# Synthesis and Characterization of New Octamolybdates containing Imidazole, 1-Methyl- or 2-Methyl-imidazole Co-ordinatively Bound to Molybdenum†

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The compounds $[H_2im]_4[Mo_8O_{26}(Him)_2]$ **1**, $[NH_2Me_2]_4[Mo_8O_{26}(Him)_2]\cdot3H_2O$ **2**, $[1\text{-Hmim}]_4[Mo_8O_{26}(1\text{-mim})_2]\cdot2H_2O$ **3** and $[2\text{-Hmim}]_4[Mo_8O_{26}(2\text{-mim})_2]\cdot3H_2O$ **4** (where Him = imidazole, 1-mim = 1-methylimidazole and 2-mim = 2-methylimidazole) have been synthesized. Compounds **1** and **3** were prepared by the reaction between molybdenum trioxide and imidazole or 1-methylimidazole in aqueous medium, whilst **2** and **4** were synthesized by reaction of molybdenum trioxide with imidazole or 2-methylimidazole in dmf–$H_2O$ (dmf = dimethylformamide). The compounds have been characterized by elemental analysis, infrared and $^1H$ and $^{13}C$ NMR spectroscopies and thermal measurements. The structures of compounds **2** and **3** were determined by X-ray crystallography and showed that both anions are composed of two $MoNO_5$ and six $MoO_6$ edge-sharing octahedra. The Mo–N and Mo–O bond strengths of both compounds have been calculated.

Polyoxometalate chemistry includes the study of compounds that are unique because of their topological and electronic versatility and their relevance to several disciplines.[1] Recently polyoxomolybdates containing organic molecules have received considerable attention because of their use as models of the interactions between organic substrates and catalytic metal oxide surfaces in heterogeneous catalysis employing solid molybdenum oxides.[2] Moreover, there is further interest in their structural complexity and reactivity and the interconversions within these large anions.[3,4] In addition, certain polyoxomolybdates, in particular some organoammonium heptamolybdates,[5] have been recognized as potential antitumour agents.

While many octamolybdates of organic bases are known[3,4] where the organic base is bonded to the $[Mo_8O_{26}]^{4-}$ anion by a hydrogen bond, only two octamolybdates containing an organic base co-ordinatively bound to molybdenum have been described.[6,7] In this paper we report new octamolybdates containing imidazole (Him), 1-methylimidazole (1-mim) or 2-methylimidazole (2-mim), namely $[H_2im]_4[Mo_8O_{26}(Him)_2]$ **1**, $[NH_2Me_2]_4[Mo_8O_{26}(Him)_2]\cdot3H_2O$ **2**, $[1\text{-Hmim}]_4[Mo_8O_{26}(1\text{-mim})_2]\cdot2H_2O$ **3** and $[2\text{-Hmim}]_4[Mo_8O_{26}(2\text{-mim})_2]\cdot3H_2O$ **4**. The compounds have been characterized by elemental analyses, infrared and $^1H$ and $^{13}C$ NMR spectroscopies and thermal measurements. The crystal structures of compounds **2** and **3** have also been determined.

## Experimental

*Materials and Apparatus.*—All reagents obtained commercially were of reagent grade. Elemental analyses (C, H and N) were performed with a Carlo Erba 1106 automatic analyser. Infrared spectra were recorded in the range 4000–250 $cm^{-1}$ on a Nicolet 5PCFT-IR spectrophotometer using KBr pellets. Hydrogen-1 and $^{13}C$ NMR spectra were recorded at 297 K on a Bruker AC 200 spectrometer at 200 MHz, with tetramethylsilane as internal standard after dilution of the sample in deuteriated dimethyl sulfoxide. Thermogravimetric and calorimetric analyses were performed on a Netzsch STA 409 EP simultaneous thermobalance and a differential scanning calorimeter, respectively, at a heating rate of 10 °C $min^{-1}$ in static air under atmospheric pressure.

