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^{95}Mo NMR Spectra of $MoO_2(C_8H_7N_2S)_2$ and X-ray Crystal Structure of $Mo_2O_4(C_8H_7N_2S)_2(C_3H_7NO)_2$

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Abstract

The facile preparation of $MoO_2(C_8H_7N_2S)_2$ is given and its complex behaviour in dimethylformamide, as revealed by ^{95}Mo NMR spectroscopy, discussed. The X-ray crystal structure of one of the products obtained from this dimethylformamide solution is briefly described. This structure indicates that the Mo(VI) has been reduced to Mo(V) and is based on the $[Mo_2O_4]^{2+}$ core.

Introduction

In previous papers we have reported the ^{95}Mo NMR spectroscopy of Mo(VI) complexes with nitrogen and oxygen donors [1, 2]. To widen these NMR studies we have extended the range of donor atoms available to Mo(VI) to include sulphur. Since one of the N,O donor ligands we studied was 2-hydroxymethylbenzimidazole its sulphur analogue 2-mercaptomethylbenzimidazole (LH) was synthesized and complexed with Mo(VI). The deprotonated form of LH is denoted L.

Experimental

$MoO_2(L)_2$

A 0.005 mol solution of MoO_2(acetylacetonate)$_2$ in methanol was added dropwise to a 0.030 mol solution of LH in methanol over a period of 1 h under dinitrogen. A brown product formed and after the solution had been stirred for a further hour it was filtered, washed with ethanol and dried over P_2O_5 under vacuum. *Anal.* Found: C, 41.8; H, 3.2; N, 12.0; Mo, 20.3. Calc. for MoO_2L_2: C, 42.3; H, 3.1; N, 12.3; Mo, 21.2%.

$Mo_2O_4(L)_2(C_3H_7NO)_2$

MoO_2L_2 (0.0075 mol) was dissolved in 100 ml dimethylformamide. The resulting dark brown solution was heated to 65 °C for 10 min and then cooled slowly with stirring. The yellow solid that formed after approximately one hour was filtered, washed with ethanol and dried at 50 °C under vacuum. Recrystallisation from dimethylformamide gave yellow crystals suitable for X-ray crystallographic study. *Anal.* Found: C, 36.1; H, 3.9; N, 11.7; Mo, 26.2. Calc. for $Mo_2O_4(L)_2(C_3H_7NO)_2$: C, 36.3; H, 3.9; N, 11.5; Mo, 26.2%.

2-Mercaptomethylbenzimidazole, $C_8H_7N_2SH$

All manipulations of solutions were carried out in an atmosphere of dinitrogen. The product is reasonably air stable but its solutions are readily oxidized.

o-Phenylenediamine (54 g, 0.5 mol) and thioglycollic acid (46 g, 0.5 mol) were heated under reflux in 4 M hydrochloric acid (500 cm^3) for 1 h. After cooling, the solution was basified using ammonium hydroxide solution (0.880) and a pink solid separated. The solution was decanted and the solid washed copiously with distilled water, again by decantation. The crude product was decolourized using charcoal and recrystallized from 95% aqueous ethanol. This yielded colourless prisms which melted with decomposition at 157–158 °C (literature m.p. 158 °C). Yield 50%.

NMR Data

All ^{95}Mo NMR spectra were recorded using a Bruker WM-250 Spectrometer, ^{95}Mo resonance frequency 16.3 MHz. Aqueous sodium molybdate (2 M) was used as an external chemical shift reference. All measurements were made using a 50 kHz sweep width and 40 ms data acquisition time. All free induction decays were multiplied by an exponential window function selected to give a minimum line width of twice the digital resolution after Fourier transformation. Experimental parameters were selected to minimise the effects of acoustic ringing in the NMR probe head.

