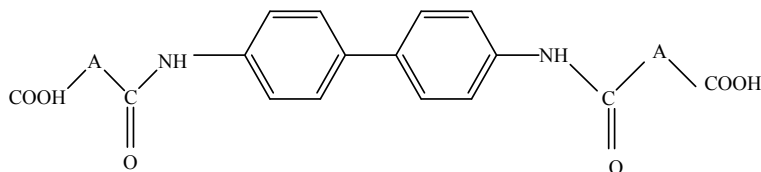
I - The structure of ligand (I) :Bd(PAH)$_2$, A=C$_6$H$_4$; Bd(SAH)$_2$, A=C$_2$H$_4$
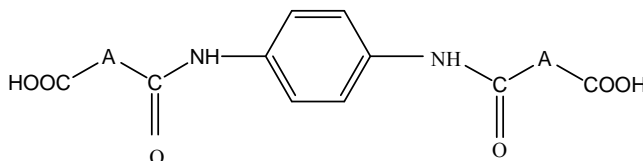


II - The structure of ligand (II) : PPD(PAH)$_2$, A=C$_6$H$_4$; PPD(SAH)$_2$, A=C$_2$H$_4$

**Figure 1.** Structure of the ligands

*Synthesis of ligands*

A solution of the appropriate diamines like 4,4'-diaminobiphenyl (Bd) or 1,4-diaminobenzene (PPD) (0.01 mol) in absolute ethanol (30 cm$^3$) was refluxed with the respective anhydrides like Phthalic (PAH) or Succinic anhydride (SAH) (0.02 mol) in ethanol (30 cm$^3$) for 2 to 4 h. On cooling the corresponding carboxyamides precipitated out. The product was filtered, washed twice with ether and dried[14].

*Synthesis of complexes*

About 0.48g of Bd(PAH)$_2$ was dissolved in 25 mL of absolute ethanol. To this 0.45 g of (PyH)$_2$ [MoOCl$_5$] in 25 mL of absolute ethanol was added. The reaction mixture was heated to reflux for about an hour. The solid, that separated out was filtered, washed with ethanol, ether and dried under vacuum. A similar procedure was followed for the synthesis using the ligands Bd(SAH)$_2$, PPD(PAH)$_2$ and PPD(SAH)$_2$.

*Measurements*

Molybdenum content was determined by a standard procedure[15]. The elemental analysis was carried out on a Heraeus model C,H,N – rapid analyser. The infrared spectra were recorded in KBr pellets on a JASCO IR-700 model spectrophotometer. The electronic spectra were recorded in DMF on a JASCO UVIDEC - 650 double beam spectrophotometer. Thermal Analysis were done on a Mettler TA 3000 micro processor with TG 50 Thermobalance and STA 1500 PL Thermal Sciences, heating at the rate of 20$^0$/min. The cyclic voltammetric studies were performed on a BAS – 100A or a BAS CV – 27 electrochemical analyzer, using a glassy carbon working electrode (area 0.07 cm$^2$), a platinum wire auxiliary electrode and a Ag/AgCl reference electrode. Tetramethylammonium perchlorate (0.1 M) was used as the supporting electrolyte with concentration of molybdenum compounds in millimolar range. The complexes were dissolved in purified and deaerated DMF. The experiments were carried out under an atmosphere of purified nitrogen.

## Results and Discussion

The oxomolybdenum(V) Complexes were prepared by reacting the precursor (PyH)$_2$ [MoOCl$_5$] with the binucleating bis-(Carboxyamide) ligands. The analytical data correlates well with the calculated values assuming a metal: ligand ratio 1:1 indicating this to be the stoichiometry.

*Analytical data of the complexes*

The analytical data for the binuclear carboxyamide ligands with oxomolybdenum(V) are given in Table 1. The experimental data correlates well with the calculated values assuming a metal: ligand ratio 1:1 indicating this to be the stoichiometry.

**Table 1.** Analytical data of the Mo(V) – oxo complexes

| Complex | Molecular Formula | Found (calcd) % | | | |
|---|---|---|---|---|---|
| | | C | H | N | Mo |
| Mo-Bd(PAH)$_2$ | Mo$_4$O$_6$(C$_{112}$H$_{72}$N$_8$O$_{24}$) | 56.02(56.19) | 3.20(3.01) | 4.44(4.68) | 16.20(16.05) |
| Mo-Bd(SAH)$_2$ | Mo$_4$O$_6$(C$_{80}$H$_{72}$N$_8$O$_{24}$) | 47.99(48.81) | 3.46(3.59) | 5.49(5.57) | 19.08(19.12) |
| Mo-PPD(PAH)$_2$ | Mo$_4$O$_6$(C$_{88}$H$_{56}$N$_8$O$_{24}$) | 50.75(50.57) | 2.70(2.68) | 5.27(5.36) | 18.39(18.39) |
| Mo-PPD(SAH)$_2$ | Mo$_4$O$_6$(C$_{56}$H$_{56}$N$_8$O$_{24}$) | 39.38(39.44) | 3.17(3.29) | 6.48(6.57) | 22.40(22.53) |

