Synthesis, Characterization and Crystal Structure of a Binuclear Molybdenum(VI) Oxo Complex of a Dianionic Tetradentate Schiff-base Ligand†

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Reaction in methanol solution of $[NBu_4]_4[Mo_8O_{26}]$ with 1,3,5,7-tetraazatricyclo$[3.3.1.1^{3,7}]$decane (hexamethylenetetramine, hmt) and salicylaldehyde yielded the complex $[Hhmt][Mo_2O_4(\mu\text{-}O)(\mu\text{-}OMe)(o\text{-}OC_6H_4CH{=}NCH_2N{=}CHC_6H_4O\text{-}o)]$ which has been characterized by elemental analysis, IR and ^1H NMR spectroscopy. A single-crystal analysis revealed that the complex possesses the usual $Mo_2O_5^{2+}$ core and that the Schiff-base ligand complexes in a tetradentate manner through the atoms ONON, acts forming two six-membered rings. The two Mo atoms are bridged by a methoxo group, giving each a distorted-octahedral configuration.

Molybdenum chemistry has aroused considerable interest in recent years in view of its importance in catalytic, material and biochemical science.[1] The presence of the *cis*-dioxomolybdenum(VI) cation, MoO_2^{2+}, in the oxidative form of certain molybdoenzymes[2] has stimulated the search for new structures in which this moiety is co-ordinated to ligands containing nitrogen, oxygen and/or sulfur donors.[3] At present, a large number of *cis*-dioxomolybdenum(VI) complexes are known, some of which have been proposed as models for the active sites of oxo-transfer molybdoenzymes, *viz.* sulfite and aldehyde oxidase, xanthine oxidase/dehydrogenase and nitrate reductase.[4]

Although many *cis*-dioxomolybdenum(VI) complexes with Schiff bases have been reported previously, there are no binuclear complexes of this cation with dianionic tetradentate Schiff bases.

Takajo *et al.*[5] and Bu *et al.*[6] have reported that aryl aldehydes react with aqueous ammonia to afford the mixed Schiff base, *N*,*N*-bis(2-hydroxybenzylidene)arylmethanediamine, but no mixed Schiff-base compound of salicylaldehyde and formaldehyde has been reported. We have synthesised a Schiff-base complex by reaction between salicylaldehyde and 1,3,5,7-tetraazatricyclo$[3.3.1.1^{3,7}]$decane (hexamethylenetetramine, hmt) in the presence of molybdates and characterized it by spectroscopy and X-ray diffraction analysis.

Experimental

All chemicals were procured commercially and used without subsequent purification. Unpurified methanol contained about 2% water, as verified by gas chromatography. Infrared spectra were recorded as KBr discs on a Nicolet 170SX spectrophotomer, ^1H NMR spectra on a Varian FT-80A spectrometer. Elemental analyses were measured on an Italy 1106 apparatus.

Preparation of Complex.—The salt $[NBu_4][Mo_8O_{26}]$[7] (10 mmol) was dissolved in methanol (50 cm^3) and hexamethylenetetramine (45 mmol) and salicylaldehyde (60 mmol) were added with refluxing and stirring for 2 h. The solution retained its yellow colour and pale yellow single crystals were isolated after slow evaporation of the solvent. Yield: 70% (Found: C, 37.8; H, 4.1; N, 11.9. Calc. for $C_{22}H_{28}Mo_2N_6O_8$: C, 37.9; H, 4.1; N, 12.1%). IR (KBr pellet): 2905m, 1595vs, 1552s, 1010m, 920s, 884vs, 796s, 610s and 565w cm^{-1}. ^1H NMR: 3.35 (s, 3 H) 4.60 (s, 2 H), 5.66 (s, 2 H), 7.05–7.60 (m, 8 H) and 8.91 (s, 2 H).

Crystal Structure Determination.—A single crystal with dimensions 0.20 × 0.20 × 0.25 mm was mounted on a glass fibre. The intensity data were collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Cu-Kα radiation (λ = 1.5418 Å). The scan mode was ω–2θ. 4076 Independent reflections were collected in the range $2 \leqslant 2\theta \leqslant 120°$, 3668 of which with $I \geqslant 3\sigma(I)$ were used for further computation.

Crystal data. $C_{22}H_{28}Mo_2N_6O_8$, $M = 696.38$, monoclinic, space group $P2_1/a$, $a = 11.978(1)$, $b = 12.723(1)$, $c = 16.620(2)$ Å, $\beta = 98.88(2)°$, $U = 2502.6$ Å^3, $Z = 4$, $D_c = 1.85$ Mg m^{-3}, $\mu = 88.9$ cm^{-1}, $F(000) = 1400$.

