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^{95}Mo NMR Studies of Complexes containing the $Mo_2O_5^{2+}$ Core and Crystal Structure of $Mo_2O_5[SC_6H_4NHCH_2C_5H_4N]_2(C_3H_7NO)_3$

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Abstract

The crystal structure of $Mo_2O_5[SC_6H_4NHCH_2C_5H_4N]_2(C_3N_7NO)_3$ is reported and seen to consist of a single oxo-bridged species with each Mo atom bonded to *cis* dioxo groups and the nitrogen atoms and thiolate group of the tridentate ligand. ^{95}Mo NMR spectra of this and three related complexes are presented and attempts made to interpret them in terms of their crystal structures.

Introduction

In a recent communication we reported the ^{95}Mo NMR spectra of $Mo_2O_5((CH_3)_2NCH_2CH_2NHCH_2CH_2S)_2$ and $Mo_2O_5((CH_3)_2NCH_2CH_2NHCH_2C(CH_3)_2S)_2$ in dimethylformamide (DMF) [1]. In both cases signals at approximately ($\approx$) 330 ppm and $\approx$125 ppm were observed. The appearance of a signal at $\approx$125 ppm in both of these complexes was unexpected and suggested to us that an $Mo_2O_5^{2+}$ species, without coordinated S, was present in solution. Isolation of white crystals from a DMF solution of $Mo_2O_5((CH_3)_2NCH_2CH_2NHCH_2CH_2S)_2$ was achieved and subsequent X-ray crystallography showed the complex to have a novel tetrameric structure in which the displaced thiolates formed disulphide bridges between diagonal molybdenum atoms [1]. To determine if this tetrameric structure was of more general occurrence we investigated the complexes formed by Mo with the tri-dentate ligand *N*-(2-pyridylmethyl)-2-mercaptoaniline.

Experimental

Synthesis of the Ligands and Complexes

N-(2-mercaptoethyl)-*N'*,*N'*-dimethylethylenediamine, $(CH_3)_2NCH_2CH_2NHCH_2CH_2SH$; *N*-(2-mercapto-2-methylpropyl)-*N'*,*N'*-dimethylethylenediamine, $(CH_3)_2NCH_2CH_2NHCH_2C(CH_3)_2SH$; and *N*-(2-pyridylmethyl)-2-mercaptoaniline, $HSC_6H_4NHCH_2C_5H_4N$, were synthesized as described in the literature [2].

(μ-Oxo)bis[[*N*,*N*-dimethyl-*N'*-(2-mercapto ethyl)-ethylenediamino]dioxomolybdenum(VI)], $Mo_2O_5[(CH_3)_2NCH_2CH_2NHCH_2CH_2S]_2$ (**I**); (μ-oxo)bis[[*N*,*N*-dimethyl-*N'*-(2-methyl-2-mercaptopropyl)-ethylenediamino]dioxomolybdenum(VI)], $Mo_2O_5[(CH_3)_2NCH_2CH_2NHCH_2C(CH_3)_2S]_2$ (**II**); and (μ-oxo)bis[[(2-(2-picolyl)amino)benzenethiolato]dioxomolybdenum(VI)], $Mo_2O_5(SC_6H_4NHCH_2C_5H_4N)_2$ (**III**), were all prepared by the same general method as described in ref. 2 *viz.* addition of a methanol solution of the ligand to a methanol solution of $MoO_2(AcAc)_2$ where AcAc is acetyl acetonate.

In the case of **III** dissolution in DMF and cooling of the filtered solution overnight in a refigerator

TABLE I. Analytical Results for the Complexes

	Complex		C	H	N	Mo
I	$Mo_2O_5(C_6H_{15}N_2S)_2$	Found	25.3	5.5	9.7	33.3
		Calculated	25.4	5.3	9.9	33.9
II	$Mo_2O_5(C_8H_{19}N_2S)_2$	Found	30.7	6.0	9.1	30.9
		Calculated	30.9	6.2	9.0	30.8
III	$Mo_2O_5(C_{12}H_{11}N_2S)_2$	Found	42.7	4.5	10.3	22.7
		Calculated	43.0	4.7	10.6	20.8

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TABLE II. Infra Red Spectral Data for the Complexes

Complex	Assignment		
	NH (cm^{-1})	Mo–O_t (cm^{-1})	Mo–O–Mo (cm^{-1})
I	3220m	920vs 880s	720s(br)
II	3240w(br)	910vs 875vs	680s
III	3350s(br)	930vs 900vs 875vs	780s

vs = very strong, s = strong, m = medium, br = broad, w = weak.

produced reddish orange crystals suitable for X-ray crystallography. The complexes **I**, **II** and **III** were identified as being the same as those reported in ref. 2 on the basis of elemental analysis (Table I) and infra-red spectra (Table II).

