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Reactions of Bis(acetylacetonato)dioxomolybdenum(VI) with Aroylhydrazines. Structure and ^{1}H NMR Spectrum of 3,5-Dimethylpyrazolium β-Octamolybdate Tetrahydrate

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Abstract

The reactions of bis(acetylacetonato)dioxomolybdenum(VI), $MoO_2(acac)_2$, with benzoylhydrazine have been investigated using a number of different solvent conditions. A 1:2 ratio of $MoO_2(acac)_2$ to benzoylhydrazine in dry methanol yields red crystals of a six-coordinate oxomolybdenum complex [OMo(MeC(O)CHC(Me)(=NNC(O)Ph))(NHNC(O)-Ph)] (1). In ordinary 'wet' methanol the same reaction yields white crystals of the octamolybdate $(C_5H_9N_2)_4[Mo_8O_{26}]$ (2) formed by hydrolysis. $C_5H_9N_2^+$ is the 3,5-dimethylpyrazolium cation which has been produced *in situ* by a cyclization reaction of acetylacetone and benzoylhydrazine. The tetrahydrate of 2, $(C_5H_9N_2)_4[Mo_8O_{26}]\cdot 4H_2O$ (4), is formed in a 1:2 reaction in 95% ethanol. A second white crystalline by-product, 3, tentatively formulated as $Mo_2O_4(NHNHC(O)Ph)_2\cdot 2H_2O$, is also formed in this reaction. Crystals of $(C_5H_9N_2)_4[Mo_8O_{26}]\cdot 4H_2O$ (4) are triclinic, space group $P\bar{1}$, $a = 12.029(6)$, $b = 10.181(5)$, $c = 12.193(6)$ Å; $\alpha = 97.04(9)°$, $\beta = 127.00(12)°$, $\gamma = 95.51(9)°$; $V = 1156.1$ Å^3, $Z = 1$. The final refinement gave $R = 0.043$ and $R_w = 0.043$ for 3610 observed reflections. The structure contains the β-octamolybdate anion and an organic-base 3,5-dimethylpyrazolium cation. The ^{1}H NMR spectra of 4 show the presence of two lines for both the C(4)H and CH_3 protons in the 3,5-dimethylpyrazolium rings. The same intensity ratio is observed for each proton. Unusual temperature dependent effects on both the line positions and intensity ratios are observed between 291–385 K. The possibility of N-bonding of 3,5-dimethylpyrazole to Mo in solution is discussed.

Introduction

As a continuation of our interest in reactions between dioxomolybdenum(VI) complexes and substituted hydrazines [1] we have investigated the products obtained on reaction of bis(acetylacetonato)dioxomolybdenum(VI) ($[MoO_2(acac)_2]$) with aroyl hydrazines in various solvents. $[MoO_2(acac)_2]$ is the parent compound used to form the thiohydroxamate, and many other, O_2MoL_2 complexes. During the course of the present study, Dutta and Pal have also described reactions of benzoylhydrazine with $[MoO_2(acac)_2]$ and found that different products could be isolated depending on the solvents used [2]. Thus, when dry methanol was employed as the solvent, they proposed that the product contained chelated diazenido and diazene groups in a six-coordinate complex $[Mo(N_2C(O)Ph)(NNHC(O)Ph)(acac)]$. A brief early report by Chatt and Dilworth [3] on the same species suggested, however, that this complex contained diazene and hydrazone groups in an oxomolybdenum complex of formula [OMo(NHNC(O)Ph)(MeC(O)-CHC(Me)(=NNC(O)Ph))]. The hydrazone is a dianionic tridentate ligand formed by the condensation of an acetylacetonato group with benzoylhydrazine. We show here by use of spectroscopic data that the Chatt and Dilworth proposal is correct. We further show, in general agreement with Dutta and Pal, that the products are indeed solvent dependent. In addition, the nature of the product is dependent on the amount of water present in the solvent. When the reactions were performed in organic solvents containing small amounts of water, an interesting result occurs in which the molybdenum complex is hydrolyzed to form an octamolybdate anion, $[Mo_8O_{26}]^{4-}$. At the same time the 3,5-dimethylpyrazolium cation is formed via a cyclization reaction between acetylacetone and benzoylhydrazine. A crystal structure determination on the complex $(C_5H_9N_2)_4[Mo_8O_{26}]\cdot 4H_2O$ (4) shows that it contains the β-isomer of the octamolybdate.

In this rather unexpected way we have, therefore, prepared an organic-base isopolymolybdate. A growing number of such molybdates have been prepared and structurally characterized in recent years [4]. They have a number of interesting applications including their use as model compounds for the study of small organic molecules with catalytic

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molybdenum oxide surfaces [5]. Small organic molecules, including organohydrazines [6], have been shown to coordinate onto the polymolybdate cluster. In their anhydrous forms organic-soluble octamolybdates such as $[n\text{-}Bu_4N]_4[Mo_8O_{26}]$ have also recently been found to be useful starting reagents for the preparation of other dioxomolybdenum(VI) complexes [7] and of substituted polymolybdates [8].