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X-Ray Crystal Structure Data

$Mo_2C_{16}H_{14}N_4O_4S_2 2C_3H_7NO$, $M = 728$, triclinic, $a = 13.568(5)$, $b = 12.124(4)$, $c = 9.398(4)$ Å, $\alpha = 107.05(3)$, $\beta = 74.68(2)$, $\gamma = 101.52(4)°$, $U = 1412.19$ Å^3, space group $P\bar{1}$, $Z = 2$, $D_c = 1.71$ g cm^{-3}, μ (Mo Kα) = 7.95 cm^{-1}. Cell dimensions were derived from angular measurements of 25 strong reflections on a Philips PW1100 four circle diffractometer. 2753 reflections were recorded ($1.5° < \theta < 25.0°$) using graphite monochromated Mo Kα radiation and a 2 θ scan. Equivalent reflections were averaged to give 2637 unique reflections. Lorentz polarisation 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 0.042. All computing was carried out using SHELX76 [3].

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.

Discussion

The infra-red spectrum of MoO_2L_2 showed two strong bands at 895 cm^{-1} and 860 cm^{-1} respectively which can be assigned to the $\nu(Mo{=}O_t)$ of a *cis* dioxo Mo(VI) core. A strong band at 364 cm^{-1} can be assigned to the ν(Mo–S). The ^{95}Mo NMR spectrum of a freshly prepared solution of MoO_2L_2 in dimethylformamide (DMF) shows a signal at 410 ppm (Fig. 1(a)) which is in the region expected for a *cis* dioxo Mo(VI) species with 2N and 2S$^-$ donor atoms [4, 5]. This evidence in conjunction with the analytical figures and method of preparation leads to the formulation of MoO_2L_2 as a *cis* dioxo Mo(VI) species with two chelating deprotonated 2 α mercaptomethylbenzimidazole ligands (L) in a distorted octahedral array.

We were not able to obtain a ^{95}Mo NMR signal of $Mo_2O_4L_2$ (dimethylformamide)$_2$ despite repeated attempts. Even with 'long runs' (approximately 3×10^6 scans) no evidence of a signal was obtained. This is surprising since signals in the region 600 to 700 ppm have been recorded for other $Mo_2O_4^{2+}$ core containing compounds [6, 7]. The structure of $Mo_2O_4L_2(DMF)_2$ is illustrated in Fig. 2 which shows it to contain the $[Mo_2O_4]^{2+}$ core. The Mo–Mo distance of 2.566(1) Å is similar to that of 2.544 Å found in $Ba[Mo_2O_4(C_2O_4)_2(H_2O)_2]$ [8]. The Mo(VI) starting material has clearly been reduced to Mo(V) and the Mo–Mo distance indicates that the Mo atoms have formed an electron pair bond. If the Mo–Mo bond is excluded the structure can be described as two edge sharing distorted trigonal bipyramids. The DMF is hydrogen bonded to the hydrogens of the benzimidazole ring amino nitrogens. A list of selected bond lengths and bond angles is given in Table I.