^{95}*Mo NMR Spectra*

The spectra of complex **I** and $Mo_4O_{12}(C_{12}H_{30}N_4S_2)_2(C_3H_7ON)_2$ were obtained from a Bruker WM 250 Spectrometer operating at 16.3 MHz. The remaining spectra were obtained from a Jeol 90 Spectrometer operating at 5.6 MHz. An aqueous 2 M sodium molybdate solution (pH 11) was used as an external chemical shift reference.

X-ray Crystal Structure Data

$Mo_2C_{33}H_{43}N_7O_8S_2$, $M_r = 921.7$, monoclinic, $a = 10.413(2)$, $b = 18.557(4)$, $c = 21.523(5)$ Å, $\beta = 98.91(2)^\circ$, $U = 4109$ Å^3, space group $P2_1/n$, $Z = 4$, $D_c = 1.49$ g cm^{-3}, μ(Cu Kα) = 63 cm^{-1}.

Refined unit cell parameters were obtained by centring 19 reflections on a Nicolet R3m diffractometer, 5158 independent reflections ($\theta \leqslant 55^\circ$) were measured for a single crystal (0.4 × 0.6 × 0.8) mm with Cu Kα radiation ($\lambda = 1.54178$ Å, graphite monochromated) and using the omega scan measuring routine. Of these 4680 had $|F_o| > 3\sigma(|F_o|)$ and were considered to be observed). The net count of two check reflections (the $15\bar{1}$ and $1\bar{5}\bar{1}$) did not change significantly during data collection indicating that no deterioriation of the crystal had occurred. The data were brought to a uniform arbitrary scale and Lorentz, polarization and numerical absorption correction applied.

The structure was solved by the heavy atom method which gave the positions of the two independent Mo atoms. The remaining non-hydrogen atoms were obtained from subsequent ΔF maps. These maps revealed the presence of three solvent molecules (DMF) one of which was disordered adopting two principal partially overlapping orientations with estimated occupancies of 0.6 and 0.4. The non-hydrogen atoms were refined non-isotropically. The hydrogen atoms on N1 and N3 were located in a ΔF map and refined isotropically. The remaining hydrogen atom positions were idealized (C–H = 0.96 Å), assigned isotropic thermal parameters, $U(H) = 1.2\ U_{eq}(C)$ and allowed to ride on their parent C atoms. The methyl groups of the DMF molecules were refined as rigid bodies. The refinement of the disordered partial occupancy DMF molecule was constrained such that equivalent bonds in the two fragments had the same bond lengths. Refinement was by block cascade full matrix least-squares to $R = 0.034$, $R_w = 0.036$, $[w^{-1} = \sigma^2(F) + 0.00026F^2]$. Computations were carried out on an ECLIPSE S140 computer using the SHELXTL program system [3].

Results and Discussion

The structure of **III** is shown in Fig. 1. Atomic coordinates and equivalent isotropic thermal parameters are given in Table III and selected bond lengths and angles in Table IV. The structure is seen to be based on the $Mo_2O_5^{2+}$ core with a bridge angle [Mo(2)–O(1)–Mo(1)] of 165.6(2)° which is more obtuse than that in **I** (147.0(5)° [4] and **II** (143.8°) [2] but very similar to that in $Mo_2O_5(C_{13}H_9N_2O)_2(DMF)_2(H_2O)_{1.5}$ (165.4(5)°) [5]. The two bridge distances Mo(1)–O(1) (1.896(3)) and Mo(2)–O(1) (1.900(3)) are comparable to those in **I** (1.908(3)) [4] and **II** (1.929(5) and 1.917(5)) [2]. Within statistical significance the four Mo to terminal oxygen distances are the same and typical for this type of bond [5]. Of the Mo–N bond lengths those to the pyridyl nitrogens are marginally longer than those to the amino nitrogens. The latter bond distances (2.334(3) and 2.341(3) Å) are comparable to the Mo to central nitrogen atom bond lengths in **I** (2.345(9) Å) [4] and **II** (2.310(6) Å) [2]. The Mo–S bond lengths of 2.469(1) and 2.462(1) in **III** are slightly longer than the corresponding bonds in **I** (2.442(3) Å) [4] and **II** (2.422(3) and 2.416(3) Å) [2].