It is interesting to note that reactions of dioxomolybdenum(VI) or of octamolybdate complexes with organohydrazines can, under appropriate conditions, also yield substituted tetramolybdate species [9–11].

Experimental

General Information

Infrared spectra were determined as Nujol mulls using a Jasco IRA-1 spectrophotometer. Far infrared spectra were recorded as Nujol mulls between KBr or polyethylene plates using a Perkin-Elmer 180 spectrophotometer. ^1H NMR spectra were obtained using either a Bruker WH90 or AM300 spectrometer. They were determined on $CDCl_3$ or $(CD_2)_2SO$ solutions, with all shifts reported downfield from internal Me_4Si. Microanalyses were determined at the Australian Microanalytical Service. Dry methanol was prepared by conventional methods and stored over molecular sieves. Other solvents were laboratory grade and used without further drying. Aroylhydrazines [12] and $MoO_2(acac)_2$ [13] were prepared by literature methods.

Synthesis

[OMe(MeC(O)CHC(Me)(=NNC(O)Ph)(NHNC(O)Ph)] (1)

$[MoO_2(acac)_2]$ (240 mg, 0.74 mmol) and $PhCONHNH_2$ (200 mg, 1.47 mmol) were refluxed in dry methanol (20 ml) for 0.5 h. The initial yellow solution turned red as the reaction proceeded. Evaporation of the reaction solution yielded red microcrystals (110 mg, 32%) which were recrystallized from dichloromethane/methanol. Melting point (m.p.) 164.5 °C (decomp.). *Anal.* Calc. for $C_{19}H_{18}MoN_4O_4$: C, 49.36; H, 3.92; N, 12.12. Found: C, 49.39; H, 3.70; N, 12.14%. IR (Nujol) cm^{-1}, 3130br,w (ν(N–H)), 1600s, 1565s, 1560s (ν(C=O), ν(N=N), ν(C=N)), 950 s (ν(Mo=O). ^1H NMR (300 MHz, $CDCl_3$) $\delta = 14.2$br,s (1H, NH), 8.04–7.96 (4H, m-C_6H_5), 7.43–7.32 (6H, o and p-C_6H_5), 5.48s (1H, CH), 2.56s (3H, Me), 2.14s (3H, Me).

$(C_5H_9N_2)_4[Mo_8O_{26}]$ (2)

The reaction described above was repeated except that laboratory grade methanol (40 ml) plus water (0.5 ml) was employed as the solvent. The reaction solution retained its yellow color and pale yellow crystals were isolated after evaporation of the solvent (115 mg, 79%). The crystals slowly changed to a pale green–aqua color upon standing for several months. *Anal.* Calc. for $C_{20}H_{36}Mo_8N_8O_{26}$: C, 15.28; H, 2.31; N, 7.13. Found: C, 15.47; H, 2.31; N, 7.28%.

Reactions of $MoO_2(acac)_2$ and $PhC(O)NHNH_2$ in 95% ethanol

When similar reaction conditions to those given for **1** were employed, but with 95% ethanol used as the solvent, a different reaction was found to occur. Thus when $[MoO_2(acac)_2]$ (120 mg, 0.37 mmol) and $PhC(O)NHNH_2$ (100 mg, 0.74 mmol) were refluxed in 95% ethanol (20 ml) for 0.5 h the initial orange suspension was taken up into solution to yield a very fine white precipitate of **3** (57 mg, 55%) in a red solution. Upon leaving the filtrate to slowly evaporate small white crystals $(C_5H_9N_2)_4[Mo_8O_{26}]\cdot 4H_2O$ (**4**) (15 mg, 20%) formed which proved suitable for an X-ray crystal structure determination. Compounds **3** and **4** were able to be prepared exclusively by the alternative reactions given below.

$Mo_2O_4(NHNHC(O)Ph)_2\cdot 2H_2O$ (3)

$(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O$ (ammonium molybdate) (180 mg, 0.146 mmol or 1.0 mmol in Mo) was dissolved in water (20 ml). A solution of benzoylhydrazine (140 mg, 1.0 mmol) dissolved in 95% ethanol (20 ml), was added to the aqueous molybdate solution and refluxed for 1 h. Evaporating the solution under reduced pressure affords a white powder (160 mg, 57%) which was filtered off and washed extensively with water and acetone and then dried. IR (Nujol) 3190m, 3080br,m (ν(N–H)), 1640s (ν(C=O)), 1565s (ν(N–N)), 935s (ν(Mo=O)), 450w (ν(MoO_2Mo)). ^1H NMR (300 MHz, $(CD_3)_2SO$) δ 16.49s (N–H), 16.10s (N–H), 8.10–7.91m (m-C_6H_5), 7.63–7.38m (o- and p-C_6H_5). *Anal.* Calc. for $C_{14}H_{18}Mo_2N_4O_8$: C, 29.91; H, 3.23; N, 9.97; O, 22.8. Found: C, 30.27; H, 2.92; N, 10.21; O, 22.7%.