The structure analysis was performed on a PDP 11/44 computer with the SDP program.[8] The positions of the two molybdenum atoms were determined by direct methods. The other non-hydrogen atoms were revealed by Fourier difference synthesis. The positions of the hydrogen atoms were calculated as idealized contributions. The structure was refined by full-matrix least squares to a final $R = 0.047$ and $R' = 0.057$ for the 3668 observed reflections.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Synthesis and Spectroscopic Properties.—The complex $[Hhmt][Mo_2O_4(\mu\text{-}O)(\mu\text{-}OMe)(o\text{-}OC_6H_4CH{=}NCH_2N{=}CH\text{-}C_6H_4O\text{-}o)]$ was obtained in methanolic solution, by the reaction of hexamethylenetetramine with salicylaldehyde in the presence of octamolybdate only. It is evident that the Schiff base *N*,*N'*-bis(*o*-hydroxybenzylidene)methanediamine could not be isolated from methanolic solution in the absence of molybdate. The hydrolysis of the amine produces formaldehyde and ammonia as shown in Scheme 1.

The IR spectral data of the complex are typical for a co-ordinated anionic Schiff base and oxygen donor. A band at 3005 cm^{-1} is associated with the C–H stretch of the methoxo group

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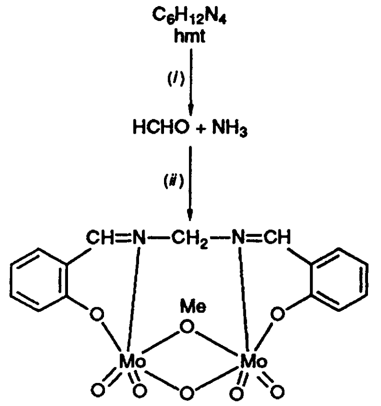
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.



Scheme 1 (*i*) Water as impurity in MeOH; (*ii*) *o*-HOC_6H_4CHO, $[Mo_8O_{26}]^{4-}$

Table 1 Atomic coordinates for non-hydrogen atoms of the complex

Atom	*x*	*y*	*z*
Mo(1)	1.194 07(5)	0.032 07(5)	0.239 65(4)
Mo(2)	0.976 92(5)	−0.048 80(5)	0.312 88(4)
O(1)	1.216 8(4)	0.018 5(4)	0.123 9(3)
O(2)	0.846 2(4)	−0.124 9(4)	0.251 8(4)
O(3)	1.275 5(4)	0.140 9(5)	0.258 8(3)
O(4)	1.279 0(4)	−0.069 6(5)	0.278 2(3)
O(5)	1.101 6(4)	0.046 6(4)	0.324 4(3)
O(6)	1.040 0(4)	−0.160 1(4)	0.358 9(3)
O(7)	0.904 0(4)	0.002 7(4)	0.384 6(3)
O(8)	1.049 3(4)	−0.069 1(4)	0.204 1(3)
N(1)	1.053 5(5)	0.150 1(5)	0.173 0(4)
N(2)	0.892 1(5)	0.086 7(5)	0.227 6(4)
N(3)	0.755 1(6)	0.211 6(6)	0.493 7(4)
N(4)	0.588 6(6)	0.200 1(6)	0.389 7(4)
N(5)	0.570 8(6)	0.248 9(6)	0.527 3(5)
N(6)	0.618 1(6)	0.070 9(6)	0.498 3(4)
C(1)	1.157 8(7)	0.182 7(6)	0.061 6(4)
C(2)	1.172 0(7)	0.260 1(7)	0.003 3(5)
C(3)	1.258 4(8)	0.251 6(8)	−0.042 6(5)
C(4)	1.326 8(7)	0.163 9(8)	−0.033 2(5)
C(5)	1.314 0(7)	0.086 4(8)	0.023 0(5)
C(6)	1.227 9(6)	0.095 4(6)	0.071 7(5)
C(7)	1.062 7(6)	0.197 2(6)	0.106 3(5)
C(8)	0.956 3(6)	0.180 9(6)	0.212 2(5)
C(9)	0.784 5(7)	0.090 3(6)	0.201 9(5)
C(10)	0.705 4(6)	0.007 9(6)	0.211 8(5)
C(11)	0.588 3(7)	0.031 4(8)	0.193 6(6)
C(12)	0.508 9(7)	−0.044 1(8)	0.201 1(6)
C(13)	0.541 0(6)	−0.144 2(8)	0.225 4(5)
C(14)	0.653 9(6)	−0.171 1(7)	0.241 9(5)
C(15)	0.737 0(6)	−0.095 1(6)	0.236 0(5)
C(16)	0.996 1(7)	−0.093 2(7)	0.122 6(5)
C(17)	0.739 5(7)	0.101 1(7)	0.513 8(5)
C(18)	0.575 5(8)	0.090 1(8)	0.412 0(5)
C(19)	0.557 9(7)	0.133 9(7)	0.547 8(5)
C(20)	0.528 2(8)	0.266 0(8)	0.437 3(6)
C(21)	0.695 4(9)	0.276 2(8)	0.542 3(6)
C(22)	0.709 9(7)	0.227 6(7)	0.407 0(5)