In the 'octahedron' defined by the six donor atoms about each Mo this atom lies 0.33 Å below the equatorial plane. The pyridyl rings are nearly parallel (8° between mean planes) and almost eclipsed with a nitrogen distance of 3.6 Å. The molecule can be said to have an approximate non-crystallographic two-fold axis through the bridge oxygen and perpendicular to the plane of the 'dished' Mo atoms.

The amino nitrogen protons form strong hydrogen bonds to the oxygen atoms of the two ordered DMF molecules. The amino nitrogen to DMF oxygen distances being N1–O7, 2.82 and N3–O6, 2.84 Å respectively.

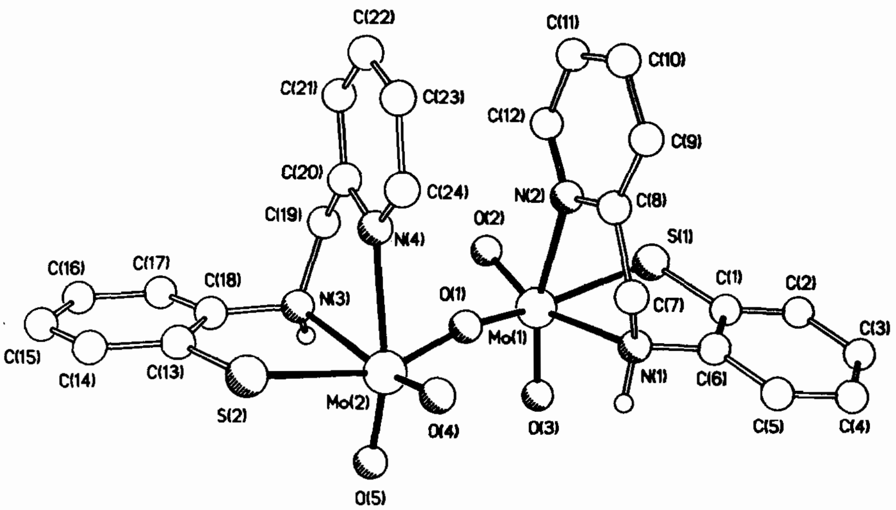

Fig. 1. The structure of **III**.

TABLE III. Atom Coordinates (×10^4) and Temperature Factors (Å^2 × 10^3)

Atom	x	y	z	U^a
Mo(1)	3430(1)	5580(1)	1045(1)	41(1)
MO(2)	5391(1)	7286(1)	1336(1)	45(1)
O(1)	4598(3)	6363(1)	1226(1)	49(1)
O(2)	3727(3)	5267(2)	333(1)	57(1)
O(3)	1991(3)	6030(2)	916(2)	64(1)
O(4)	5780(3)	7386(2)	2135(1)	67(1)
O(5)	4073(3)	7817(2)	1094(2)	61(1)
S(1)	2497(1)	4390(1)	1228(1)	59(1)
C(1)	2097(4)	4498(2)	1985(2)	51(1)
C(2)	1306(5)	4001(3)	2230(3)	75(2)
C(3)	942(5)	4105(4)	2813(3)	93(2)
C(4)	1373(6)	4696(4)	3172(3)	90(2)
C(5)	2190(5)	5178(3)	2943(2)	70(1)
C(6)	2565(4)	5080(2)	2362(2)	48(1)
N(1)	3423(4)	5599(2)	2129(2)	46(1)
C(7)	4775(4)	5566(2)	2475(2)	53(1)
C(8)	5582(4)	5033(2)	2182(2)	48(1)
C(9)	6567(5)	4633(3)	2524(2)	60(1)
C(10)	7304(5)	4182(3)	2215(3)	74(2)
C(11)	7033(5)	4132(3)	1575(3)	70(1)
C(12)	6025(5)	4533(3)	1256(2)	58(1)
N(2)	5297(3)	4969(2)	1553(2)	45(1)
S(2)	7029(1)	8215(1)	1228(1)	62(1)
C(13)	7086(4)	8211(2)	417(2)	51(1)
C(14)	7767(5)	8741(3)	150(2)	68(1)
C(15)	7789(6)	8749(3)	−492(3)	83(2)
C(16)	7134(6)	8230(3)	−870(2)	79(2)
C(17)	6461(5)	7698(3)	−612(2)	63(1)
C(18)	6440(4)	7679(2)	22(2)	49(1)
N(3)	5744(3)	7110(2)	299(2)	44(1)
C(19)	6327(4)	6382(2)	233(2)	50(1)
C(20)	7360(4)	6226(2)	768(2)	50(1)
C(21)	8371(5)	5761(3)	714(3)	66(1)
C(22)	9259(5)	5600(3)	1230(3)	88(2)
C(23)	9142(5)	5917(3)	1799(3)	88(2)
C(24)	8100(5)	6390(3)	1832(3)	73(2)
N(4)	7220(3)	6537(2)	1318(2)	53(1)
O(6)	3298(4)	7255(2)	−486(2)	93(1)
C(25)	2312(5)	7151(3)	−270(3)	85(2)
N(5)	1102(5)	7265(3)	−554(3)	94(2)
C(26)	847(8)	7588(4)	−1166(3)	129(2)
C(27)	1(7)	7080(5)	−237(5)	153(2)
O(7)	2266(4)	6882(2)	2468(2)	89(1)
C(28)	1918(6)	7318(3)	2043(3)	79(2)
N(6)	1071(4)	7837(2)	2058(2)	68(1)
C(29)	784(6)	8357(4)	1561(3)	111(2)
C(30)	422(6)	7919(3)	2597(3)	100(2)
O(8)	9197(4)	386(2)	961(2)	145(2)
C(31)	8421(4)	595(2)	523(2)	119(2)
N(7)	7162(4)	781(2)	502(2)	116(2)
C(32)	6504(4)	670(2)	1068(2)	165(2)
C(33)	6396(4)	924(2)	−136(2)	141(2)
C(31′)	7929(4)	487(2)	856(2)	167(2)
N(7′)	7385(4)	716(2)	280(2)	114(2)
C(32′)	8215(4)	866(2)	−215(2)	126(2)
C(33′)	5965(4)	893(2)	187(2)	116(2)