$(C_5H_9N_2)_4[Mo_8O_{26}]\cdot 4H_2O$ (4)

$MoO_2(acac)_2$ (120 mg, 0.37 mmol) and $PhC(O)NHNH_2$ (50 mg, 0.37 mmol) were refluxed in 95% ethanol (20 ml) for 0.5 h. The yellow reaction solution was filtered, if necessary, to remove a small amount of white powder, evaporated under reduced pressure and left to stand at room temperature to crystallize. White needles/microcrystals (67 mg, 89%) of **4** were isolated. *Anal.* Calc. for $C_{20}H_{44}Mo_8N_8O_{30}$: C, 14.61; H, 2.70; N, 6.82; O, 29.2. Found: C, 14.68; H, 2.49; N, 6.76; O, 29.7%.

X-ray Crystallography

Crystal data and details of the structure determination for the octamolybdate **4** are given in Table 1. Unit cell parameters were determined from 24 accurately centered reflections and were calculated by the standard Philips program. A representative clear prismatic crystal was used to collect data on a Philips PW1100 diffractometer. Three standard reflections every 6 h showed no significant variation in intensity over the data collection period.

Intensity data were processed as described previously [14]. A numerical absorption correction was applied [15], the maximum and minimum transmission factors being 0.888 and 0.776 respectively. The atomic scattering factors for neutral atoms were taken from ref. 16, and were corrected for anomalous dispersion by using values from ref. 16. All calculations were performed on a DEC/VAX 11/780 computer. The program used for least-squares refinement was that due to Sheldrick [15].

TABLE 1. Crystal Data and Details of the Structure Analysis of $(C_5H_9N_2)_4[Mo_8O_{26}]\cdot 4H_2O$ (**4**)

(a) Crystal Data	
M	1644.2 ($C_{20}H_{44}Mo_8O_{30}$)
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	12.029(6)
b (Å)	10.181(5)
c (Å)	12.123(6)
α (°)	97.04(9)
β (°)	127.00(12)
γ (°)	95.51(9)
V (Å^3)	1156.1
Z	1
D_c (g cm^{-3})	2.36
D_m (g cm^{-3})	2.32(3)
F(000)	791.6
μ(Mo Kα) (cm^{-1})	21.1
Crystal size (mm)	0.06 × 0.11 × 0.12
Max., min. transmission	0.888, 0.776
(b) Data Collection	
Radiation	graphite-monochromated Mo Kα, $\lambda = 0.7107$ Å
Temperature (K)	298
θ_{min}, θ_{max} (°)	3, 30
$\omega/2\theta$ scan (°)	$\pm(1.30 + 0.2 \tan\theta)$
Total unique data	6732
Observed data $I \geqslant 3\sigma(I)$	3610
(c) Refinement	
No. refined parameters	178
Weighting scheme	$w = \sigma^{-2}(F)$ (or $w^{-1} = \sigma^2(F)$)
Final $R_F = \Sigma(\lvert F_o\rvert - \lvert F_c\rvert)/\Sigma\lvert F_c\rvert$	0.043
Final $R_w = \Sigma(w^{1/2}(\lVert F_o\rvert - \lvert F_c\rVert)/\Sigma w^{1/2}\lvert F_o\rvert$	0.043

The structure was solved by direct methods, positions for 4 unique Mo atoms being found in the first E map. Subsequent difference Fourier synthesis revealed the molecule, which consisted of an octamolybdate ion, $Mo_8O_{26}^{4-}$, four cations of formula $C_5H_9N_2$ and four waters of crystallization. Full-matrix least-squares refinement employing anisotropic thermal parameters for Mo and isotropic thermal parameters for all other atoms, with hydrogen in geometrically idealized positions (C–H, 1.08 Å and N–H, 1.01 Å) and a common thermal parameter reduced R to 0.043 and R_w to 0.043 at convergence. Final atomic parameters are given in Table 2, and selected interatomic distances in Table 3.