*Preparation of Compounds.*—$[H_2im]_4[Mo_8O_{26}(Him)_2]$ **1**. A suspension of $MoO_3$ (3.50 g, 24.3 mmol) and imidazole (1.66 g, 24.4 mmol) in water (1 $dm^3$) was refluxed with stirring for 12 h. The resulting yellow solution was cooled and allowed to stand at room temperature. White crystals of **1** appeared after several weeks. They were filtered off, washed with water, then dried in air for a few hours and stored in a desiccator over $CaCl_2$ (Found: C, 13.25; H, 1.65; N, 10.25; $MoO_3$, 72.40. $C_{18}H_{24}Mo_8N_{12}O_{26}$ requires C, 13.55; H 1.75; N, 10.55; $MoO_3$, 72.15%). A structural study of **1** was discarded because of its instability in air.

$[NH_2Me_2]_4[Mo_8O_{26}(Him)_2]\cdot3H_2O$ **2**. A suspension of $MoO_3$ (3.00 g, 20.8 mmol) and imidazole (1.42 g, 20.8 mmol) in dmf–$H_2O$ (200 $cm^3$, 3:1) (dmf = dimethylformamide) was refluxed with stirring for 12 h. The resulting solution was cooled and allowed to stand at room temperature whereupon a white dust appeared after several weeks, which was filtered off. Prismatic transparent crystals of **2** were deposited on slow evaporation (Found: C, 11.10; H, 2.90; N, 7.30; $MoO_3$ 73.40. $C_{14}H_{46}Mo_8N_8O_{29}$ requires C, 10.80; H, 2.95; N, 7.20; $MoO_3$, 73.90%).

$[1\text{-Hmim}]_4[Mo_8O_{26}(1\text{-mim})_2]\cdot2H_2O$ **3**. This compound was prepared as described above for **1** from $MoO_3$ (3.20 g, 22.2 mmol) and 1-methylimidazole (1.90 g, 23.1 mmol). White crystals of **3** were washed with water and stored in a desiccator over $CaCl_2$ (Found: C, 16.75; H, 2.50; N, 9.80; $MoO_3$ 66.95. $C_{24}H_{44}Mo_8N_{12}O_{28}$ requires C, 16.80; H, 2.60; N, 9.80; $MoO_3$, 67.10%). Yellow crystals were obtained upon recrystallization from water which had the same chemical composition as the white ones.

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

**Table 1** Summary of crystallographic data for $[NH_2Me_2]_4[Mo_8O_{26}(Him)_2]\cdot 3H_2O$ **2** and $[1\text{-Hmim}]_4[Mo_8O_{26}(1\text{-mim})]\cdot 2H_2O$ **3***

| | **2** | **3** |
|---|---|---|
| Molecular formula | $C_{14}H_{40}Mo_8N_8O_{26}\cdot 3H_2O$ | $C_{24}H_{40}Mo_8N_{12}O_{26}\cdot 2H_2O$ |
| $M$ | 1558.07 | 1716.20 |
| Space group | $P2_1/n$ | $C2/c$ |
| $a$/Å | 11.414(2) | 21.449(6) |
| $b$/Å | 18.390(4) | 10.372(4) |
| $c$/Å | 20.570(4) | 23.240(5) |
| $\beta$/° | 101.13(1) | 102.84(2) |
| $U$/Å$^3$ | 4237(1) | 5040.8(8) |
| $D_c$/g cm$^{-3}$ | 2.43 | 2.19 |
| $\mu$(Mo-K$\alpha$)/mm$^{-1}$ | 2.33 | 1.949 |
| $F$(000) | 3016 | 3328 |
| Crystal dimensions/mm | 0.10 × 0.03 × 0.6 | 0.40 × 0.30 × 0.35 |
| Scan range $\omega$–2$\theta$/° | $1.9 + 0.35 \tan\theta$ | $0.8 + 0.35 \tan\theta$ |
| 2$\theta$ Range/° | 0–60 | 2–50 |
| Range of $hkl$ | 0–16, 0–25, −28 to 28 | −23 to 23, 0–12, 0−27 |
| No. of reflections collected | 12301 | 4872 |
| No. of reflections in refinement | 9473 | 3977 |
| $R\ [\Sigma(\lvert F_o\rvert - \lvert F_c\rvert)/\Sigma\lvert F_o\rvert]$ | 0.030 | 0.046 |
| $R'\{[\Sigma(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma\lvert F_o\rvert^2]^{\frac{1}{2}}\}$ | 0.0356 | 0.046 |