^{a}Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

The crystal structures of **I** [4] and **II** [2] are based on the $Mo_2O_5^{2+}$ core with six coordination about each Mo being completed by the two N atoms and an S atom of the corresponding ligand. In dichloromethane (DCM) **I** gave a single peak at 340 ppm (Table V) and **II** a similar peak at 324 ppm. Since DCM is a non coordinating solvent it seems reasonable to suppose that the solid state structure persists in solution and that a signal at about 330 ppm is characteristic of the species exemplified by **I** and **II**. Complexes with an $Mo_2O_5^{2+}$ core in which six coordination about each Mo is completed by N or O

TABLE IV. Selected Bond Lengths and Bond Angles

Mo(1)–O(1)	1.896(3)	Mo(1)–O(2)	1.711(3)
Mo(1)–O(3)	1.700(3)	Mo(1)–S(1)	2.469(1)
Mo(1)–N(1)	2.334(3)	Mo(1)–N(2)	2.367(3)
Mo(2)–O(1)	1.900(3)	Mo(2)–O(4)	1.714(3)
Mo(2)–O(5)	1.704(3)	Mo(2)–S(2)	2.462(1)
Mo(2)–N(3)	2.341(3)	Mo(2)–N(4)	2.364(4)
O(1)–Mo(1)–O(2)	104.2(1)	O(1)–Mo(1)–O(3)	100.3(1)
O(2)–Mo(1)–O(3)	107.3(1)	O(1)–Mo(1)–S(1)	155.3(1)
O(2)–Mo(1)–S(1)	88.2(1)	O(3)–Mo(1)–S(1)	96.1(1)
O(i)–Mo(1)–N(1)	83.4(1)	O(2)–Mo(1)–N(1)	158.3(1)
O(3)–Mo(1)–N(1)	91.0(1)	S(1)–Mo(1)–N(1)	78.0(1)
O(1)–Mo(1)–N(2)	79.5(1)	O(2)–Mo(1)–N(2)	90.1(1)
O(3)–Mo(1)–N(2)	162.0(1)	S(1)–Mo(1)–N(2)	79.2(1)
N(1)–Mo(1)–N(2)	71.0(1)	O(1)–Mo(2)–O(4)	104.7(1)
O(1)–Mo(2)–O(5)	99.8(1)	O(4)–Mo(2)–O(5)	107.4(2)
O(1)–Mo(2)–S(2)	156.0(1)	O(4)–Mo(2)–S(2)	87.7(1)
O(5)–Mo(2)–S(2)	95.9(1)	O(1)–Mo(2)–N(3)	83.4(1)
O(4)–Mo(2)–N(3)	157.5(1)	O(5)–Mo(2)–N(3)	91.6(1)
S(2)–Mo(2)–N(3)	78.1(1)	O(1)–Mo(2)–N(4)	78.7(1)
O(4)–Mo(2)–N(4)	90.8(1)	O(5)–Mo(2)–N(4)	161.5(1)
S(2)–Mo(2)–N(4)	80.7(1)	N(3)–Mo(2)–N(4)	69.9(1)
Mo(1)–O(1)–Mo(2)	165.6(2)		