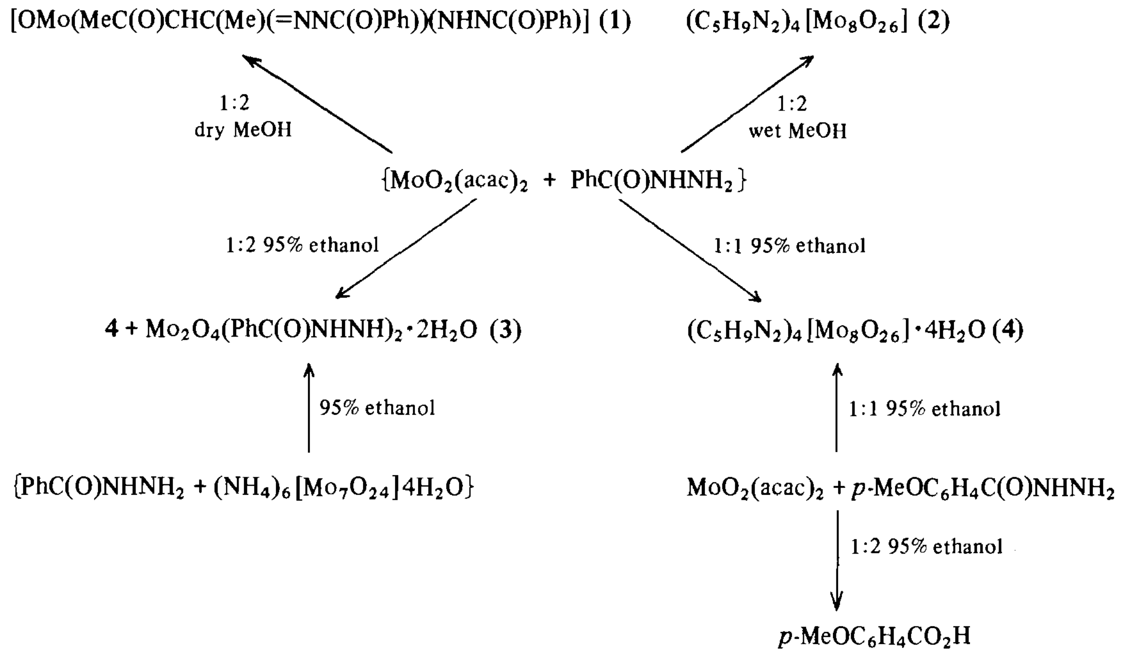
Results and Discussion

Synthesis and Characterization

The products formed by reacting $MoO_2(acac)_2$ and $PhC(O)NHNH_2$ under a variety of conditions are shown in Scheme 1.

Red crystals of **1** are formed from reaction in pure dry methanol. Compound **1** has the IR stretching frequency ν(Mo=O) at 950 cm^{-1} and an NH proton resonance shifted considerably downfield to 14.2 ppm. These and other spectroscopic data are compatible with the presence of a tridentate hydrazone ligand formed by partial condensation of one of the coordinated acac groups with the hydrazine. The six-coordinate geometry around Mo is completed by an oxo and a bidentate diazene ligand *viz.* [OMo(MeC(O)CHC(Me)(=NNC(O)Ph)-(NHNC(O)Ph)] as described by Chatt and Dilworth [3]. A similar condensation has been reported for the reaction of $VO(acac)_2$ with benzoylhydrazine by Diamantis *et al.* [17], and the crystal structure of the non-oxo product, $[V(MeC(O)CHC(Me)(=NNC(O)Ph)_2]$, has confirmed the tridentate {O,O,N} coordinate mode of the hydrazone ligand. An alternative formulation of **1**, recently proposed by Dutta and Pal [2], containing bidentate diazene, diazenide and acetylacetonate groups, $[Mo(N_2C(O)Ph)(NNHC(O)Ph)(acac)]$, does not, therefore, appear to be correct. Interestingly, Jeannin *et al.* [18] have recently shown that reaction of $MoO_2(acac)_2$ with excess phenylhydrazine in methanol produces the deep purple coloured binuclear bis-diazenido complex $[Mo_2(N_2Ph)_4(acac)_2(OMe)_2]$. In this case the acac group is chelated rather than condensed with the hydrazine.

When the reaction between $MoO_2(acac)_2$ and $PhC(O)NHNH_2$ was carried out in 'wet' methanol, the reaction solution did not turn red, as in the formation of **1**, but pale yellow. Nicely formed pale yellow crystals of **2** were isolated from the solution. Crystallographic examination showed that



Scheme 1.