* Details in common: crystal system, monoclinic; $Z = 4$; colour, white; scan type $\omega$–2$\theta$.

$[2\text{-Hmim}]_4[Mo_8O_{26}(2\text{-mim})_2]\cdot H_2O$ **4**. This compound was obtained in the same way as **1**, starting from $MoO_3$ (3.20 g, 22.2 mmol) and 2-methylimidazole (1.90 g, 23.1 mmol). After several weeks white crystals were deposited, which were washed with water and stored in a desiccator over $CaCl_2$ (Found: C, 16.30; H, 2.55; N, 9.30. $C_{24}H_{42}Mo_8N_{12}O_{27}$ requires C, 16.95; H, 2.50; N, 9.90%). When the synthesis was carried out in dmf–$H_2O$ (150:20) the compound $[2\text{-Hmim}]_4[Mo_8O_{26}(2\text{-mim})_2]\cdot 3H_2O$ **4** was obtained (Found: C, 16.80; H, 2.50; N, 9.45. $C_{24}H_{46}Mo_8N_{12}O_{29}$ requires C, 16.60; H, 2.65; N, 9.70%).

Crystals suitable for X-ray crystallography were obtained only for compounds **2** and **3**.

*X-Ray Structure Determination and Refinement.*—$[NH_2Me_2]_4[Mo_8O_{26}(Him)_2]\cdot 3H_2O$ **2**. Diffraction data were collected at 298 K using an Enraf Nonius CAD-4 diffractometer with graphite-monochromated Mo-K$\alpha$ ($\lambda$ = 0.7107 Å) radiation. The crystal was sealed in a capillary under a nitrogen atmosphere. The cell parameters were determined by least squares from 25 automatically centred reflections in the range $18 \leqslant 2\theta \leqslant 30°$. Crystal parameters and the results of the refinement are summarized in Table 1. 12301 Independent reflections were measured with $\omega$–2$\theta$ scans up to 2$\theta$ = 60°. Three standard reflections (−7, −4, 2; −6, −7, −9, 8; and −5, 7, 14) were measured for every 100 reflections, which showed only random deviation from the mean intensity. After completion of the experiment the crystal was black. Lorentz and polarization, but not absorption, corrections were applied. Only 9473 reflections $[I > 3\sigma(I)]$ were considered observed and were included in the refinement. The structure was solved by direct methods using SHELXS 86[8] and the refinement carried out by least squares using SHELX 76.[9] The function $\Sigma w(\Delta F)^2$ was minimized with anisotropic thermal parameters for the non-hydrogen atoms. The hydrogen atoms were included in the refinement in calculated positions, except for those of the ammonium groups, with an overall isotropic thermal parameter. The final $R$ and $R'$ values were 0.030 and 0.0356 $\{w = K/[\sigma^2(F) + 0.002102F^2]\}$ respectively, and the goodness of fit was 0.9835. Atomic scattering factors were taken from ref. 10 and the anomalous scattering factors were those of Cromer and Liberman.[11] The maximum and minimum electron densities in the final difference map were +0.94 and −1.04 e Å$^{-3}$ and the maximum $\Delta/\sigma$ was −0.575 for O(6). All graphic representations were produced using the SCHAKAL program.[12]

