X-ray Crystal Structure and ^{95}Mo NMR Spectroscopic Investigation of $MoO_2(C_{13}H_9N_2O)_2(C_2H_5OH)_2$

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The ^{95}Mo NMR spectra of a series of *cis*-dioxo Mo(VI) complexes with 2 substituted benzimidazoles have been reported [1]. The ligand in the title compound *i.e.* 2-*ortho*-hydroxyphenylbenzimidazole (HPB) is similar to these benzimidazoles, differing only in the position of the hydroxyl group. Because of this and particularly its relationship to the interesting single oxo bridged species $Mo_2O_5(HPB)_2(C_3H_7NO)_2(H_2O)_{1.5}$ [2] it was decided to determine the X-ray crystal structure and measure the ^{95}Mo NMR spectrum of the title compound.

Experimental

Addition of an ethanolic solution of MoO_2(acetylacetonate)$_2$ (0.006 mol) to a boiling ethanolic solution of 2-*ortho*-hydroxyphenylbenzimidazole (0.031 mol) over a period of 3–4 h gave a dark orange solution which on slow evaporation produced large orange crystals. One of these crystals was coated with epoxy resin and used in the X-ray diffraction study.

Crystal Data

$MoC_{30}H_{30}N_4O_6$, M = 638.532, monoclinic, a = 10816(4), b = 19.355(9), c = 14.194(6) Å, U = 2951.2 Å^3, β = 96.69(2)°, space group $P2_1/c$, Z = 4, D_c = 1.44 gm cm^{-3}, μ(Mo Kα) = 7.95 cm^{-1}. Cell dimensions were derived from the angular measurements of 25 strong reflections on a Phillips PW 1100 diffractometer. 3284 reflections were recorded (1.5° $< \theta <$ 25.0°) using graphite monochromated Mo-Kα radiation and a 2θ scan. Equivalent reflections were averaged to give 3033 unique observed intensities ($F > 4\sigma(F)$). Lorentz, polarization but no absorption corrections were applied. The structure was solved using Patterson and Fourier methods and least squares refinement gave a final R value of 0.048. All computing was carried out using SHELX 76 and ORTEP(II) [3]. Full crystallographic details are reported in [4].

NMR Data

Attempts were made to record the ^{95}Mo NMR spectrum of a saturated ethanolic solution of the title compound in a 5.87 T field (Bruker WM-250 F.T. spectrometer). A chemical shift range of ±150 ppm (with reference to 2 N aqueous Na_2MoO_4) was covered, but no signals were observed after 2 million scans. Acoustic ringing effects in the probe head were controlled by appropriate delays between the R.F. pulse and data acquisitions.

Discussion

The arrangement of atoms in $MoO_2(HPB)_2(C_2H_5OH)_2$ is shown in Fig. 1 (the hydrogen bonded ethanol molecules are not shown). The MoO_2^{2+} core has the *cis* configuration with an average Mo–O$_t$ bond length of 1.70 Å indicative of multiple bonding [5]. The O_t–Mo–O_t^* angle of 103.5(2) is in the usual range for oxomolybdenum(VI) complexes [6]. Within the ligand the Mo–O and Mo–N bond distances of 1.938(5), 2.059(4) and 2.142(5), 2.325(5) Å are unexceptional [7, 8]. The differences between the two Mo–O bonds (0.12 Å) and the two Mo–N bonds (0.18 Å) can be attributed to the ***trans*** influence of the *cis*-dioxo groups [6].

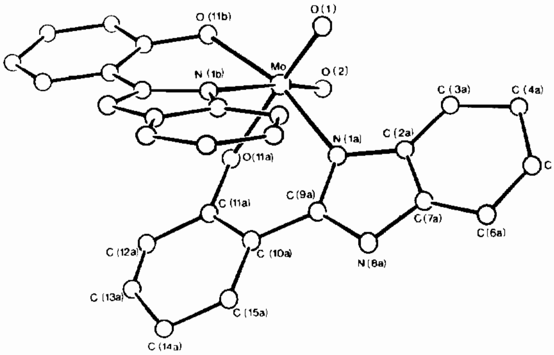

Fig. 1. X-ray crystal structure of $MoO_2(C_{13}H_9N_2O)_2(C_2H_5OH)_2$.

It has been observed that the weaker π bonding donor atoms in octahedral *cis*-dioxo Mo(VI) complexes lie ***trans*** to the terminal oxygen atoms [9]. In $MoO_2(HPB)_2(C_2H_5OH)_2$ this would mean that either both imino nitrogen or both phenoxide oxygen atoms, depending on which is argued to be the weaker π donor, should be ***trans*** to the terminal oxygen atoms. From Fig. 1 this is clearly not the case. This anomalous coordination is observed in two complexes of Mo(VI) with quadridentate Schiff bases of salicylaldehyde *viz.* MoO_2L [10–13]. However, in these the anomalous coordination is forced on the complex by constraints within the ligand. In the case of HPB no such internal constraints exist. To investigate the cause of this molecular models of $MoO_2(HPB)_2$ were built with: (i) both phenoxide oxygen atoms ***trans*** to $Mo-O_t$, (ii) both imino nitrogen atoms ***trans*** to $Mo-O_t$, (iii) as in Fig. 1. Of the three models iii) is the one in which interligand steric interactions are minimized.

The absence of a ^{95}Mo NMR signal in the title compound is puzzling since related complexes have been shown to give signals at approximately 50 ppm [1]. The reason for this absence is not known but a suggestion is that the relaxation time is such that severe line broadening occurs.

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