TABLE 2. Atomic Parameters for $(C_5H_9N_2)_4[Mo_8O_{26}]\cdot 4H_2O$

Atom[a]	x	y	z	U(Iso)[b]
Mo(1)	0.34791(7)	−0.04349(7)	0.31931(7)	*
Mo(2)	0.29701(7)	−0.04975(7)	0.54889(8)	*
Mo(3)	0.45082(7)	0.26018(7)	0.56507(7)	*
Mo(4)	0.49877(8)	0.26802(7)	0.32920(7)	*
C(1)	−0.0815(9)	0.3872(8)	0.0669(9)	0.032(2)
C(2)	0.0331(9)	0.3254(8)	0.1407(9)	0.030(2)
C(5)	−0.0343(9)	0.5220(8)	0.1369(9)	0.031(2)
C(6)	−0.1099(11)	0.6363(10)	0.1111(11)	0.047(2)
C(7)	0.0429(11)	0.1810(10)	0.1123(11)	0.047(2)
C(1) (B)	0.6377(11)	0.1048(11)	0.0095(11)	0.052(3)
C(2) (B)	0.7534(11)	0.0757(10)	0.1269(10)	0.046(2)
C(5) (B)	0.6308(11)	0.2374(11)	0.0518(11)	0.051(3)
C(6) (B)	0.5303(13)	0.3225(12)	−0.0309(13)	0.066(3)
C(7) (B)	0.8103(14)	−0.0496(13)	0.1438(14)	0.072(4)
N(3)	0.1433(9)	0.4186(8)	0.2519(8)	0.044(2)
N(4)	0.1027(9)	0.5382(8)	0.2508(9)	0.045(2)
N(3) (B)	0.8162(9)	0.1844(8)	0.2345(8)	0.043(2)
N(4) (B)	0.7405(9)	0.2803(8)	0.1874(9)	0.044(2)
O(1)	0.2049(6)	−0.1741(5)	0.2089(6)	0.030(1)
O(2)	0.1572(6)	−0.1825(6)	0.4249(6)	0.034(1)
O(3)	0.2308(6)	0.0500(6)	0.6104(6)	0.037(1)
O(4)	0.6022(6)	0.3782(6)	0.6833(6)	0.034(1)
O(5)	0.3279(6)	0.3090(6)	0.5784(6)	0.035(1)
O(6)	0.6500(6)	0.3891(6)	0.4559(6)	0.035(1)
O(7)	0.4170(7)	0.3237(6)	0.1778(6)	0.040(2)
O(8)	0.2871(5)	0.0534(5)	0.4162(5)	0.020(1)
O(9)	0.5538(5)	0.1241(5)	0.4961(5)	0.019(1)
O(10)	0.5909(6)	0.1356(5)	0.3034(6)	0.029(1)
O(11)	0.3887(5)	0.3059(5)	0.3911(5)	0.023(1)
O(12)	0.3278(6)	0.0723(5)	0.2172(5)	0.025(1)
O(13)	0.5041(5)	0.1164(5)	0.6744(5)	0.023(1)
O(14)	0.0400(7)	0.2282(6)	0.5224(7)	0.045(2)
O(15)	0.8234(10)	0.4980(10)	0.3846(10)	0.094(3)

(continued)

TABLE 2. *(continued)*

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo(1)	0.0167(3)	0.0191(3)	0.0165(3)	0.0048(3)	0.0081(3)	0.0022(3)
Mo(2)	0.0208(4)	0.0247(4)	0.0271(4)	0.0071(3)	0.0166(3)	0.0074(3)
Mo(3)	0.0242(4)	0.0179(3)	0.0244(4)	0.0075(3)	0.0148(3)	0.0039(3)
Mo(4)	0.0260(4)	0.0229(4)	0.0244(4)	0.0080(3)	0.0147(3)	0.0089(3)

[a] (B), atoms in ligand B. [b] Starred items: anisotropic thermal parameters are of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^*b^* + \ldots)]$.

TABLE 3. Bond Lengths for $(C_5H_9N_2)_4[Mo_8O_{26}]\cdot 4H_2O$[a]

Atom[b]	d (Å)
Mo(1)–O(1)	1.695(5)
Mo(1)–O(12)	1.747(6)
Mo(1)–O(8)	1.949(7)
Mo(1)–O(13)′	1.957(7)
Mo(1)–O(9)′	2.139(5)
Mo(1)–O(9)	2.356(4)
Mo(2)–O(3)	1.707(9)
Mo(2)–O(2)	1.716(5)
Mo(2)–O(10)′	1.875(6)
Mo(2)–O(8)	1.985(6)
Mo(2)–O(13)	2.319(5)
Mo(2)–O(9)′	2.332(7)
Mo(3)–O(4)	1.683(5)
Mo(3)–O(5)	1.695(9)
Mo(3)–O(11)	1.917(6)
Mo(3)–O(13)	1.990(6)
Mo(3)–O(9)	2.337(7)
Mo(3)–O(8)	2.360(4)
Mo(4)–O(7)	1.696(7)
Mo(4)–O(6)	1.713(5)
Mo(4)–O(11)	1.924(8)
Mo(4)–O(10)	1.936(7)
Mo(4)–O(12)	2.287(5)
Mo(4)–O(9)	2.453(6)

Atom	d (Å) Ligand A	Ligand B
C(1)–C(2)	1.39(1)	1.36(1)
C(1)–C(5)	1.38(1)	1.41(2)
C(2)–N(3)	1.33(1)	1.34(1)
C(2)–C(7)	1.50(1)	1.48(2)
C(5)–N(4)	1.34(1)	1.32(1)
C(5)–C(6)	1.49(1)	1.48(2)
N(3)–N(4)	1.35(1)	1.34(1)

