Inorganica Chimica Acta, 98 (1985) L53–L55

X-Ray Crystal Structure and ^{95}Mo NMR Spectroscopy of the Single Oxo-bridged Species $Mo_2O_5(C_{13}H_9N_2O)_2(C_3H_7NO)_2(H_2O)_{1.5}$

MARIO V. CAPARELLI

Escuela de Quimica, Facultad de Ciencias, Universidad Central de Venezuela, Caracas, Venezuela

BRIAN PIGGOTT, SIMON D. THORPE

Inorganic Chemistry Research Laboratory, School of Natural Sciences, Hatfield Polytechnic, Hatfield AL10 9AB, U.K.

and RICHARD N. SHEPPARD

Department of Chemistry, Imperial College of Science and Technology, London SW7 2AY, U.K.

Received October 2, 1984

As part of our work on the structural characterization of Mo(VI) complexes we have synthesized and determined the X-ray crystal structure of $Mo_2O_5(HPB)_2(dmf)_2(H_2O)_{1.5}$ where HPB is the deprotonated form of 2-*o*-hydroxyphenylbenzimidazole ($C_{13}H_{10}N_2O$) and dmf is dimethylformamide (C_3H_7NO). In addition we have recorded the ^{95}Mo NMR spectrum of the title compound. We now report these results and suggest that the ^{95}Mo NMR spectrum which shows a single peak at approximately 120 ppm is characteristic of the $MoO_2–O–MoO_2{}^{2+}$ core where each six coordinate Mo(VI) atom is ligated to oxygen and nitrogen donors.

Experimental

Addition of an ethanolic solution of MoO_2(acetylacetonate)$_2$ (0.006 mol) to a boiling ethanolic solution of 2-*o*-hydroxyphenylbenzimidazole (0.030 mol) over a period of 3–4 hours gave a dark orange solution which on slow evaporation produced large orange crystals. Repeated crystallisation of the product from dimethylformamide using diethyl ether diffusion yielded long yellow needles the analysis and ^{1}H NMR spectrum of which are consistent with the formulation $Mo_2O_5(HPB)_2(dmf)_2(H_2O)_{1.5}$. A saturated solution of this material in dimethylformamide gave a ^{95}Mo NMR spectrum consisting of a single peak at 123 ppm with a line width of 130 Hz. A crystalline fragment suitable for X-ray structure determination was obtained by careful sorting and cutting the best formed and least striated crystal of the crop.

Crystal Data

$Mo_2C_{32}H_{32}O_9N_6$*, 836.52*, monoclinic (c unique), a = 15.545(3), b = 9.504(2), c = 29.247(9) Å, γ = 90.17(2), U = 4321(2) Å^3, space group $P2_1/n$, Z = 4, D_c = 1.29 g cm^{-3}*, F(000) = 1688°, μ = 52.6 cm^{-1}*.

Data were measured on a Nicolet R3m diffractometer with graphite monochromated Cu-K$_\alpha$ radiation and using ω scans. The structure was solved by direct methods and refined anisotropically using absorption corrected data to R = 0.079 for the 3558 independent observed reflections. Selected

TABLE I. Selected Bond Distances and Angles.[a]

		Mo–O–Mo (°)	Mo–O*b* (Å)	Mo–O*t* (Å)	Ref.
(*a*)	$Mo_2O_5(C_2O_4)_2(H_2O)_2{}^{2-}$	180	1.876	1.68, 1.70	1
(*b*)	$[Mo_2O_5(O_2)_4(H_2O)_2]K_2(H_2O)_2$	136.1	1.93	1.66	2
(*c*)	$Mo_2O_5(DMF)_4Cl_2$	171	1.90	1.68	3
(*d*)	$Mo_2O_5(phen)_2(NCS)_2$	162.7	1.865, 1.885	1.685, 1.688 1.691, 1.694	4
(*e*)	$Mo_2O_5(Hnta)_2{}^{2-}$	180	1.88	1.68, 1.71	5
(*f*)	$Mo_2O_5[(CH_3)_2NCH_2CH_2NHCH_2C(CH_3)_2S]_2$	143.8	1.929, 1.917	1.715, 1.715 1.714, 1.709	6
(*g*)	$Mo_2O_5(NCS)_2(Me_2SO)_4$	180	1.864	1.691, 1.686	7
(*l*)	$Mo_2O_5[HB(Me_2pz)_3]_2$	167.1	1.889	1.701, 1.696	8

[a] O*t* = terminal oxygen; O*b* = bridging oxygen.