*Infrared spectra*

The infrared spectral data of the Mo(V) complexes from binucleating carboxyamide derivative shown in Table 2, a wide range of absorptions due to the vMo=O stretching, (O-Mo-O) stretching frequencies and also the amide carbonyl, acid carbonyl and vNH stretching frequency of the amide group. In the present system, when compared to the spectral data of ligands, there is no appreciable change in vNH amide stretching frequency. The peaks are merged vOH stretching frequency of water (whose presence is inferred from the thermograms) and forms a broad band around ca.3430 cm$^{-1}$. The amide II absorption due to vNH bending of the secondary amide occurs at 1500 -1600 cm$^{-1}$. This band is not affected by complexation with the metal. The amide carbonyl group frequency appears around 1650-1600 cm$^{-1}$ in the ligands. In the case of complexes, this absorption shifted to lower values by nearly 10-30 cm$^{-1}$. This shift indicates the binding of the amide carbonyl group to metal on complexation. The acid carbonyl which appears around 1706-1715 cm$^{-1}$ in the ligands, gets shifted to higher values by 10-15 cm$^{-1}$ upon complexation, implying the involvement of acid carbonyl in binding to the metal. The infrared spectra of all Mo(V) complexes exhibit a strong band at ca.970 cm$^{-1}$, indicating the Mo$_2$O$_3^{4+}$ core and is assigned to the molybdenum-terminal oxygen vibration (υMo=O). All Complexes exhibit medium intensity absorptions at ca.750-721 cm$^{-1}$ and 451-424 cm$^{-1}$, which are attributed to the antisymmetric and symmetric vibrations of Mo-O-Mo bridge[16-18]. The infrared data point to the ligands binding through the acid carbonyl and the amide carbonyl group to the metal ion in the complexes. All complexes show only one band in the region 970 cm$^{-1}$ in presence of Mo$_2$O$_3^{4+}$ core and also a medium intense absorption at 750 and 451 cm$^{-1}$ indicating the presence of Mo-*O*-Mo bridge. The other characteristic absorption in the ligands do not undergo any distinct shift upon complexation.

**Table 2.** IR Spectral data (in cm$^{-1}$) and CV data of the Mo(V) – oxo complexes

| Complex | Amide I C=O Amide II (N-H bend) | Acid C=O | Mo =O | Epc (V) | Epa (V) |
|---|---|---|---|---|---|
| Mo-Bd(PAH)$_2$ | 1620,1508 | 1720 | 970 | -0.76 -0.30 | -0.39 +0.34 |
| Mo-Bd(SAH)$_2$ | 1624,1587 | 1715 | 969 | -0.78 -0.38(Sh) | +0.39(Sh) |
| Mo-PPD(PAH)$_2$ | 1623,1560 | 1725 | 969 | -0.78 -0.36(Sh) | -0.38 +0.40(Sh) |
| Mo-PPD(SAH)$_2$ | 1626,1561 | 1718 | 969 | -0.77 +0.36(Sh) | -0.38 +0.39(Sh) |

*UV-Visible spectra*

The spectra of oxomolybdenum(V) complexes exhibit a shoulder at ca.19,600-19,800 cm$^{-1}$. Which has been attributed to a transition involving the Mo-*O*-Mo bridge. This interpretation has been previously proposed to explain the origin of similar bands in the electronic spectra of analogous xanthate and dithiocarbamate dimmers[16-21]. The electronic spectrum shows a shoulder in the region ca. 19,608-19,724 cm$^{-1}$ due to the transition $^2B_2 \longrightarrow {}^2B_1$ (dxy$\longrightarrow$ dx$_2$-y$_2$). The band appearing as a shoulder in the region around 21,740 – 23,256 cm$^{-1}$ is due to the transition $^2B_2 \longrightarrow {}^2A_1$ (dxy $\longrightarrow$ dz$_2$). Other shoulders are possibly obscured by the intra ligand transitions.[22]

*Cyclic voltammetric study*

The data from the cyclic voltammograms for the complexes is given in the Table 2. In the present system, all the oxomolybdenum(V) complexes exhibit a reduction peak at -0.56 to -0.78 V. The corresponding anodic wave is seen at -0.35 to -0.38 V in the case of the Bd(PAH)$_2$, PPD(PAH)$_2$ and PPD(SAH)$_2$ complexes. Such a wave is not present in the Bd(SAH)$_2$ complexes. An anodic peak is present in the range +0.34 to +0.40 V in the cyclic voltammograms of the complexes. When the scan rate increases from 0.050 to 0.500 Vs$^{-1}$, the height of the reduction as well as oxidation peak increases. Sayer *et al.*,[15] have studied the electrochemistry of molybdenum (VI) and (V) with 8 – quinolinol complexes in dimethylsuphoxide. They observed that the oxobridged dimeric Mo(V) complex shows three cathodic peaks and an anodic peak. They decided that the anodic peak produces the Mo(VI) complexes in an irreversible process. From the above data, the oxomolybdenum(V) complexes have a well-defined reduction peak in the range -0.56 to -0.78 V. It is inferred that the reduction is quasi reversible since the anodic wave is obscured. ΔEp is much larger than that theoretically predicted confirming the quasi-reversible nature of the reduction. The anodic peak found in the range +0.40 V indicates a one electron oxidation to produce Mo(VI) and is a totally irreversible process.

