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Comparison of structural features of three new *cis*-dioxomolybdenum(VI) complexes with 2-hydroxy-1-naphthaldehyde-*S*-methylisothiosemicarbazone: Possible role of intermolecular interactions on the geometry of the *cis*-MoO_2 unit ☆

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Abstract

Three closely related $[MoO_2(L)(ML)]$ complexes, where L is the 2-hydroxy-1-naphthaldehyde-*S*-methylisothiosemicarbazone ligand, and ML is EtOH (**I**), Py (**II**) and DMSO (**III**), were synthesized, characterized by NMR and IR spectra, and their X-ray crystal structures were determined. The crystal structure properties of these three closely related complexes were compared. Two *cis*-Mo–O bond lengths were almost the same in the crystal structure of complexes **II** and **III**, while in complex **I** a significant difference between the two *cis*-Mo–O bond lengths was observed. At the same time, the geometry of L ligand in complex **I** is different, compared to **II** and **III**. DFT calculations on the isolated molecule **I**, as well as geometrical analysis of the complexes indicate that intramolecular interactions are not responsible for these structural differences. On the other hand, the pattern of intermolecular contacts in the crystal structure of **I** differs from those observed in **II** and **III**. Analyses indicate that differences in *cis*-Mo–O bond lengths and in the geometry of ligand L could be related to intermolecular interactions. These results suggest the possibility that in enzymes oxotransferases or in their model systems, the Mo–O bond length could be designed by the interactions of chelate ligands with the surroundings.

Keywords: Intermolecular interactions; *cis*-Dioxomolybdenum(VI); Hydrogen bonds; Isothiosemicarbazone

1. Introduction

Many enzymes that catalyze redox reactions [1] and many potential catalysts [2–4] contain molybdenum as the metal ion in an active site. Investigation of the structure of molybdenum containing enzymes has revealed the presence of a chelated *cis*-MoO_2 unit in the active site of sulfite-oxidase enzymes [5]. This observation has prompted

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investigations of molybdenum complexes with ligands whose structural features bear a relationship to the active site of molybdenum enzymes [6–9]. A number of Mo(VI) and Mo(IV) complexes were synthesized to model oxo-molybdenum enzymes. These complexes range from having four monodentate ligands [10] to a single tetradentate ligand [11] attached to the molybdenum center.

The complexes of MoO_2^{2+} with tridentate ligands of the general formula $[MoO_2(TL)(ML)]$ (TL = tridentate ligand, ML = monodentate ligand) were synthesized as the model systems of molybdoenzymes catalyzing redox reactions. The model proposed for oxo-transfer reactions considers the direct transfer of an oxygen atom from/to the molybdenum center, and involves terminal O atoms [12–14]. This raises the question of the identification of those structural features of the chelated *cis*-MoO_2 fragment that influence catalytic capacity of the molybdenum compounds [15]. Some investigations treat the influence of changes in the conformation of the chelate ring [16,17] and attached substituents [4,18], on the redox potential and the catalytic activity of the compounds. However, much less is known about the influence of the nonbonding interaction on the structural properties of the chelate ring, and accordingly, on the catalytic activity of the molecule. The crystal structure and ^1H NMR spectra of $[MoO_2(L\text{-}cysOR)_2]$, complex [19] suggest that different conformations of the chelate ring can be correlated with different hydrogen bonding patterns of chelate ring atoms.

The complexes of *S*-alkylisothiosemicarbazone based ligands were extensively studied. The synthesis and X-ray characterization of complexes of the general formula $[MoO_2(L_s)(ML)]$ (L_s = the dianion of the tridentate ONN ligand salicylaldehyde-*S*-methylisothiosemicarbazone, ML = py, MeOH, EtOH, DMF and DMSO) were reported [20,21]. We present here the synthesis, characterization by NMR and IR spectra, X-ray characterization, and theoretical study of complexes of the general formula $[MoO_2(L)(ML)]$ (L = the dianion of the tridentate ONN ligand 2-hydroxy-1-naphthaldehyde-*S*-methylisothiosemicarbazone [22] (Chart 1) and ML = EtOH (**I**), py (**II**), and DMSO (**III**)). Crystal structures of these three closely related complexes were compared in order to study the influence of intramolecular and intermolecular interactions on differences in the structural properties of $[MoO_2(L)(ML)]$ molecules.