and a strong band at 1010 cm^{-1} to its bridging nature (Mo–OMe–Mo). The band at 796 cm^{-1} is associated with the bridging oxo group (Mo–O–Mo), and that at 1595 cm^{-1} to the C=N stretch, indicating co-ordination of the nitrogen to molybdenum.[9–11] The complex does not show a phenolic ν(OH) and the ν(C–O) band at 1552 cm^{-1} has shifted to lower wavenumber compared to the free ligand,[9] both suggestive of co-ordination of the phenolic C–O group. Bands at 610 and 565 cm^{-1}, respectively, are assigned to ν(Mo–N) and ν(Mo–O).[9,10] The tendency of MoO_2^{2+} to form a *cis* configuration is well established, and is attributed to the maximum utilization of the available d orbitals for bonding with the oxo-group.[1]

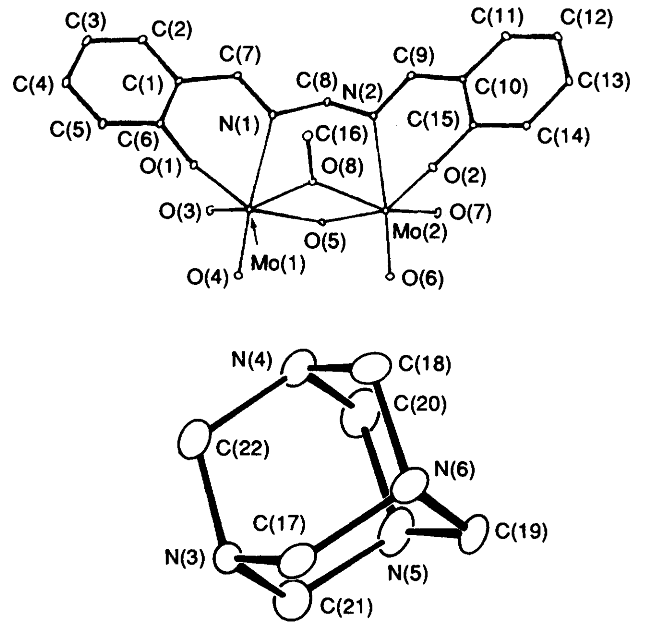


Fig. 1 A view of the structure of $[Mo_2O_4(\mu\text{-}O)(\mu\text{-}OMe)(o\text{-}OC_6H_4CH{=}NCH_2N{=}CHC_6H_4O\text{-}o)]^-$ and $[Hhmt]^+$

Dioxomolybdenum(VI) complexes with a *cis*-MoO_2 moiety exhibit two strong bands at 905–948 and 875–914 cm^{-1} assignable to symmetric and asymmetric ν(O=Mo=O) respectively.[9,10] A *trans*-MoO_2 species would show only one IR-active band. The complex exhibits bands at 920 and 884 cm^{-1} indicating the presence of a *cis*-MoO_2 moiety. A band at 2905 cm^{-1} is associated with the NH^+ stretch of the protonated hexamethylenetriamine.

The ^1H NMR spectra of the complex have been recorded in $(CD_3)_2SO$ using $SiMe_4$ as the internal standard. As expected, OH resonances are absent. The azomethine proton signal (CH=N) at δ 8.9 of the complex has shifted downfield upon coordination of the nitrogen to molybdenum.[6,12] The peak at δ 5.66 is assigned to the protons of NCH_2N, and that at δ 3.35 to OMe. The NCH_2N protons of the cation appear at δ 4.60. The NH^+ resonance is not observed, being obscured by 'noise'.

