Synthesis and characterization of molybdenum oxo complexes of two tripodal ligands – reactivity studies of a functional model for molybdenum oxotransferases

Anders Thapper, a Axel Behrens, a, b Jacob Fryxelius, a Maria H. Johansson, a Fabio Prestopino, a Miklos Czaun, a Dieter Rehder b and Ebbe Nordlander a*

a. Inorganic Chemistry, Center for Chemistry and Chemical Engineering, Lund University, Box 124, SE-221 00 Lund, Sweden. E-mail: Ebbe.Nordlander@inorg.lu.se
b. Institute of Inorganic and Applied Chemistry, University of Hamburg, Martin-Luther-King Platz 6, D-20146 Hamburg, Germany

SUPPLEMENTARY MATERIAL
Synthesis of bis-pyridin-2-ylmethyl-amine hydrochloride (DPA·3HCl). To a solution of 15.0 ml 2-(aminomethyl)pyridine (0.146 mol) in 150 ml ethanol, 13.9 ml of 2-pyridinecarboxaldehyde (0.145 mol) dissolved in 40 ml ethanol was added dropwise. The mixture was left stirring for 15 min. Sodium borohydride (14.0 g, 0.370 mol) was added in small portions and the reaction was refluxed for 50 minutes. The mixture was cooled in an ice bath and 15 ml of conc. HCl dissolved in 10 ml ethanol was added dropwise during 30 minutes while the flask remained in the ice bath. The flask was left in the refrigerator overnight. The resultant precipitated white product was isolated by filtration and the remaining solution reduced to dryness and dissolved in 150 ml ether and 240 ml ethanol. To this solution 60 ml of HCl was added with stirring and more product precipitated. This product was also isolated by filtration and the combined products were dissolved in 180 ml of water. Sodium hydroxide (24g, 0.6 mol) dissolved in 60 ml water was added and a two-phase system with the product on top formed. The product was extracted with 5 x 80 ml diethyl ether evaporated to dryness, dissolved in 250 ml ethanol and filtered. The filtered solution was cooled in an ice bath and 65 ml of conc. HCl was added and a white precipitate formed. The product was isolated by filtration and dried in vacuo to give 38.6 g of white crystals (0.125 mol, 86% yield). To obtain the free base, a water solution of DPA·3HCl was made basic by the addition of solid KOH and the DPA was extracted with 3 x 10 ml dichloromethane. The organic phase was dried with MgSO₄, filtered and evaporated to give DPA as a yellow oil. ¹H-NMR (CD₃OD): δ 8.48 (d, 2H) 7.79 (t, 2H), 7.49 (d, 2H), 7.28 (t, 2H), 3.92 (s, 4H)
Figure S1. $^1$H-$^1$H COSY spectrum of [MoO$_2$(L-O)]$^+$ 1.