---

*These values are calculated for a crystal *not* containing water molecules.

0020-1693/85/\$3.30

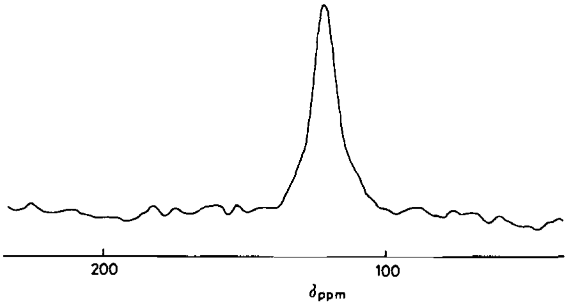

Fig. 1. ^{95}Mo FT NMR spectrum of $Mo_2O_5(HPB)_2(dmf)_2(H_2O)_{1.5}$.

bond distances and angles are given in Table I [$\theta \leqslant 50°$, $|F_o| > 3\sigma(|F_o|)$].

The final Fourier difference map showed a large number of peaks, which could not be attributed to absorption effects, located in empty regions of the unit cell and out of bonding range of the molecule. Attempts to identify water molecules in these peaks were unsuccessful and undoubtedly contributes to the rather high R value.

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 1EWK. Any request should be accompanied by the full literature citation for this communication.

NMR Data

The spectrum was measured in a 5.87 T applied field using a Bruker WM-250 spectrometer. Approximately 1.5 million pulses were required to obtain the signal shown in Fig. 1. A 500 μ sec delay was

TABLE II. Selected Values of Bond Lengths and Angles.

	a	b
Mo–N	2.193(8)	2.212(8)
Mo–O(1)	2.021(6)	2.015(8)
Mo–O(2)	2.353(7)	2.390(7)
Mo–O(3)	1.717(7)	1.710(8)
Mo–O(4)	1.709(8)	1.708(6)
Mo–O(12)	1.906(8)	1.855(8)
Mo–O(12)–Mo	165.4(5)	
N–Mo–O(1)	77.6(3)	78.1(3)
N–Mo–O(2)	84.5(3)	79.1(3)
N–Mo–O(3)	85.0(3)	85.6(3)
N–Mo–O(4)	90.8(3)	93.3(3)
N–Mo–O(12)	164.4(3)	161.0(3)
O(1)–Mo–O(2)	76.2(3)	76.2(3)
O(1)–Mo–O(3)	151.1(3)	154.3(3)
O(1)–Mo–O(4)	99.9(3)	98.4(4)
O(1)–Mo–O(12)	90.0(3)	87.9(3)
O(2)–Mo–O(3)	79.3(3)	81.3(3)
O(2)–Mo–O(4)	174.4(3)	171.4(3)
O(2)–Mo–O(12)	83.4(3)	85.2(3)
O(3)–Mo–O(4)	103.3(4)	102.3(4)
O(3)–Mo–O(12)	102.3(3)	102.5(4)
O(4)–Mo–O(12)	100.7(4)	101.5(3)

Average lengths in ligands (range 0.012–0.023 Å)

C(7)–C(1)	1.446	C(9)–C(10)	1.368
C(7)–N(1)	1.360	C(10)–C(11)	1.380
C(7)–N(2)	1.341	C(11)–C(12)	1.358
C(8)–N(1)	1.398	C(12)–C(13)	1.376
C(8)–C(9)	1.368	C(2)–O(1)	1.323
C(8)–C(13)	1.405	O(2)–C(14)	1.234
C(9)–N(2)	1.386	C(14)–N(3)	1.318
		N(3)–C(Me)	1.443
Phenyl ring (a) C–C	1.391		
Phenyl ring (b) C–C	1.382		