*Thermal study*

Thermograms were recorded for the Mo(V) complexes with Bd(SAH)$_2$, Bd(PAH)$_2$ and PPD(SAH)$_2$. All the complexes lose water or solvent molecule below 100 $^0$C. In addition all three complexes undergo decomposition in three stages. The first stage occurs around 200 $^0$C, the second stage around 300$^0$-350 $^0$C and the third stage around 800$^0$C. All three stages appear to be exothermic as indicated by DTA curve for the Mo(V) –PPD(SAH)$_2$ complex. It has not been possible to identify the fractions volatilizing at different stages of the thermal loss. The thermograms of the Mo(V) –Bd(PAH)$_2$ and Mo(V) - Bd(SAH)$_2$ were subjected to a kinetic analysis using the method of Coats and Redfern[23]. A linear regression of the values of the terms with n=0, 1/2,2/3 and n=1 against 1/T was carried out[24]. The weight loss step from 290-410 $^0$C in the thermogram of Mo(V)-Bd(PAH)$_2$ corresponds to a zero order decomposition as indicated by a fair correlation coefficient for the line involving n=0. For this step an energy of activation of 105.30 Jmol$^{-1}$ has been calculated. Similar analysis of the weight loss step starting at 600 $^0$C shows this step also follows a zero order decomposition, for this step the energy of activation has a value of 94.72 Jmol$^{-1}$. In the case of Mo(V) – Bd(SAH)$_2$, the weight loss step from 65-150 $^0$C shows a first order decomposition as indicated by the large correlation coefficient for the line involving n=1. For this step an energy of activation of 35.93 Jmol$^{-1}$ has been calculated. Similar analysis of the weight loss steps between 270-400 $^0$C and 830-890 $^0$C follow a first order and zero order decay with an energy of activation of 103.75 and 341.92 Jmol$^{-1}$ respectively.

## Conclusion

Based on the results of elemental analysis, spectral, electrochemical and thermal studies data, it is inferred that the ligand molecule binds to the metal through the amide oxygen and the carboxyl oxygen atoms and bridges two molybdenum centers. The basic unit containing molybdenum appears to be the $Mo_2O_3$ unit with two terminal oxygen atoms and a bridging oxygen. This is a common observation with regards to complexes of oxomolybdenum(V). Thus the basic unit appears to contain four molybdenum atoms and four ligands, the proposed structure of the compound is depicted in Figure 2. The complexes are found to be soluble in DMF and DMSO, and negligibly soluble in other common solvents. This may be indicative of a polynuclear structure formed by the ligands acting as bridges between molybdenum centers. A part of the polymeric structure is depicted in Figure 3.
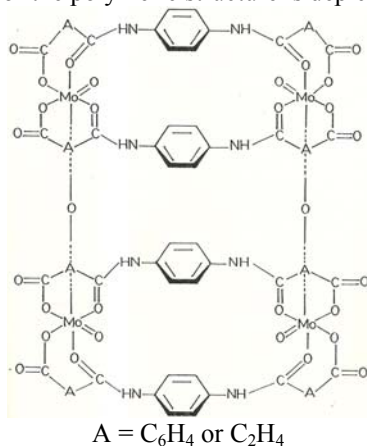


$A = C_6H_4$ or $C_2H_4$

**Figure 2.** The structure of the Mo-Oxo complexes: $A=C_6H_4$ or $C_2H_4$



$A = C_6H_4$ or $C_2H_4$

X = ⬡⬡ for Bd Complexes
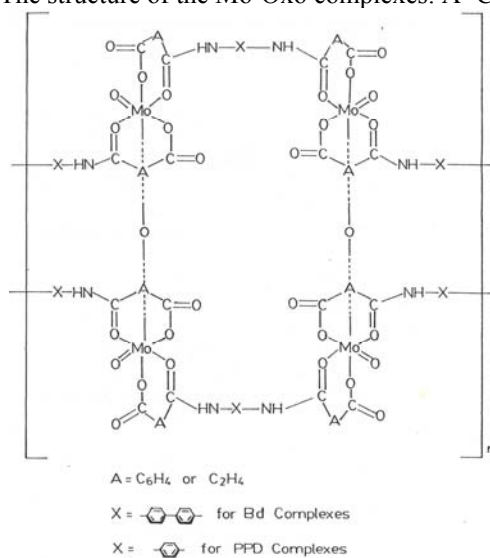
X = ⬡ for PPD Complexes

**Figure 3.** The structure of the Mo-Oxo complexes: $A=C_6H_4$ or $C_2H_4$: X= ⬡⬡ for Bd complexes and ⬡ for PPD complexes

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