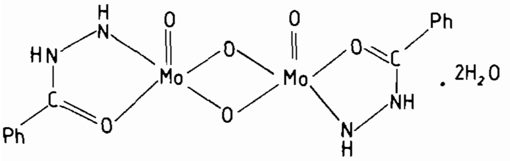
Hydrogen bond distances <3.2 Å

O(14) ... N(3) (B)	2.79(1)
O(14) ... H(N(3)) (B)	1.84(6)
O(14) ... O(15)	2.80(1)
O(14) ... O(2)	2.82(1)
O(14) ... O(3)	2.83(1)
O(15) ... N(4) (B)	2.66(1)
O(15) ... H(N(4)) (B)	1.78(11)
O(15) ... O(6)	2.88(2)
O(15) ... O(5)	2.97(2)
N(3) (A) ... O(11)	2.83(1)
N(4) (A) ... O(6)″	2.88(1)
O(14) ... O(5)	3.10(1)
N(3) (A) ... O(6)″	3.07(1)
N(3) (A) ... O(4)″	3.12(1)
N(4) (A) ... O(2)‴	3.08(1)
N(4) (A) ... O(4)″	3.13(1)

[a] e.s.d.s given in parentheses. [b] Primed atoms: ′ $1 - x, -y, 1 - z$; ″ $1 - x, 1 - y, 1 - z$; ‴ $x, 1 + y, z$. (A), atoms in ligand A; (B), atoms in ligand B.

they were twinned and hence unsuitable for structure determination. Interestingly, they change color slowly in the light to a pale aqua–green colour. While it was initially difficult to interpret the analytical and spectroscopic data for 2 it became clear that this product was an octamolybdate of formula $(C_5H_9N_2)_4[Mo_8O_{26}]$ by analogy with the spectroscopic data and crystal structure of the related tetrahydrate 4 prepared in 95% ethanol (*vide infra*). Both 2 and 4 contain the 3,5-dimethylpyrazolium cation formed by an initial cyclization reaction between benzoylhydrazine and acetylacetone with subsequent hydrolysis and release of the benzoyl moiety. This kind of cyclization of β-diketones and hydrazines to form pyrazoles is well known [19]. In the present situation the acac groups initially coordinated to Mo are presumably protonated and displaced from the metal by a combination of the solvent medium and presence of hydrazine.

Reaction of $MoO_2(acac)_2$ and PhC(O)NHNH$_2$ in 1:2 mole ratio in 95% ethanol leads to a fine white precipitate, 3, being initially formed in the solution. Small white crystals of 4 could be isolated from the mother liquor in low yield, but the crystals were not big enough for X-ray determination. The analytical and spectroscopic data of 3 show that no acac fragments are present and a dinuclear structural formula of the type $Mo_2O_4(NHNHCOPh)_2\cdot 2H_2O$ is proposed. Crystal structures [20] on related $Mo_2O_4^{2+}$ species show a *cis*-disposition of the terminal Mo=O bonds and ν(Mo=O) frequencies are generally observed similar to those displayed in **3**, *viz.* 935 cm^{-1}. A weak band observed at 450 cm^{-1} is probably due to the $\nu(MoO_2Mo)$ vibration. The chelated benzoylhydrazido(1–) ligand is characterized by the following IR stretching frequencies; ν(NH) 3190, 3080; ν(C=O) 1640; ν(N=N) 1565 cm^{-1}. Low field ^1H NMR resonances at 16.49 and 16.10 ppm are assigned to NH protons of the hydrazido(1–) moiety. Complex **3** could also be prepared by refluxing together aqueous ammonium molybdate and ethanolic benzoylhydrazine. If the proposed formulation is correct then presumably the hydrazine acts, in part, as a reducing agent to yield the Mo(V) state. The white colour and analytical data are also compatible with the binuclear Mo(VI) formulation, $Mo_2O_5(NHNHCOPh)_2H_2O$, while the insolubility of **3** in organic solvents may be indicative of a more polymeric solid state structure than a dinuclear one. A tetramolybdate structure of the type referred to in the 'Introduction' is conceivable [9–11].



3

It is possible to obtain the tetrahydrate of 3,5-dimethylpyrazolium β-octamolybdate (**4**) exclusively and in higher yield by using a 1:1 mole ratio of $MoO_2(acac)_2$ and benzoylhydrazine in 95% ethanol as solvent. A short reflux period followed by evaporation of the solvent favour high yields of the white needle-like crystalline product. Longer periods of heating yield green solutions from which samples of **4** are deposited and tainted a pale blue colour. As indicated above, the formation of the 3,5-dimethylpyrazolium ion involves hydrolysis of the benzoyl fragment of the hydrazine. Thus, it is possible to obtain **4** from *p*-methoxybenzoylhydrazine under the reaction conditions just described. Interestingly, if this particular hydrazine is used in a 1:2 Mo:hydrazine reaction, the only crystalline product obtained is p-$MeOC_6H_4COOH$ formed, presumably, by hydrolysis of the (unisolated) 3,5-dimethylpyrazole precursor.

