

Synthesis and characterization of seven-coordinated polymeric mono[anti-*cis*-bis(2-hydroxy-1-naphthaldehyde)oxaloyldihydratonato]monoquoobis-*cis*-dioxomolybdenum(VI)dihydrate complex

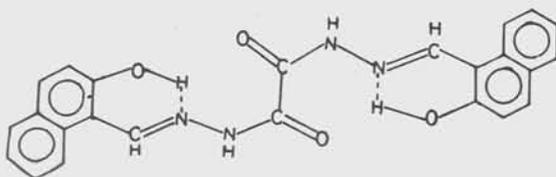
R A Lal* & S Adhikari

Department of Chemistry, Tripura University,
Agartala 799 004, Tripura

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The title compound synthesized from the reaction of $\text{MoO}_2(\text{acac})_2$ with bis(2-hydroxy-1-naphthaldehyde)-oxaloyldihydrazone in ethanol-acetonitrile in 3:1 molar ratio under reflux is proposed to be a hexamer in which ligands are arranged in sets of three in two parallel planes one above the other. The intraplanar metal atoms are bonded to each other by naphthoxo-bridges whereas the interplanar metal atoms are bonded to each other by $\text{Mo}=\text{O} \cdots \text{Mo}$ type of bridging. The anti-*cis*-configuration of the dihydrazone moieties leads to the chair conformation of the complex.

Molybdenum is a biologically trace element that occurs in the redox enzymes which are involved in nitrogen, sulphur and carbon metabolism¹. Such a feature associated with the molybdenum has kindled renewed interest in its coordination chemistry². Although oxomolybdenum(VI), (V), (IV), complexes of several monoacyl, and aroyldihydrazone bearing N_2O_2 and N_2O_3 donor systems are reported³, the molybdenum complexes of the dihydrazones derived from condensation of acyl, aroyl, and pyridoyl, dihydrazines with *o*-hydroxy aromatic aldehydes and ketones, have remained to be examined. Accordingly, the present note describes a hexameric molybdenum(VI) complex with the polyfunctional ligand bis(2-hydroxy-1-naphthaldehyde)oxaloyldihydrazone.



Bis(2-hydroxy-1-naphthaldehyde)oxaloyldihydrazone
(napoxih₄)

Experimental

Ammonium heptamolybdate tetrahydrate, diethyloxalate, hydrazinehydrate, 2-hydroxy-1-naphthaldehyde and acetylacetone were of BDH (AR) grade. Bis(acetylacetonato)dioxomolybdenum(VI) was synthesized by following literature procedure⁴. Oxaloyldihydrazone was prepared by reacting diethyloxalate(1 mol) with hydrazine hydrate(2 mols)⁵. Bis(2-hydroxy-1-naphthaldehyde)oxaloyldihydrazone was prepared by refluxing for 4 h, a hot dilute ethanolic solution of oxaloyldihydrazone(1 mol) with *o*-hydroxynaphthaldehyde(2.5 mols). The yellow precipitate obtained on cooling the resultant solution was recrystallized from ethanol, and dried in hot air oven at *ca.* 70°C (m.p. > 300°C). [Found: C, 68.00; H, 4.25; N, 13.32. Reqd. for $\text{C}_{24}\text{H}_{18}\text{N}_4\text{O}_4$, C, 67.61; H, 4.23; N, 13.15%].

Molybdenum in the complex was determined by standard literature method⁶. Carbon, hydrogen, and nitrogen were determined by microanalysis, water molecules were determined by heating the samples for 4 h in an electric oven at *ca.* 110° and *ca.* 180°C, respectively, and passing the vapour through a trap containing anhydrous copper sulphate which turned blue and estimating the weight loss. The molar conductance of the complex at 10^{-3} M dilution in DMSO was measured using Direct Reading Conductivity meter 303 with a diptype conductivity cell. IR spectra were recorded on a Perkin-Elmer 983 spectrophotometer in the range 4000-180 cm^{-1} using KBr discs. The ¹H NMR spectrum of the complex was recorded on a EM-90, 90 MHz spectrometer in DMSO solution using TMS as an internal standard. The magnetic susceptibilities were determined by the Faraday method at room temperature using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as the calibrant. Molecular weight of the complex was determined by freezing point depression method in DMSO.

Synthesis of $[(\text{MoO}_2)_2(\text{napoxlh})(\text{H}_2\text{O})].2\text{H}_2\text{O}$

To an ethanolic solution of $\text{MoO}_2(\text{acac})_2$ (0.1 M, 120 cm^3) was added a hot ligand solution (0.1 M, 40 cm^3) in ethanol. The solution was refluxed for 2 h and cooled, which yielded an orange and precipitate which was filtered hot and washed with ethanol. Again it was suspended in hot ethanol (40 cm^3) and stirred for 10 min at 70°C. To this suspension, CH_3CN (30 cm^3) was quickly added which changed the colour of the suspension to black green. This reaction

mixture was digested over water bath for 1 h and then filtered hot, washed with acetonitrile, ether and dried over anhydrous CaCl_2 . D.P. > 300°C. [Found: Mo, 26.50; C, 39.50; H, 2.70; N, 7.91. Reqd. for $[(\text{MoO}_2)_2(\text{napoxlh})(\text{H}_2\text{O})].2\text{H}_2\text{O}$, $(\text{Mo}_2\text{C}_{24}\text{H}_{20}\text{N}_4\text{O}_{11})$ Mo, 26.22; C, 39.34; H, 2.73; N, 7.65%].