Structural Studies.—The atomic positional parameters and selected bond lengths and angles are given in Tables 1 and 2, respectively. The structure of the complex anion and the cation are displayed in Fig. 1. The X-ray analysis establishes that the ligand is doubly deprotonated. The structure of the monoanion consists of the well documented $Mo_2O_5^{2+}$ core[5] ligated to the Schiff base and methoxo group. The Schiff base functions as a chelating and bridging moiety. The two Mo atoms are bridged by the methoxo group, thereby achieving the customary requirement[13] of molybdenum(VI) for six-co-ordination. From Table 2 it is seen that the geometry around each molybdenum is a distorted octahedron. The ligand bonds to each *cis*-MoO_2 moiety through O(1), N(1), O(2) and N(2) and is thus tetradentate. To a large extent the distortion stems from the incorporation of Mo into two six-membered rings. The average Mo–O bond length 1.713(3) Å and the O–Mo–O bond angle 104.5(1)° are comparable to other such data reported for the *cis*-MoO_2 group.[9–12] However the average distances, Mo–O [O(1) and O(2)] 1.987(3) Å and Mo–N 2.379(4) Å in the binuclear complex are longer than those found in other six-membered rings of mononuclear molybdenum complexes,[9,14] but similar to those in a salicylhydroximato molybdenum complex.[15] The Mo–N bonds are relatively long, due in part to the *trans* influence.[16] The distances N(1)–C(7) [1.279(5) Å] and N(2)–C(9) [1.294(6) Å] indicate that these correspond to double bonds (single bond 1.364 Å[9]). The Mo(1)–O(5)–Mo(2)

Table 2 Important bond distances (Å) and angles (°) in the complex

Mo(1)–O(1)	1.991(3)	Mo(1)–O(3)	1.706(3)	Mo(1)–O(4)	1.708(3)
Mo(1)–O(5)	1.931(2)	Mo(1)–O(8)	2.167(3)	Mo(1)–N(1)	2.397(4)
Mo(2)–O(2)	1.982(3)	Mo(2)–O(5)	1.911(2)	Mo(2)–O(6)	1.726(3)
Mo(2)–O(7)	1.713(3)	Mo(2)–O(8)	2.139(3)	Mo(2)–N(2)	2.360(4)
O(1)–C(6)	1.329(5)	O(2)–C(15)	1.349(5)	O(8)–C(16)	1.437(5)
N(1)–C(7)	1.279(5)	N(1)–C(8)	1.474(5)	N(2)–C(8)	1.468(6)
N(2)–C(9)	1.294(6)				
O(1)–Mo(1)–O(3)	95.3(1)	O(1)–Mo(1)–O(4)	97.8(1)	O(1)–Mo(1)–O(5)	153.2(2)
O(1)–Mo(1)–O(8)	84.7(2)	O(1)–Mo(1)–N(1)	78.4(1)	O(3)–Mo(1)–O(5)	99.3(1)
O(3)–Mo(1)–O(4)	105.1(1)	O(3)–Mo(1)–O(8)	161.4(1)	O(3)–Mo(1)–N(1)	85.0(1)
O(4)–Mo(1)–O(5)	100.1(1)	O(4)–Mo(1)–O(8)	93.4(1)	O(4)–Mo(1)–N(1)	169.5(1)
O(5)–Mo(1)–O(8)	74.5(2)	O(5)–Mo(1)–N(1)	80.6(1)	O(8)–Mo(1)–N(1)	76.7(1)
O(2)–Mo(2)–O(5)	154.9(1)	O(2)–Mo(2)–O(6)	94.8(1)	O(2)–Mo(2)–O(7)	95.5(1)
O(2)–Mo(2)–O(8)	84.2(2)	O(2)–Mo(2)–N(2)	79.4(1)	O(5)–Mo(2)–O(6)	101.2(1)
O(5)–Mo(2)–O(7)	99.3(1)	O(5)–Mo(2)–O(8)	75.4(2)	O(5)–Mo(2)–N(2)	81.6(1)
O(6)–Mo(2)–O(7)	103.9(1)	O(6)–Mo(2)–O(8)	93.9(1)	O(6)–Mo(2)–N(2)	169.6(1)
O(7)–Mo(2)–O(8)	162.1(1)	O(7)–Mo(2)–N(2)	85.4(1)	O(8)–Mo(2)–N(2)	76.9(1)
Mo(1)–O(5)–Mo(2)	113.2(3)	Mo(1)–O(8)–Mo(2)	119.2(3)		
C(7)–N(1)–C(8)	116.1(4)	C(8)–N(2)–C(9)	115.9(4)		

angle (113.2°) is similar to that in a phenanthrenequinone complex[17] which has the same μ-O bridge.

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