Crystal Structure of 4

The crystal structure viewed approximately along the *b* axis is shown in Fig. 1, whilst Fig. 2 shows the 3,5-dimethylpyrazolium cation. The β-$Mo_8O_{26}^{4-}$ anion consists of eight edge shared molybdenum–oxygen octahedra, with geometry similar to those of other β-$Mo_8O_{26}^{4-}$ anions [4]. Bond lengths for the octamolybdate anion are given in Table 3 and, as can be seen, each molybdenum–oxygen octahedra has two short, two medium and two long bonds, similar to that found in solid state molybdate structures [21].

The two crystallographically independent 3,5-dimethylpyrazolium cations A and B, are hydrogen

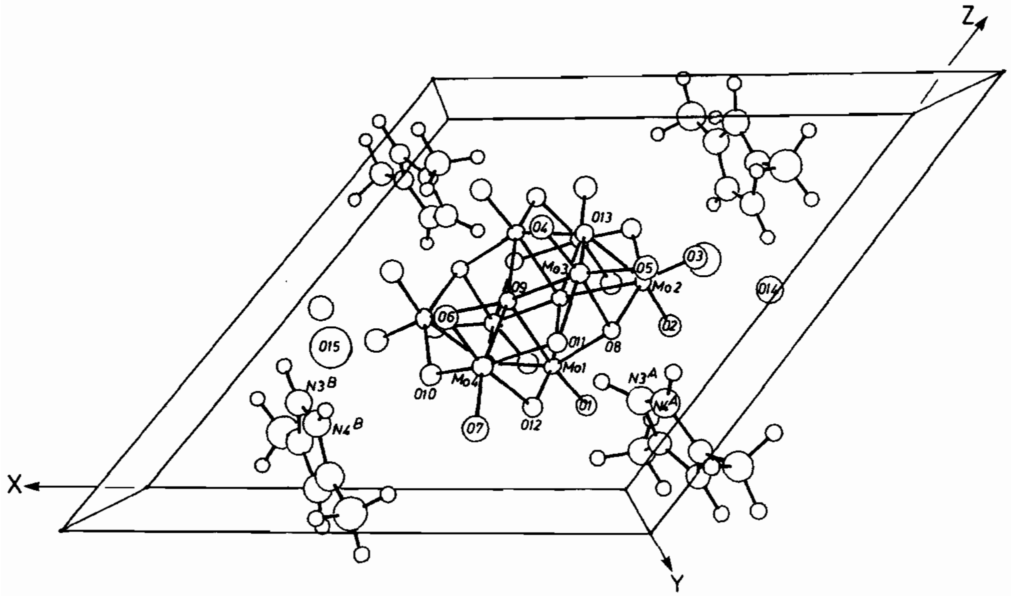


Fig. 1. A view approximately down *b* showing the packing of the β-$Mo_8O_{26}^{4-}$ anion, the cations and water molecules. Hydrogen atom thermal parameters have been reduced for clarity.

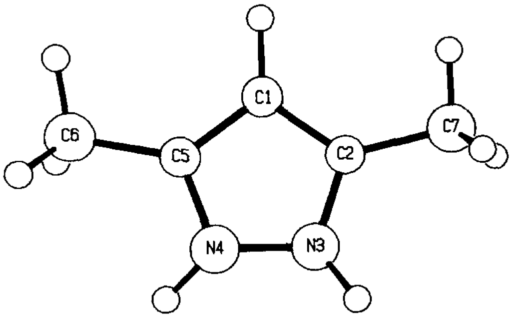


Fig. 2. A view of the 3,5-dimethylpyrazolium cation, with atomic labelling scheme (NB, numbering is different to that commonly accepted for nomenclature purposes). Thermal parameters for hydrogen have been reduced for clarity.

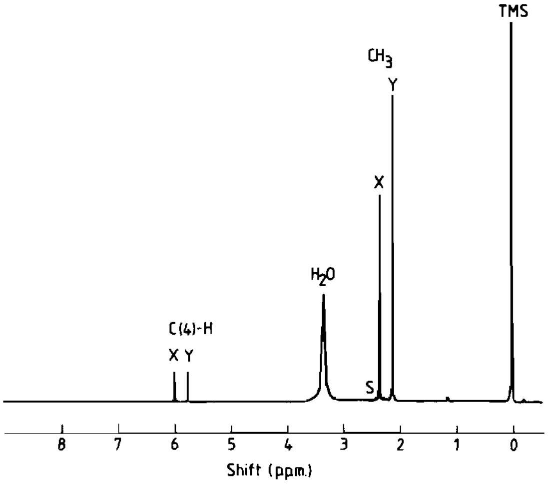


Fig. 3. ^1H NMR spectrum for $(C_5H_9N_2)_4[Mo_8O_{26}]\cdot 4H_2O$ (4) in $(CD_3)_2SO$ at 297 K and 300 MHz. The solvent peak (S) has been removed for clarity. NH^+ resonances could not be detected over a wide sweep and many scans.

