

A bimetallic dioxomolybdenum(VI) complex containing coordinated dihydrazone in staggered configuration

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The reaction between bis(acetylacetonato)dioxomolybdenum(VI) and bis(2-hydroxy-1-naphthaldehyde)malonoyldihydrazone yields homobimetallic complex $[(\text{MoO}_2)_2(\text{CH}_2\text{L})(\text{H}_2\text{O})_2]$ in which dihydrazone coordinates to the metal centres in the staggered configuration. The complex undergoes a dynamic process in solution in which the dissociated form remains in equilibrium with the undissociated form.

Molybdenum occurs in the redox active sites of over a dozen molybdoenzymes involved in nitrogen, sulfur and carbon metabolism¹. All these contain a dissociable cofactor at the centre of which molybdenum is present in a form which bears a terminal oxo group or groups. The presence of such a group is believed to be obligatory for the oxo-transfer activity of these enzymes. The formal oxidation state of molybdenum in this cofactor changes² from +6 to +5 to +4. All these observations have rekindled renewed interest in the coordination chemistry of molybdenum. The chemical information gained in studying the molybdenum complexes may be applicable to understand the enzyme structure/function questions not readily obtainable by studying the enzymes themselves. Further, interest has been shown very recently in the synthesis of molybdenum complexes of macrocyclic and macroacyclic ligands with a view to understand the role that the ligand backbone, and side-chains of the metallacycle play in determining the redox and spectroscopic properties of a molybdenum centre³. Besides, the metal complexes derived from polyfunctional ligands exhibit interesting properties as electrocatalysts, as models for biological systems and more recently, as precursors for electrically conducting polymers⁴.

Dihydrzones are examples of polyfunctional ligands possessing amide, azomethine and phenol functions which possess potential to yield polynuclear complexes⁵. Although oxomolybdenum complexes of several monoacyl- and aroyldihydrzones are reported⁵, the molybdenum complexes of polyfunctional dihydrzones are scarcely studied⁶. The present note describes a monomeric dioxomolybdenum(VI) complex with the polyfunctional dihydrazone ligand bis(2-hydroxy-1-naphthaldehyde)malonoyldihydrazone which bears active methylene function, azomethine, amide and phenol functions.

Results and Discussion

Elemental analyses of the complex suggest $[(\text{MoO}_2)_2(\text{CH}_2\text{L})(\text{H}_2\text{O})_2]$ composition. It is orange coloured, air-stable and melts with decomposition at 270°. It is insoluble in water and common organic solvents, poorly soluble in CH_3CN and soluble in DMSO and DMF. The complex does not show any weight-loss at 110° ruling out the possibility of the presence of lattice water or ethanol. Its weight-loss corresponding to two water molecules at 180° indicates that they are coordinated to the molybdenum centre. The experimental value of the molecular weight (820) for the complex in DMSO is very close to the theoretical value (728) calculated on the basis of monomer formula, suggesting monomeric nature of the complex. The complex is non-electrolyte¹¹ (10^{-3} M in DMSO, $1.2 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$). It has zero μ_B value and is EPR silent, consistent with the occurrence of molybdenum as Mo^{VI} in the complex.

Electronic spectrum : The uncoordinated dihydrazone shows bands at 320 ($\epsilon_{\text{max}}, 9500$) and 390 nm ($\epsilon_{\text{max}}, 15700 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) which arise due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of naphtholic, azomethine and carbonyl groups. The band at 320 nm is shifted to 340 nm while the band at 390 nm shifts to 415 nm in the complex. The complex shows a broad new band centred at 600 nm ($\epsilon_{\text{max}}, 780 \text{ dm}^3 \text{ cm}^{-1} \text{ mol}^{-1}$). In view of very high extinction coefficient of this band and d^0 -electronic configuration of M_O^{VI} , this band is assigned to have its origin in the charge-transfer from naphtholate oxygen atoms to the metal centre⁷.

¹H NMR spectra : The presence of four resonances at δ 11.11–12.96 (OH + NH) and 3.60, 3.90 (methylene proton) suggests that dihydrazone exists in keto-enol equilibrium in solution⁶.

The ¹H NMR spectrum of the complex is clean in the δ 11.00–20.00 region (OH + NH) corresponding to signals in

the uncoordinated dihydrazone. The protons of the azomethine group coordinated to the molybdenyl ion are deshielded, the average chemical shift changing from 8.95 ppm in the free ligand to 9.72 ppm in the complex. The two resonances due to the protons of the CH₂ group change into a singlet and experience upfield shift of 0.15 ppm due to coordination of the enolate oxygen atom with the molybdenum ion. The most crucial point in the spectrum of the compound is the collapse of the four resonances corresponding to CH=N signal in the free ligand into a single resonance. This suggests that the dihydrazone, which exists in the *anti-cis*-configuration in the uncoordinated state, isomerises to attain staggered configuration in the complex⁸.