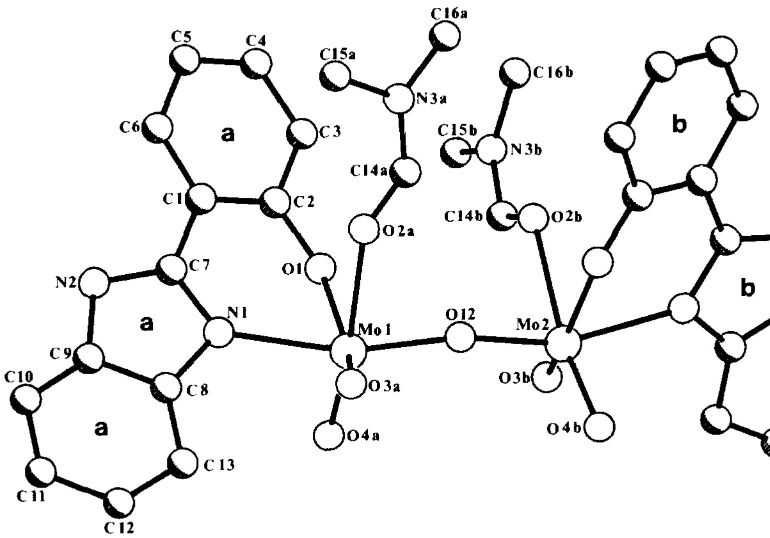

Fig. 2. Structure of $Mo_2O_5(C_{13}H_9N_2O)_2(C_3H_7NO)_2(H_2O)_{1.5}$.

inserted between the RF pulse and the start of data acquisition to control the effects of acoustic ringing in the NMR probe. The data were multiplied by an appropriate exponential window function before transformation. Chemical shifts are referenced to 2 M aqueous Na_2MoO_4 (external reference).

Discussion

The title compound is an example of the relatively rare structural type in which two distorted octahedral *cis* dioxo Mo(VI) units are linked by a single oxo bridge. Table I lists various bond distances and angles found in complexes of this type.

Since the terminal and bridging oxo groups (Mo–O_3, Mo–O_4 and Mo–O_{12}) in $Mo_2O_5(HPB)_2(dmf)_2$ define a face about each distorted octahedral Mo(VI) atom they can best be described as adopting *fac* stereochemistry (Fig. 2). The bidentate HPB (Mo–N_1 and Mo–O_1) and the dmf (Mo–O_2) define the remaining *fac.* positions. In $Mo_2O_5(HPB)_2(dmf)_2$ the Mo–O–Mo angle shows pronounced deviation from linearity, only complexes (*b*), (*d*) and (*f*) of Table I having a more acute bridge angle. The assymmetry of the Mo–O–Mo bridge is more pronounced in the title compound (Mo–O_{12} = 1.906 and 1.855 Å) than in compounds (*d*) and (*f*) of Table I, which are the only other examples with unequal Mo–O_{12} distances. From Table II it can be seen that the Mo–O_3, Mo–O_4 distances and O_3–Mo–O_4 angles are unexceptional. The structural *trans* effect is not obviously manifest in the Mo–O_1 bond distances. However the Mo–O_2 bonds which are also *trans* to the terminal oxygens show a pronounced lengthening which can be attributed to this effect.

The assumption that the structure of $Mo_2O_5 \cdot (HPB)_2(dmf)_2$ is retained in solution leads us to suggest that the ^{95}Mo NMR signal observed at 123 ppm could be a characteristic of this structural type and hence provide a diagnostic for identifying it in solution. We are currently investigating this suggestion.

References

1 F. A. Cotton, S. M. Morehouse and J. S. Wood, *Inorg. Chem., 3,* 1603 (1964).
2 R. Stomberg, *Acta Crystallogr., Sect. B:, 37,* 56 (1968).
3 L. O. Atovmyan, Y. A. Sokovova and V. V. Thachey, *Dokl. Akad. Nauk SSSR, 195,* 1355 (1970).
4 B. Viossat and N. Rodier, *Acta Crystallogr., Sect. B:, 37,* 56 (1981).
5 C. B. Knobler, W. T. Robinson, C. J. Wilkins and A. J. Wilson, *Acta Crystallogr., Sect. B:, 39,* 443 (1983).
6 C. P. Marabella, H. H. Enemark, K. F. Miller, A. E. Bruce, K. Paritadath, J. L. Corbin and E. I. Stiefel, *Inorg. Chim. Acta, 22,* 3456 (1983).
7 T. Shibahara, H. Kuroya, S. Ooi and Y. Mori, *Inorg. Chim. Acta, 76,* L315 (1983).
8 K. M. Barnhart and J. H. Enemark, *Acta Crystallogr., Sect. C:, 40,* 1362 (1984).