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A Bridged Mo(VI) Complex Containing Six and Five Coordinate Mo: Synthesis, ^{95}Mo N.m.r. Spectroscopy and X-Ray Crystal Structure of $Mo_2O_5(C_{17}H_{17}N_2O)_2$

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Introduction

1-*n*-2-α-hydroxybenzylbenzimidazole (nPHOBB) forms complexes with Ni(II) ions one of which has been shown to be an excellent model for the active site of the enzyme urease [1]. To extend our knowledge of the electronic and steric properties of nPHOBB we have synthesized some Mo(VI) complexes and measured their ^{95}Mo n.m.r. spectra. We now report the preparation, ^{95}Mo n.m.r. spectrum and X-ray crystal structure of $Mo_2O_5(nPOBB)_2$ where nPOBB is the deprotonated form of nPHOBB.

Experimental

Rapid stirring of 0.0108 mol nPHOBB and 0.0054 mol MoO_2Cl_2 in dry ethanol under argon for 6 h gave a white product. Subsequent washing with distilled water followed by hot ethanol and recrystallisation from dichloromethane gave a white product which analysed for $C_{34}H_{34}MoN_4O_7$. A saturated solution of this product in dichloromethane gave the ^{95}Mo n.m.r. spectrum shown (Fig. 1). Crystals suitable for X-ray structure determination were obtained by slow evaporation of a saturated dichloromethane solution.

Crystal Data

$Mo_2O_5(nPOBB)_2$, orthorhombic, $a = 16.854(2)$, $b = 18.453(3)$, $c = 21.720(2)$ Å, $U = 6755$ Å^3, space group Pbca, $z = 8$, $M = 802.5$, $D_c = 1.58$ g cm^{-3}, μ(Cu-Kα) = 66 cm^{-1}. Data were measured on a Nicolet R3m diffractometer with graphite monochromated Cu-Kα radiation and using ω scans. The structure was solved by direct methods and refined anisotropically using absorption corrected data to $R = 0.032$ for the 3418 independent observed reflections. Selected bond distances and angles are given in Fig. 2 [$\theta \leqslant 53°$, $|F_o| > 3\sigma(|F_o|)$].

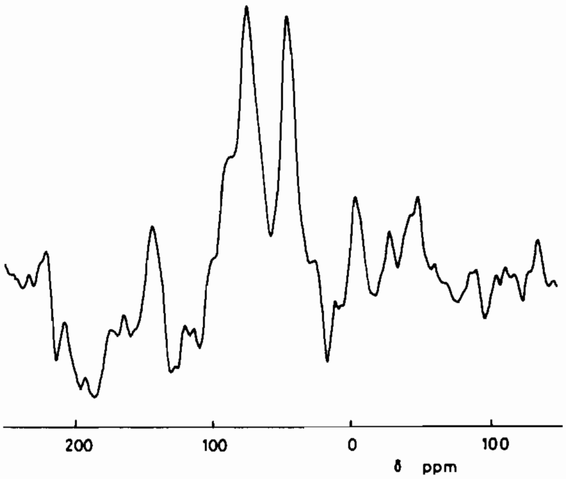

Fig. 1. ^{95}Mo FT n.m.r. spectrum of $Mo_2O_5(nPOBB)_2$.

The atomic coordinates for this work are available on request from the Director of Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

N..m.r. Data

The spectrum was measured in a 5.87T applied field. (Bruker WM-250 spectrometer). Approximately 3.5 million pulses were required to obtain an S:N ratio of 6:1. A 500 sec delay was inserted between the RF pulse and the start of data acquisition to control the effects of acoustic ringing in the n.m.r. probe. The data were multiplied by an appropriate exponential window function before transformation. Chemical shifts are referenced to 2 *N* aqueous Na_2MoO_4 (external reference).

Discussion

^{95}Mo n.m.r. of the title compound show two resonances, one at 76 ppm and the other at 47 ppm (Fig. 1). This suggested to us that $Mo_2O_5(nPOBB)_2$ was not a 'simple' $Mo_2O_5^{2+}$ core dimer with two bridging ligands since this would be expected to give a single ^{95}Mo n.m.r. signal, but a mixed coordination number dimer. The crystal structure of $Mo_2O_5(nPOBB)_2$ supported this suggestion. In the title compound the Mo(2)–O(2)–Mo(1) bridge angle of 116.6(1)° shows considerable deviation from the linearity found in $K_2[Mo_2O_5(C_2O_4)_2](H_2O)_2$ [2] and near linearity found in $[MoO_2Cl(dmf)_2]_2O$ [3] and is considered to be a consequence of the steric requirements of the nPOBB bridge. The oxygen