¹³C NMR spectra: The numbering scheme of the carbon atoms in both the ligand and complex is the same as shown in Fig. 1. The carbon atoms in the axial and equatorial positions have been designated by the letters 'a' and 'b', respectively⁹.

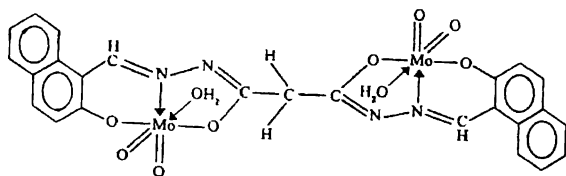
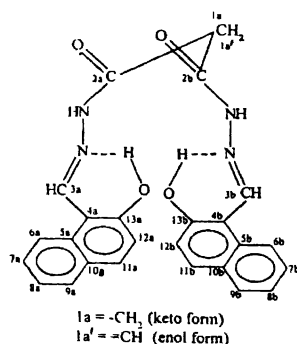


Fig. 1. The numbering scheme of the carbon atoms in CH₂LH₄ and [(MoO₂)₂L(H₂O)₂] complex

The signals relating to the carbons near the coordinated sites in complex are remarkably deshielded in comparison to the free ligand. The effect of molybdenyl ion on carbon resonance of naphthyl ring thus shifts downfield the signals for C(6), C(7), C(8) and C(9) by at least 1.50–4.65 ppm while those due to C(11) and C(12) by 2.85 and 1.85 ppm. The C(2), C(13) and C(3) resonances are shifted downfield more since they are closer to the coordinated oxygen and nitrogen atoms. As a consequence, the signals for C(2a) and C(2b), which in the free ligand are at δ 168.3 and 167.8 ppm, respectively, could in complex be at either δ 169.1 or 205.8 ppm. The latter assignment is much more likely, since it gives a deshielding of 40.6 ppm whereas the δ 169.1 ppm assignment only gives a small deshielding (3.8 ppm). On this basis, the signal at δ 169.1 ppm can only be as-

signed to the C(13) alone which in free ligand are at δ 157.8 and 156.7 ppm giving a chemical shift change of 11.85 ppm. Similarly, the signal at δ 152.2 ppm is assigned to the azomethine carbon which in free ligand are at δ 146.0 and 145.4 ppm giving rise to chemical shift change of 6.5 ppm. The signals at δ 148.0 and 138.2 ppm could be assigned to C(10) and C(5) carbon atoms which in free dihydrazone are at δ 142.9, 142.5 and 132.8, 132.4 ppm giving chemical shift change of 5.3 and 5.6 ppm, respectively. The signal at δ 121.4 ppm is assigned to C(4) carbon atoms which in free ligand appears at δ 121.0 and 120.8 ppm, giving a chemical shift change of 0.5 ppm. Such a small chemical shift change for C(4) resonances may be attributed to the combined effect of drainage of electron density from azomethine nitrogen atoms and naphtholate oxygen atoms in opposite direction.

It is remarkable to note that complex shows a signal at δ 95.5 ppm corresponding to methylene group which appears at 110.1 ppm in free dihydrazone. The upfield shift of the signal in the complex indicates that the electron density at methylene carbon atom is increased in the coordinated dihydrazone as compared to that in the free dihydrazone. This signal may be assigned to the methylene form of the ligand. However, the signal due to methylene form is not visible. The appearance of this signal indicates that the complex is undergoing a dynamic process in solution in which the dissociated complex remains in equilibrium with the undissociated complex.

The ligand shows 15 resonances each of which appears as pairs except the signals due to methylene carbon atoms which appear at 41.5 and 110.1 ppm due to keto and enol forms giving rise in total 28 resonances. Each resonance from a pair corresponds to the axial and equatorial carbon atoms⁹. On the other hand, ¹³C NMR spectrum of the complex shows 13 signals only, each of which corresponds to different carbon atoms. Such features of ¹³C NMR spectrum of the complex support the staggered configuration of the ligand in coordinated state.

IR spectra: The strong $\nu_{C=O}$ bands observed at 1697 and 1661 cm⁻¹ in free dihydrazone disappears on complexation. This together with the presence of a new strong band at 1554 cm⁻¹ due to newly created NCO⁻ group indicates coordination of dihydrazone in enol form. The $\nu_{C=N}$ band, which appears as a couple of bands at 1617 and 1596 cm⁻¹ in free dihydrazone, also appears as a single band at 1593 cm⁻¹. The medium intensity band observed at 1278 cm⁻¹ in the free ligand assigned to ν_{C-O} (naphtholic) appears at 1277 cm⁻¹ in the complex, indicating bonding between naphtholic oxygen atoms and molybdenum centre. The strong intensity bands observed at 591, 567 cm⁻¹ and weak intensity band at 432 cm⁻¹ are assigned to ν_{M-O} (naphtholic)¹⁰ and ν_{M-O} (carbonyl)¹¹ moieties, respectively. Two very strong new bands at 938 and 915 cm⁻¹ indicate the presence of *cis*-

MoO₂²⁺ grouping in the complex.