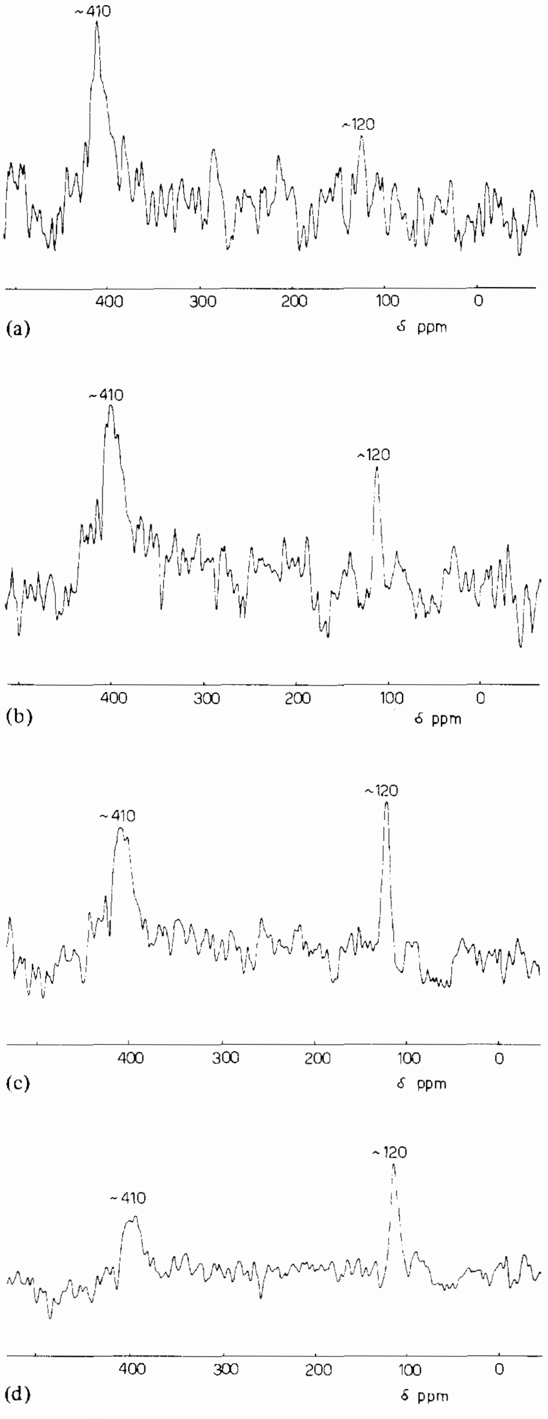


Fig. 1. ^{95}Mo FT NMR spectrum of MoO_2L_2 in dimethylformamide: (a) after 6 h; (b) after 18 h; (c) after 36 h; (d) after 58 h.

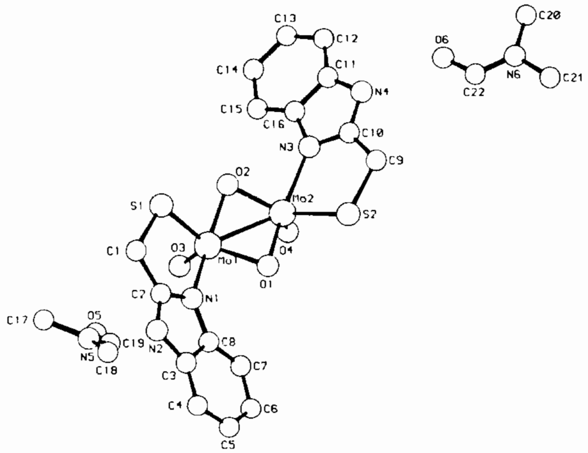
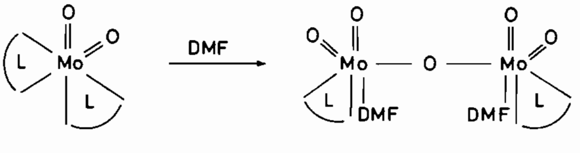


Fig. 2. The structure of $Mo_2O_4L_2(DMF)_2$.

TABLE I. Bond Lengths (Å) and Bond Angles (°)