$[1\text{-Hmim}]_4[Mo_8O_{26}(1\text{-mim})_2]\cdot 2H_2O$ **3**. Diffraction data were collected at 294 K with an Enraf Nonius CAD-4 diffractometer using graphite monochromated Mo-K$\alpha$ radiation ($\lambda$ = 0.7107 Å). Cell parameters were determined from the least-squares refinement of 25 centred reflections in the range $12 < 2\theta < 20°$. Crystal parameters and the results of the refinements are summarized in Table 1. A total of 4872 reflections were recorded in the range $2 < 2\theta < 50°$ with a scan speed of 0.091° s$^{-1}$. Three reference reflections monitored throughout the data collection showed no significant sign of crystal deterioration. The usual corrections for Lorentz and polarization effects were carried out and an empirical absorption correction using the $\psi$ scan was applied. The structure was solved by the Patterson method and refined by the full-matrix least-squares method. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located in a Fourier difference map and were refined with an overall isotropic thermal parameter. The maximum $\Delta/\sigma$ was 0.1. The final full-matrix least-squares refinement, minimizing $\Sigma w(\lvert F_o\rvert - F_c\rvert)^2$, including 3977 reflections with $I \geqslant 3\sigma(I)$, converged at $R$ and $R'$ = 0.046 and 0.046. Atomic scattering factors were taken from ref. 10. All calculations were performed using SHELXS 86,[8] SHELX 76[9] and SCHAKAL.[12]

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

## Results and Discussion

The structures of compounds **2** and **3** are discussed comparatively. For compound **2** the final fractional atomic coordinates for the non-hydrogen atoms and a list of bond lengths and angles are reported in Tables 2 and 3, respectively. Fig. 1 shows a stereoscopic view of the molecular structure. For **3**, final atomic coordinates and bond lengths and angles are given in Tables 4 and 5, respectively and its molecular structure is shown in Fig. 2. The anions of both compounds have crystallographic inversion symmetry and **2** has two independent centrosymmetric anions.

Both anions are composed of two $MoNO_5$ and six $MoO_6$ edge-sharing octahedra and are similar to those described by McCarron *et al.*[6] and more recently in ref. 7. As shown previously[6,7] the polyanions are related to $\beta$-$[Mo_8O_{26}]^{4-}$ by a simple shearing of the $[Mo_4O_{13}]^{2-}$ asymmetric units of the parent $\beta$-$[Mo_8O_{26}]^{4-}$ anion parallel to one another, producing

**Table 2** Fractional atomic coordinates with estimated standard deviations (e.s.d.s.) in parentheses for $[NH_2Me_2]_4[Mo_8O_{26}(Him)_2]\cdot 3H_2O$ **2**