TABLE V. ^{95}Mo NMR Data for the Complexes

Complex	Solvent	Chemical shift^a δ (ppm)		$\Delta\nu_{1/2}$^{b} (Hz)
I	DMF	332 > 127	after 6 h	
		332 > 124	after 12 h	
		331 > 123	after 24 h	
		328 > 124	after 36 h	
		331 < 123	after 48 h	
		328 < 124	after 60 h	
	DCM	340		160
II	DMF	329		120
		129		50
	DCM	324		120
III	DMF	430		340
	DMF	125		80
IV^c	DMF	124		195

^{a}>, Intensity greater than; <, intensity less than. $^b\Delta\nu_{1/2}$, Line width at half peak height. ^{c}IV, $Mo_4O_{12}(C_{12}H_{30}N_4S_2)_2(C_3H_7NO)_2$.

donors give an NMR signal at 125 ppm [6]. The shift from 125 ppm to ≈330 ppm on replacing O by S in these complexes is in accord with the deshielding nature of the S atoms. This effect is also seen in the complexes $MoO_2(C_8H_7N_2O)_2$ and $MoO_2(C_8H_7N_2S)_2$ which give peaks in their ^{95}Mo NMR spectra at 57 and 410 ppm respectively [7]. On the basis of these observations and the structure of **III** a signal at approximately 330 ppm in its ^{95}Mo NMR spectrum may be expected.

Unfortunately **III** is only sparingly soluble in DCM and no signal could be observed after 3×10^6 scans. Dissolving **III** in DMF that had been cooled in an acetone/'dry ice' slush bath and cooling the probe to 223 K gave a broad signal centred at approximately 430 ppm. On raising the probe temperature the signal very quickly disappeared, there was no sign of it at room temperature, and a signal at 125 ppm began to appear after several minutes. At 353 K this signal was quite pronounced. The interesting feature of the 430 ppm signal, apart from its rapid disappearance, is its position. If it is due to a solution species identical in structure to the solid state form then its occurrence ≈100 ppm from the signals for **I** and **II** is at first puzzling.

However, since one of the N donors in **III** is pyridyl the other, together with the S, being benzene ring substituents, it may be naive to expect the same degree of deshielding of the Mo nucleus as observed in **I** and **II** in which the N, S donor atoms are 'aliphatic'.

A solution of **I** in DMF was studied over a period of 60 h. After 6, 12, 24, 36, 48 and 60 h the spectrum was plotted out and it could be seen that the signal at ≈125 ppm, initially weaker than the one at ≈330 ppm, increased in intensity with time until after 48 h it was stronger than the 330 ppm signal. **II** in DMF gave a signal at 329 ppm and a slightly weaker one at 129 ppm; this system was not studied as a function of time. As reported in ref. 1 we isolated from a DMF solution of **I** a tetrameric species $Mo_4O_{12}(C_{12}H_{30}N_4S_2)_2(C_3H_7NO)_2$ (**IV**) which is based on an Mo_4O_4 ring with each Mo atom achieving six coordination through *cis* dioxo groups and 2N atoms, the displaced thiolates forming disulphide bridges between diagonal Mo atoms. A solution of this tetramer in DMF gave a single peak at 124 ppm in its ^{95}Mo NMR spectrum. It is almost certainly the case that the signal at 129 ppm in the spectrum of **II** is due to a similar tetrameric species, and it is not unreasonable to make the same claim for **III**. However, attempts to isolate the species responsible for the 125 ppm signal in the spectrum of **III** have so far been unsuccessful.

From the ^{95}Mo NMR data it would seem that **III** converts to a tetrameric form in DMF much more rapidly than either **I** or **II**. Since the formation of the tetramer involves two, almost certainly concomitant, redox process *viz.* (1) reduction of two molecules of water, probably present in trace amounts in the DMF, to give two O^{2-} (4 electron gain) and (ii) oxidation of four S^- to give two disulphides (4 electron loss), the tendency for tetramer formation could be determined, in part, by the redox potential of the thiolate ligand.

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