Mo(1)•••Mo(2)	2.566(1)
Mo(1)•••O(1)	1.892(5)
Mo(1)•••O(2)	1.949(6)
Mo(1)•••O(3)	1.656(5)
Mo(1)•••N(1)	2.122(7)
Mo(1)•••S(1)	2.370(3)
Mo(2)•••O(1)	1.949(6)
Mo(2)•••O(2)	1.886(6)
Mo(2)•••O(4)	1.666(6)
Mo(2)•••N(3)	2.132(8)
Mo(2)•••S(2)	2.379(2)
O(1)•••Mo(1)•••O(2)	92.0(2)
O(1)•••Mo(1)•••O(3)	116.2(3)
O(2)•••Mo(1)•••O(3)	107.8(3)
O(3)•••Mo(1)•••Mo(2)	106.8(3)
N(1)•••Mo(1)•••Mo(2)	133.0(2)
N(1)•••Mo(1)•••O(1)	84.3(3)
N(1)•••Mo(1)•••O(2)	153.1(2)
N(1)•••Mo(1)•••O(3)	97.7(3)
S(1)•••Mo(1)•••Mo(2)	122.6(1)
S(1)•••Mo(1)•••O(1)	129.3(2)
S(1)•••Mo(1)•••O(2)	82.1(2)
S(1)•••Mo(1)•••O(3)	113.6(2)
S(1)•••Mo(1)•••N(1)	79.8(2)
O(2)•••Mo(2)•••O(1)	92.2(3)
O(4)•••Mo(2)•••Mo(1)	106.5(3)
O(4)•••Mo(2)•••O(1)	106.6(3)
O(4)•••Mo(2)•••O(2)	117.0(3)
N(3)•••Mo(2)•••Mo(1)	136.1(2)
N(3)•••Mo(2)•••O(1)	155.1(2)
N(3)•••Mo(2)•••O(2)	87.2(3)
N(3)•••Mo(2)•••O(4)	95.8(3)
S(2)•••Mo(2)•••Mo(1)	119.9(1)
S(2)•••Mo(2)•••O(1)	80.9(2)
S(2)•••Mo(2)•••O(2)	125.2(2)
S(2)•••Mo(2)•••O(4)	117.1(2)
S(2)•••Mo(2)•••N(3)	79.2(2)
Mo(2)•••O(1)•••Mo(1)	83.8(2)
Mo(2)•••O(2)•••Mo(1)	84.0(2)
C(2)•••N(1)•••Mo(1)	122.1(5)
C(8)•••N(1)•••Mo(1)	132.2(6)

A saturated solution of MoO_2L_2 in dimethylformamide was prepared immediately before the start of the NMR study, and its spectrum is shown after 6 h (Fig. 1(a)), 18 h (Fig. 1(b)), 36 h (Fig. 1(c)) and 58 h (Fig. 1(d)). The interesting feature in these figures is the increase in intensity with time of the signal at 120 ppm and the decrease in intensity of the 410 ppm signal. Since the peak at 410 ppm is attributed to MoO_2L_2 and this undergoes reduction to give $Mo_2O_4L_2$ then a decrease in its intensity with time might be expected. In a recent paper of ours we claim that a ^{95}Mo NMR signal at approximately 120 ppm is characteristic of the $[O_2Mo{-}O{-}MoO_2]^{2+}$ core with six coordination about each Mo atom being completed by additional oxygen and nitrogen donors [2]. If this claim is modified to include sulphur atoms in these additional donors then a possible explanation of figures 1(a) to 1(d) involves the slow conversion of MoO_2L_2 to $Mo_2O_5L_2(DMF)_2$.



Replacement of the O^- donors in $MoO_2(C_8H_7N_2O)_2$ with S^- to give MoO_2L_2 causes a shift in the ^{95}Mo NMR signal from 57 ppm [1] to 410 ppm, which is similar to the shift seen in going from MoO_2(8-hydroxyquinoline)$_2$, 58 ppm [9], to MoO_2(8-mercaptoquinoline)$_2$, 460 ppm, [5].

In view of this it seems most unlikely that substitution of O^- with S^- in complexes of the form $Mo_2O_5(L)_2(DMF)_2$, where L is an O^-, N donor ligand, which give a signal at 120 ppm [2], causes no shift. The most likely explanation, which is currently being investigated, is that during the reduction from Mo(VI) to Mo(V) the ligand undergoes oxidation to a sulphoxide and this is the ligand (now an N, O donor) which together with dimethylformamide completes the six coordination about the Mo atoms of the $Mo_2O_5{}^{2+}$ core.

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