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Mo(1) | 0.544 54(3) | 0.419 80(2) | 0.124 07(2) |
| Mo(2) | 0.504 61(3) | 0.423 13(2) | −0.050 14(2) |
| Mo(3) | 0.273 33(3) | 0.404 47(2) | 0.038 85(2) |
| Mo(4) | 0.211 63(3) | 0.430 95(2) | −0.118 14(2) |
| Mo(5) | 0.127 10(3) | 0.161 38(2) | 0.111 22(2) |
| Mo(6) | −0.139 84(3) | 0.157 61(2) | 0.018 81(2) |
| Mo(7) | −0.000 47(3) | 0.003 87(2) | −0.083 21(2) |
| Mo(8) | −0.259 15(3) | 0.004 52(2) | −0.036 22(2) |
| O(1) | 0.658 90(30) | 0.362 12(18) | 0.153 91(17) |
| O(2) | 0.492 37(30) | 0.448 29(18) | 0.192 10(15) |
| O(3) | 0.594 32(24) | 0.385 78(15) | 0.020 86(14) |
| O(4) | 0.413 24(24) | 0.355 60(14) | 0.088 39(14) |
| O(5) | 0.572 46(23) | 0.519 63(14) | −0.042 96(13) |
| O(6) | 0.374 61(23) | 0.491 28(14) | −0.109 48(14) |
| O(7) | 0.558 58(27) | 0.384 47(17) | −0.113 66(15) |
| O(8) | 0.359 13(23) | 0.375 02(14) | −0.049 09(13) |
| O(9) | 0.196 78(23) | 0.467 86(15) | −0.034 06(14) |
| O(10) | 0.183 23(26) | 0.330 55(16) | 0.022 34(16) |
| O(11) | 0.221 21(27) | 0.450 24(18) | 0.099 94(15) |
| O(12) | 0.137 56(29) | 0.493 80(18) | −0.170 17(16) |
| O(13) | 0.117 61(29) | 0.357 96(18) | −0.124 32(16) |
| O(14) | 0.035 10(25) | −0.090 20(14) | −0.110 38(13) |
| O(15) | −0.154 20(23) | −0.059 48(14) | −0.072 67(14) |
| O(16) | 0.143 50(24) | 0.041 72(16) | −0.061 45(14) |
| O(17) | −0.060 63(30) | 0.046 99(17) | −0.154 68(15) |
| O(18) | −0.076 05(23) | 0.055 61(14) | −0.020 01(13) |
| O(19) | −0.322 80(33) | 0.046 54(20) | −0.108 44(18) |
| O(20) | −0.367 04(29) | −0.052 62(20) | −0.019 00(20) |
| O(21) | −0.262 65(25) | 0.085 62(15) | 0.021 42(16) |
| O(22) | −0.183 84(28) | 0.218 70(17) | 0.072 35(17) |
| O(23) | 0.027 88(24) | 0.186 43(15) | 0.030 24(14) |
| O(24) | −0.187 86(30) | 0.193 85(18) | −0.057 71(16) |
| O(25) | 0.261 73(27) | 0.196 74(17) | 0.103 99(17) |
| O(26) | 0.074 20(27) | 0.216 33(17) | 0.167 20(15) |
| N(1) | 0.285 31(33) | 0.375 47(20) | −0.195 90(17) |
| C(1) | 0.348 80(48) | 0.403 21(35) | −0.236 28(27) |
| N(2) | 0.359 40(33) | 0.355 91(22) | −0.284 29(18) |
| C(2) | 0.300 60(57) | 0.293 16(34) | −0.273 61(30) |
| C(3) | 0.254 68(55) | 0.305 16(29) | −0.218 29(27) |
| N(5) | 0.455 42(42) | 0.219 44(27) | 0.031 68(29) |
| N(7) | 0.536 20(55) | 0.193 35(37) | 0.091 68(35) |
| C(8) | 0.507 73(63) | 0.213 80(35) | −0.028 68(37) |
| N(6) | 0.851 31(43) | 0.378 01(30) | 0.041 66(34) |
| C(9) | 0.883 70(75) | 0.372 86(41) | −0.022 99(42) |
| C(10) | 0.954 05(54) | 0.373 00(35) | 0.096 15(37) |
| N(3) | 0.218 50(33) | 0.101 09(20) | 0.200 08(18) |
| C(4) | 0.173 83(58) | 0.071 53(35) | 0.247 59(28) |
| N(4) | 0.258 48(38) | 0.040 97(24) | 0.292 73(19) |
| C(5) | 0.364 90(63) | 0.049 67(40) | 0.272 59(33) |
| C(6) | 0.339 52(51) | 0.086 70(39) | 0.215 58(30) |
| N(7) | 0.327 13(53) | 0.076 55(32) | −0.139 28(28) |
| C(11) | 0.370 90(69) | 0.002 03(43) | −0.137 60(43) |
| C(12) | 0.227 90(79) | 0.093 78(47) | −0.196 45(39) |
| N(8) | −0.180 52(54) | 0.180 25(30) | −0.198 84(25) |
| C(13) | 0.271 16(76) | 0.345 16(46) | 0.233 32(35) |
| C(14) | 0.428 67(83) | 0.274 95(56) | 0.298 39(66) |
| O(W1) | 0.620 30(43) | 0.268 13(24) | −0.193 24(22) |
| O(W2) | 0.208 33(47) | 0.200 61(24) | −0.064 24(25) |
| O(W3) | −0.486 34(55) | 0.137 06(35) | −0.181 80(36) |