Results and discussion

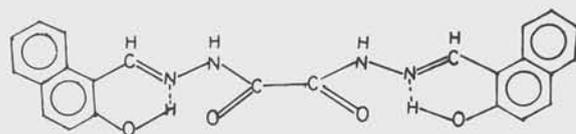
Bis(2-hydroxy-1-naphthaldehyde)oxaloyldihydrazone (napoxlh H_4) is a polyfunctional octadentate ligand which can coordinate to the metal centre in keto (I), keto-enol (II), and enol (III) forms in the metal complexes. Further, the dihydrazone can exist in the metal complexes either in the staggered configuration (structure IV) or anti-cis-configuration (structure V) or syn-cis-configuration (structure VI).

The dihydrazones containing azomethine, amide and phenol functions are polyfunctional ligands. These are capable of yielding polynuclear complexes involving ligand bridging and oxo-bridging. On the assumption that ligands containing bulky fragments in their molecular skeleton can prevent formation of polymers, the title complex $[(\text{MoO}_2)_2(\text{napoxlh})(\text{H}_2\text{O})].2\text{H}_2\text{O}$ was synthesized from the reaction of $\text{MoO}_2(\text{acac})_2$ with the title ligand in 3:1 molar ratio in ethanol-acetonitrile medium. The insertion of naphthyl ring in the dihydrazone prevents the larger polymerisation and yields the complex having discrete molecularity. The complex is air stable and decomposes above 300°C. The molar conductance of this complex is $1.50 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ in DMSO indicating that it is non-electrolyte⁷. The complex shows weight loss corresponding to two water

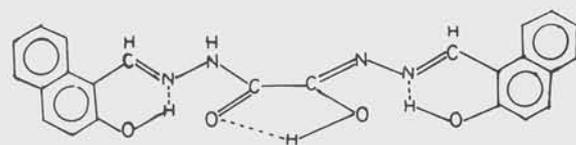
molecules at 110°C indicating their presence in the lattice structure of the complex while the weight loss at 180°C corresponds to one water molecule indicating that it is bonded to the metal centre.

The complex is only sparingly soluble in acetonitrile which prevented the determination of its molecular weight in this medium. Hence an attempt was made to determine the molecular weight of the complex in DMSO solution by freezing point depression method. The molecular weight of the complex was found to be 4500 ± 250 which is approximately six times the empirical formula weight of the compound. This suggests that the complex exists as a hexamer. The complex is diamagnetic. This shows that the reduction of metal centre does not occur under the influence of the ligand and confirms the presence of molybdenum(VI) in the complex. The DMSO solution of the complex is dark red coloured which does not change even on long standing. This suggests that the dihydrazone remains coordinated to the metal centre even in DMSO.

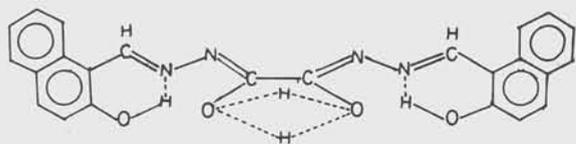
The four proton signal observed at 12.72 ppm assigned to $\delta\text{OH} + \delta\text{NH}$ in free dihydrazone⁸ does not appear in the ^1H NMR spectrum of the complex. The strong amide-I band at 1655 cm^{-1} in the free ligand is absent in the IR spectrum of the complex. Further, the IR spectrum of the complex shows strong to very strong pair of bands at 1617 and 1592 cm^{-1} characteristic of the $>\text{C}=\text{N}-\text{N}=\text{C}<$ group⁹. The $\delta-\text{CH}=\text{N}$ -signal splits into a doublet



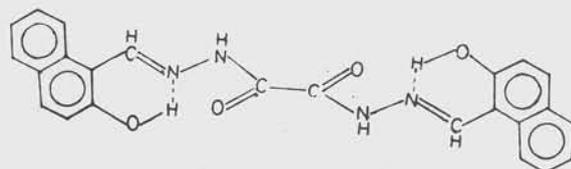
keto form (I)



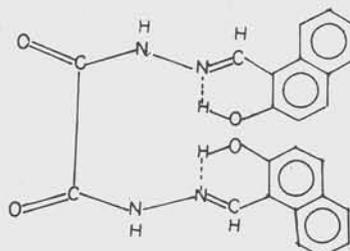
keto-enol form (II)