bonded in dissimilar ways. The A cation is bound to the β-$Mo_8O_{26}^{4-}$ anion whereas the B cation is bound to the water molecules, which are themselves bonded to the octamolybdate anion (Table 3, Fig. 1). This difference in hydrogen bonding has no apparent statistical influence on the bond lengths of the cation (Table 3). Hydrogen bonding is a characteristic feature of organic amine salts of octamolybdates [4].

^1H NMR Spectrum of 4

The ^1H NMR spectrum of the octamolybdate complex **4** shows some interesting features which are difficult to interpret precisely. Perusal of Table 4 shows that the spectrum of 3,5-dimethylpyrazole or its hydrochloride shows single C(4)–H and CH_3 resonances. In contrast, the 297 K spectrum of **4** shows two C(4)–H and CH_3 resonances (labelled X and Y) both in the % ratio of 44:56 (Fig. 3), which indicates in solution the presence of inequivalent cations. The NH resonances were too broad to be able to detect. The crystal structure of **4** indicated two inequivalent cations due to differences in hydrogen bonding to the octamolybdate cluster. It may be possible that these interactions persist in $(CD_3)_2SO$ solution. However, upon D_2O exchange the C(4)–H lines shift a little to 6.03 and 5.88 ppm but they do not become equivalent, which would tend to rule out significant hydrogen bonding effects in solution.

It was thought that maybe the octamolybdate cluster interconverts (e.g. to the α-form) and so perturbs the pyrazolium cations. However, ^{95}Mo and ^{17}O NMR studies would be required to verify

TABLE 4. ^1H NMR Data for $(C_5H_9N_2)_4[Mo_8O_{26}]\cdot 4H_2O$ (4) (in $(CD_3)_2SO$ at 300 MHz relative to Me_4Si)

Compound	Temperature (K)	H atom			Ratio (%) X:Y
		C(4)–H[a]	H_2O	CH_3	
$C_5H_8N_2$[b]	297	5.75		2.12	
$C_5H_8N_2\cdot HCl$	297	6.02		2.21	
		X, Y		X, Y	
Complex **4**	291	6.02, 5.78	3.38	2.37, 2.14	27:73
	297	6.00, 5.76	3.36	2.36, 2.12	44:56
	301	5.99, 5.77	3.33	2.36, 2.13	45:55
	311	5.97, 5.76	3.37	2.36, 2.13	43:57
	333	5.94, 5.76	3.45	2.37, 2.13	34:66
	365	5.92, 5.75	3.46	2.37, 2.13	29:71
	385	5.90, 5.75	3.43	2.37, 2.13	24:76
4 + $C_5H_8N_2$[c]	297	6.01, 5.91	5.05	2.36, 2.18	21:79
4 + $C_5H_8N_2\cdot HCl$[c]	297	6.01, 5.85	5.5v, br	2.36, 2.16	27:73

[a] Note that in Fig. 2 C(4) is labelled C(1). [b] 3,5-Dimethylpyrazole. [c] Concentration ratio of **4** to the pyrazole = 1:2.

this [22]. It is known that pyridine will bind weakly to Mo in an octamolybdate to form $(pyH)_4[py_2Mo_8O_{26}]$ [5c], so it is also conceivable that pyrazole can bind likewise. We endeavoured to test this hypothesis by adding 3,5-dimethylpyrazole and 3,5-dimethylpyrazolium chloride separately to $(CD_3)_2SO$ solutions of **4** in the hope that we may see an enhancement of a pair of peaks. The results, given in Table 4, are unfortunately rather ambiguous. Again, two resonances (only) are observed for the C(4)–H and CH_3 hydrogens. Neither X nor Y lines are precisely in the free base (or base hydrochloride) position. These experiments suggest that the pyrazole moiety exists in the protonated and non-protonated forms in solution.

The temperature study (between 291–385 K) is also interesting as the area ratio of the peaks change, becoming more equal up to 301 K and then reverting gradually back to the 291 K value above 365 K. Also the X C(4)–H peak gradually shifts from 6.02 to 5.90 ppm. On balance, we feel that these data are indicative of the presence, in $(CD_3)_2SO$ solutions of **4**, of unbound pyrazolium groups and of weakly bound pyrazole groups, which can exchange with each other, and the relative proportions of which change with temperature. Another, somewhat related situation has recently been reported by Hill *et al.* [23].

Supplementary Material

Tables of positional coordinates for hydrogen atoms, all bond angles and structure factor amplitudes (24 pages) are available on request from Dr K. S. Murray.

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