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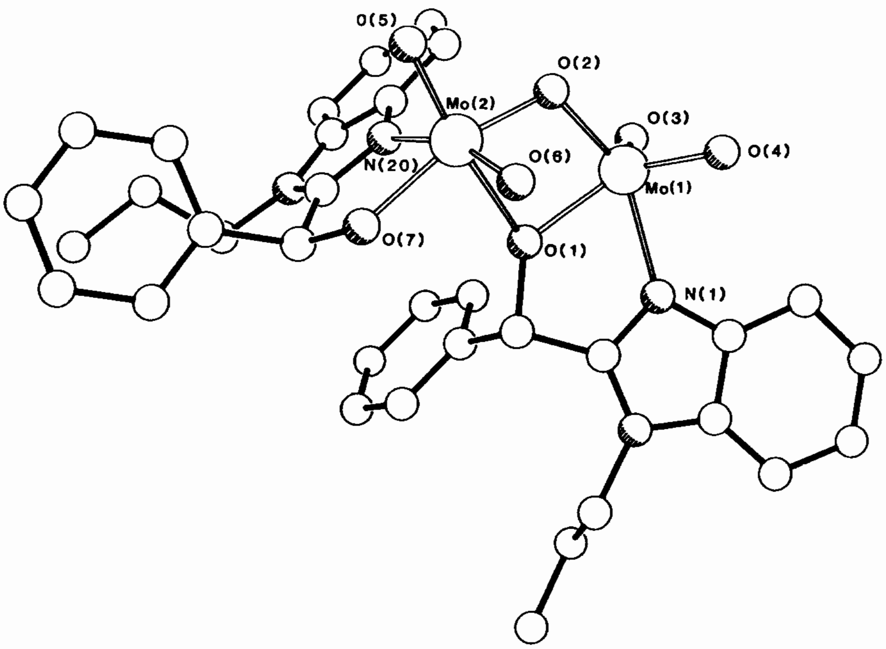

Fig. 2. The molecular structure of $Mo_2O_5(nPOBB)_2$ showing selected bond lengths with e.s.d.'s in parentheses. Mo(1)–O(1) 2.026(3), Mo(1)–O(2) 1.872(3), Mo(1)–O(3) 1.698(3), Mo(1)–O(4) 1.691(3), Mo(1)–N(1) 2.141(3), Mo(2)–O(1) 2.358(3), Mo(2)–O(2) 1.959(3), Mo(2)–O(5) 1.683(3), Mo(2)–O(6) 1.699(3), Mo(2)–O(7) 1.928(3), Mo(2)–N(20) 2.273(3) Å.

atom of the nPOBB bridge, in which the Mo(2)–O(1)–Mo(1) angle is 95.8(1)°, is closer to Mo(1) (Mo(1)–O(1) 2.026(3) Å) than Mo(2) (Mo(2)–O(1) 2.358(3) Å). This bridge asymmetry is also found for the 9,10-phenanthrenesemiquinone ligands in $Mo_2O_5(O_2C_{14}H_8)_2$ [4]. Since O(I) is *trans* to the terminal oxo group O(5) on Mo(2), the long Mo(2)–O(1) bond length of 2.358(3) Å (*cf.* the Mo(2)–O(7) bond length of 1.928(3) Å) can be attributed to the structural *trans* effect. This also accounts for the long Mo(2)–N(20) bond length of 2.273(3) Å, since N(20) is *trans* to the terminal oxo group O(6) on Mo(2). The second nPOBB ligand does not bridge but chelates exclusively to Mo(2). This results in an interesting Mo(VI) structural type, *viz.* a Mo(VI) dimer in which one of the molybdenum atoms is six coordinate and the other is five coordinate. The 'dimer' can be viewed in terms of edge sharing by an octahedral Mo(VI) and a square pyramidal Mo(VI) species. This is in contrast to $Mo_2O_5(O_2C_{14}H_8)_2$ and compounds of related structural type, in which both ligands bridge to produce dimers based on edge sharing by two octahedral Mo(VI) species. It is claimed that the presence of two coordinately different Mo atoms in the same molecule gives rise to the observed ^{95}Mo n.m.r. spectrum. The signal at 47 ppm is in a similar position to that found for $MoO_2(nPOBB)_2$ which is a monomeric, six coordinate Mo(VI) complex [5], and is assigned to the octahedrally coordinated Mo atom in $Mo_2O_5(nPOBB)_2$. The signal at 76 ppm being down field of that at 47 ppm indicates deshielding of a Mo(VI) atom relative to that of a six coordinate species. Such deshielding would probably result from a change in coordination number from six to five and it is therefore suggested that the 76 ppm peak is due to the five coordinate Mo(VI) atom.

References

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