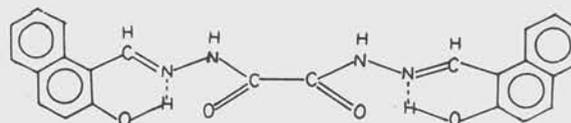
enol form (III)



staggered-configuration (IV)



anti-cis-configuration (V)



syn-cis-configuration (VI)

as against a singlet in the ^1H NMR spectrum of the dihydrazone. These observations indicate that the dihydrazone coordinates to the molybdenum centres in the enol form as a tetrabasic hexadentate ligand through phenolic oxygen, enolate oxygen and azomethine nitrogen atoms. The complex shows strong bands at 1548, 1539 and 1519 cm^{-1} assigned to $\nu(\text{C}-\text{O})$ (phenolic) and νNCO^- vibrations as against a single band at 1528 cm^{-1} assigned to have composite nature due to $\nu\text{amide II} + \nu(\text{C}-\text{O})$ (phenolic) in the IR spectrum of the uncoordinated dihydrazone. The shift of $\nu(\text{C}-\text{O})$ (phenolic) by more than 10 cm^{-1} to higher frequency indicates the presence of oxo-bridging in the complex¹⁰. The complex exhibits medium to strong bands at 593, 566 and weak bands at 455, 437 cm^{-1} which may be assigned to $\nu(\text{M}-\text{O})$ (phenolic) and $\nu(\text{M}-\text{O})$ (carbonyl)¹¹. The complex shows a very strong band at 944 cm^{-1} and a medium intensity band at 912 cm^{-1} which are not present in the IR spectrum of the free dihydrazone molecule. Further, it shows a very strong band at 852 cm^{-1} masking weak ligand bands occurring in this region. The feature of this band suggests the $\text{Mo}=\text{O}-\text{Mo}$ type of bridging in the complex¹². A very strong band at 944 cm^{-1} and a medium intensity band at 912 cm^{-1} are characteristic of *cis*- MoO_2^+ grouping in the complex¹³. The essential feature of these two bands suggests that out of the two *cis*- MoO_2^+ groups, only one is involved in $\text{Mo}=\text{O}-\text{Mo}$ bridging while both retain their identity as *cis*- MoO_2^+ grouping¹⁴.

The presence of ligand bridging, $\text{Mo}=\text{O}-\text{Mo}$ and $\text{Mo}-\text{O}-\text{Mo}$ linkages in combination with molecular weight determination suggests that the complex is a hexamer consisting of two sets of coordinated ligands each of which is arranged in separate planes one above the other. The dihydrazone molecules in one plane are presumed to be present in inverted position as compared to those in the other plane. The metal centre bonded to enolate oxygen atoms is oxo-bridged to phenolic oxygen atoms of the succeeding dihydrazone molecule in the same plane and is thus present in O_2O_2 coordination chamber. The metal centre present in N_2O_2 coordination chamber in one plane is bonded to metal centre present in O_2O_2 coordination chamber in the other plane through $\text{Mo}=\text{O}-\text{Mo}$ linkage.

It may be noted that $\delta-\text{CH}=\text{N}$ -peaks in the ^1H NMR spectrum of the complex appear as a doublet as compared to a singlet in the free ligand. Such a feature of the ^1H NMR spectrum of the complex may be rationalized by proposing that the complex exists in chair conformation. The chair conformation of the complex arises due to steric

crowding in the molecule resulted from coordination of both azomethine nitrogen atoms and both phenolic oxygen atoms of the same dihydrazone molecule to the same metal centre in the anti-*cis*-configuration¹⁵. In this conformation, the axial azomethine protons absorb at higher field¹⁶ (δ 9.52 ppm) than the equatorial azomethine protons which absorb at δ 9.99 ppm. The pattern of $\delta-\text{CH}=\text{N}$ -proton signals is asymmetric in nature which arises as a consequence of interchange between the two types of azomethine groups as a result of nitrogen inversion at the metal centre. The chair conformation of the complex is also confirmed from IR spectrum of the complex which shows two bands clearly corresponding to axial and equatorial counterparts of $>\text{C}=\text{N}-\text{N}=\text{C}<$ and $\geq\text{C}-\text{O}$ (phenolic) groups. The difference between the equatorial and axial counterparts of various groups lies in the region $9-27\text{ cm}^{-1}$ which is quite reasonable for compounds existing in chair conformation¹⁷.

On the basis of the physicochemical data presented and discussed above, the complex may be proposed to be a hexamer with three dihydrazone molecules arranged in one plane in anti-*cis*-configuration in the hexagonal fashion with the other set of three dihydrazone molecules also arranged in another plane in anti-*cis*-configuration in inverted position relative to those in the first plane. Each molybdenum centre in the hexamer probably involves a hepta-coordination with pentagonal bipyramidal arrangement.

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