

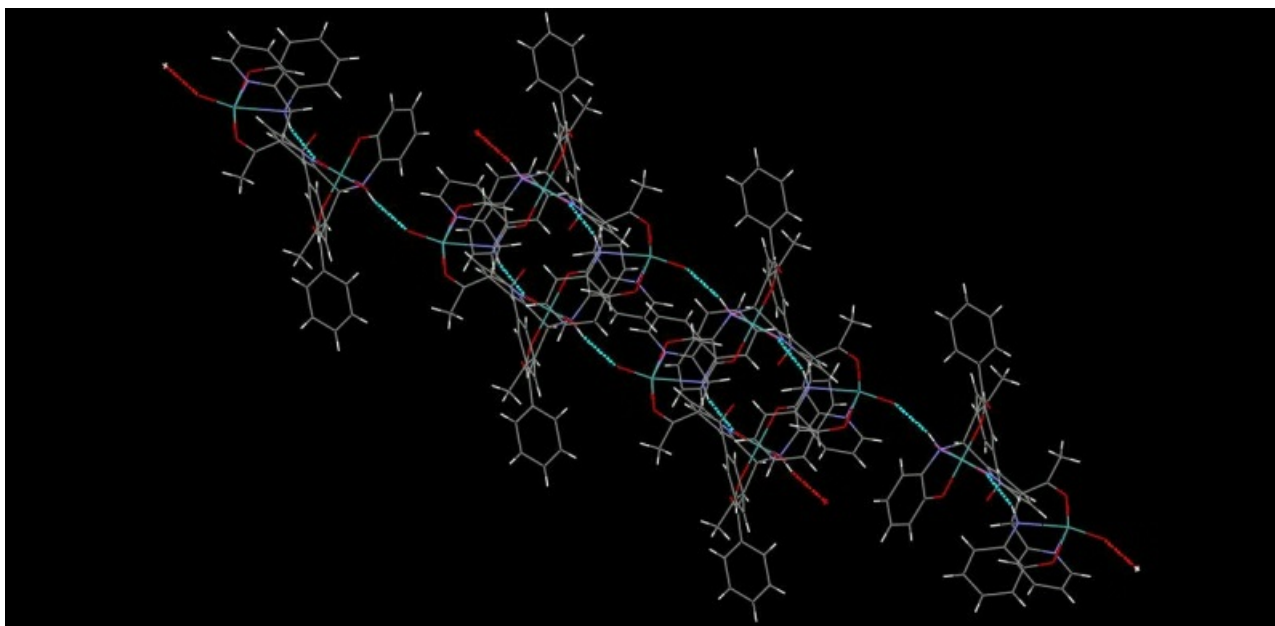
Structures of cis-Dioxomolybdenum(VI) with chiral tetradentate tripodal ligands

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Racemic complexes of the general formula $\text{cis-}[\text{MoO}_2(\text{bzacLn})_2]$ (1–3) were produced in the reactions of $[\text{MoO}_2(\text{bzac})_2]$ (bzac = benzoylacetate) with the potentially N2O-donor 5,5-membered fused chelate rings forming Schiff bases 4/5-R-2-(2-pyridylaldimine)phenols (HLn; n = 1-3 for R = H, 4-Me and 4-Cl, respectively).[1] Here (bzacLn)₂⁻ represents the chiral N2O2 donor tripodal ligand system in 1-3, which was formed via Mannich-type addition of benzoylacetate methine to the azomethine of the N2O-donor Schiff base (HLn). Analogous complexes with (acaLn)₂⁻ had also been reported by our group.[2] The complexes crystallize as 1, 2•MeOH and 3•MeOH from the corresponding methanol solutions. X-ray structures revealed that a distorted octahedral N2O4 coordination environment around the molybdenum atom is formed by the pyridine-N, the secondary amine-N, the enolate-O and the phenolate-O donor (bzacLn)₂⁻ and two mutually cis oriented oxo groups in each of 1–3. The (bzacLn)₂⁻ unit has a chiral tripodal-like motif with three different coordinating arms - the N-donor 2-pyridyl arm, the enolate-O donor 1-phenyl-1-one-2-butenyl-3-olate arm, and the bidentate secondary amine-N and the phenolate-O donor aminophenolate arm. Various characterization techniques such as IR, UV-Vis and NMR measurements were used to confirm the molecular structures of 1–3. The structure of (bzacLn)₂⁻ clearly indicates its formation via Mannich-type addition of the central =CH- of (bzac)- across the azomethine bond of (Ln)-. To the best of our knowledge, there is no such report on cis- $\{\text{MoO}_2\}^{2+}$ assisted ligand transformation of the same type except for our earlier observation.[2] The molecules of 1–3 are chiral due to the presence of two chiral centers, the pivotal carbon atom and the metal coordinated secondary amine nitrogen atom in (bzacLn)₂⁻. In each of 1–3, the N-H•••O hydrogen bond assisted self-assembly patterns are not identical. The enantiomers of unsolvated 1 form parallel inversion symmetry related one-dimensional chain-like structures, whereas for each of 2•MeOH and 3•MeOH, the enantiomers form discrete centrosymmetric dimers via a pair of reciprocal N-H•••O interactions.

[1] Ghosh, S., Kurapati, S. K. and Pal S. (2017). *Polyhedron*. 125, 26-33.

[2] Kurapati, S. K. and Pal S. (2015). *Dalton Trans.* 44, 2401-2408.



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