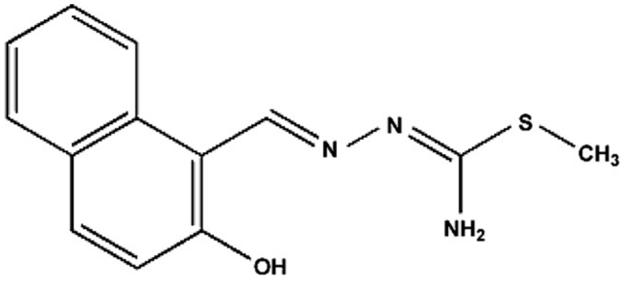

Chart 1. 2-Hydroxy-1-naphthaldehyde-*S*-methylisothiosemicarbazone.

2. Experimental

2.1. Syntheses of complexes

All chemicals used were commercial products of analytical purity. Initial complex $[MoO_2(acac)_2]$ and ligand 2-hydroxy-1-naphthaldehyde-*S*-methylisothiosemicarbazone (L) were synthesized according to the procedures reported in the literature [23,24]. The air-dried samples of complexes were used for all analyses.

Selected IR absorptions for $[MoO_2(L)(EtOH)]$, $[MoO_2(L)(py)]$, $[MoO_2(L)(DMSO)]$ and ligand 2-hydroxy-1-naphthaldehyde-*S*-methylisothiosemicarbazone (L) are summarized in Table 1.

2.1.1. $[MoO_2(L)(EtOH)]$ (I)

EtOH (10 cm^3) was added to a mixture of $[MoO_2(acac)_2]$ (0.5 mmol) and H_2L (0.5 mmol), the resulting mixture refluxed for 1 h, the solution filtered off and the filtrate left to crystalize. The precipitated crystals were separated by filtration, washed with methanol and dried in air. Yield: 0.24 mmol, 47%.

2.1.2. $[MoO_2(L)(py)]$ (II)

This complex was synthesized in the above described manner, by adding 1 cm^3 of pyridine to methanolic solution of $[MoO_2(acac)_2]$ and H_2L. Yields: 0.29 mmol, 58%.

2.1.3. $[MoO_2(L)(DMSO)]$ (III)

This complex was synthesized in the above described manner, by adding 1 cm^3 of DMSO to methanolic solution of $[MoO_2(acac)_2]$ and H_2L. Yields: 0.26 mmol, 52%.

2.2. IR and ^1H NMR spectroscopy

IR spectra of the compounds were recorded on a Perkin–Elmer FT-IR 31725X spectrophotometer at room temperature using the KBr technique. NMR spectra were obtained with a Varian Gemini-200 spectrometer a 199.98 MHz in a dimethyl-d_6 sulphoxide solvent.

2.3. X-ray crystallography

The crystals of complexes **I**, **II** and **III** were selected and mounted on a Stoe 4-circle diffractometer equipped with a graphite monochromator and Mo Kα radiation ($\lambda = 0.71013$ Å). Diffraction data were measured using $\omega/2\theta$ scans. Unit cell dimensions and intensity data were measured at 293 K (complex **I**, **II**) and at 173 K (complex **III**). The structure was solved by direct methods using the SIR92 program [25] (**I**, **II**) as implemented in the WINGX program system [26] and SHELXS-97 for compound **III**. All three structures were refined by full-matrix least-squares based on F^2 with anisotropic thermal parameters for non-hydrogen atoms using SHELXL-97 [27]. During the refinement procedure, a disorder was noticed in the position of the solvent molecule (DMSO) in compound **III**. In the final