Experimental

All the materials used were the same as described earlier⁶, except 2-hydroxy-1-naphthaldehyde (E. Merck). Malonyldihydrazine was prepared by reacting diethyl malonate (1 mol) with hydrazine hydrate (2 mol).

Preparation of ligand : Bis(2-hydroxy-1-naphthaldehyde)malonyldihydrazine (CH₂LH₄), malonyldihydrazine (1.32 g, 10.0 mmol) in dilute ethanol (40 ml) was added to 2-hydroxy-1-naphthaldehyde (4.40 g, 25.0 mmol) in ethanol (100 ml). The reaction mixture was stirred at 70–75° with stirring for 45–30 min. The precipitated yellow polycrystalline dihydrazone was filtered in warm condition, washed with ethanol and dried under reduced pressure, (3.0 g, 70%), m.p. 265° (Found : C, 68.45; H, 4.62; N, 13.00. C₂₅H₂₀N₄O₄ requires : C, 68.18; H, 4.55; N, 12.73%); ν_{max} (KBr) 3450, 3200, 3047 (OH + NH), 1697, 1661 (C=O), 1617, 1596 (C=N), 1532 (amide II (CN + NH) + (C–O) (naphtholic)), 1278 cm⁻¹, (C–O); δ_H ((CD₃)₂SO) 3.60, 3.90 (2H, d, CH₂), 7.00–8.30 (12H, m, naphthyl), 8.40, 8.79, 9.14, 9.48 (2H, dd, CH=N), 11.11, 11.88, 12.33, 12.96 ppm (4H, dd, OH + NH); λ_{max} (ε_{max}, dm³ cm⁻¹ mol⁻¹) 320 (9500), 390 nm (15700); δ_C ((CD₃)₂-SO) 168.3, 167.8 (C(2a), C(2b)), 162.6, 162.2 (C(2a'), C(b')), 157.8, 156.7 (C(13a), C(13b)), 146.0, 145.0 (C(3a), C(3b)), 142.9, 142.5 (C(10a), C(10b)), 132.8, 132.4 (C(5a), C(5b)), 131.4, 131.1 (C(9a), C(9b)), 128.9, 128.6 (C(7a), C(7b)), 127.8, 127.6 (C(8a), C(8b)), 123.5, 123.3 (C(6a), C(6b)), 121.0, 120.8 (C(4a), C(4b)), 118.7, 118.0 (C(12a), C(12b)), 108.4, 108.3 (C(11a), C(11b)), 41.5 (C(1a)), 110.1 ppm (C(1b)).

Elemental analyses and physicochemical measurements were carried out as described earlier⁶. ¹³C NMR (DMSO-d₆) spectra were recorded on a Bruker ACF-300 FT-NMR spectrometer (75.47 MHz) using TMS as an internal standard.

[(MoO₂)₂(CH₂L)(H₂O)₂] : To a solution of MoO₂(acac)₂ (1.96 g, 6.0 mmol) in ethanol (50 ml) was added hot ligand solution (0.88 g, 2.0 mmol) in ethanol (40 ml). The solution was stirred for 2 h at 70–75° which resulted a dark coloured solution. Its volume was reduced to one-third by cooling to room temperature and the resulting orange coloured solid was washed with ethanol, ether and dried under reduced pressure, (1.0 g, 70%), d.p. 270° (Found : C, 41.64; H, 2.70; N, 7.91; Mo, 25.94. C₂₅H₂₀N₄O₁₀Mo₂ requires : C, 41.21; H, 2.71; N, 7.69; Mo, 26.37%); ν_{max} (KBr) 3450 (OH), 1593 (C=N), 1554 (NCO⁻), 1277 (C–O), 938, 915 (MoO₂²⁺),

591, 567 (M–O)(naphtholic), 432 cm⁻¹ (M–O)(enolic); δ_H ((CD₃)₂SO) 3.72 (2H, s, CH), 7.14–8.80 (12H, m, naphthyl), 9.72 ppm (2H, s, CH=N); λ_{max} (ε_{max}, dm³ cm⁻¹ mol⁻¹) 340 (8790), 415 (14760), 600 nm (780); δ_C ((CD₃)₂SO) 205.8 (C(2a) = C(2b)), 205.8 (C(2a') = C(2b')), 169.1 (C(13a) = C(13b)), 152.2 (C(3a) = C(3b)), 148.0 (C(10a) = C(10b)), 138.2 (C(5a) = C(5b)), 135.9 (C(9a) = C(9b)), 131.8 (C(7a) = C(7b)), 128.6 (C(8a) = C(8b)), 124.6 (C(6a) = C(6b)), 121.4 (C(4a) = C(4b)), 120.2 (C(12a) = C(12b)), 111.2 (C(11a) = C(11b)), 95.5 ppm (C(1a) = C(1b)).

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