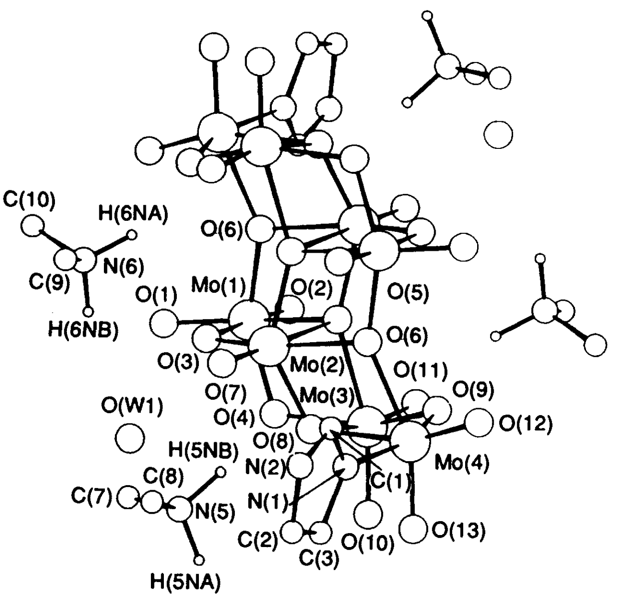


**Fig. 1** Perspective view of one asymmetric unit of **2**, showing hydrogen atoms only on the ammonium cations

the observed stoichiometry. In compounds **2** and **3** where a non-oxygen-bound ligand co-ordinates directly to a molybdenum atom of an isopolymolybdate anion, the co-ordination site is always the apical one and thus the structure of the $[Mo_8O_{26}]^{4-}$ anion can also be considered to be γ-molybdate with two additional terminal positions satisfying the octahedral co-ordination of all eight molybdenum atoms.[7]

$$\Delta l = \tfrac{1}{6}\Sigma[(R_i - R)/R]^2 \qquad (1)$$

$$\Delta e = \tfrac{1}{12}\Sigma[(D_i - D)/D]^2 \qquad (2)$$

$$\Delta\alpha = \tfrac{1}{3}\Sigma[(\alpha_i - 180)/180]^2 \qquad (3)$$

The octahedral distortion has been calculated using equations (1)–(3).[7,13] where $R_i$ = an individual Mo–O or Mo–N distance, $R$ = the mean Mo–O or Mo–N distance, $D_i$ = an individual O–O or O–N distance, $D$ = the mean O–O or O–N distance and $\alpha_i$ = an individual O–Mo–O or O–Mo–N angle. The values obtained are given in Table 6.

In compound **2** the octahedra of Mo(4) and Mo(5), which contain the $MoNO_5$ units, are the least distorted with respect to Δ*l* and Δα and neither occupies a central position in the polyanion as occurs in the pyrazole octamolybdate,[7] while in *N*,*N*-dimethylanilinium β-octamolybdate dihydrate[13] and bis(tetrabutylammonium)bis(triethylammonium) β-octamolybdate dihydrate the least distorted octahedron occupies the central position. In compound **3**, the least distorted octahedron with respect to Δ*l* and Δ*e* is that of Mo(3) which does not contain the $MoNO_5$ unit. Octahedra in central positions are not observed in this compound.

The strengths of the Mo–O and Mo–N interactions, *s*, within the $MoNO_5$ octahedra are calculated from equation (4),[14]

$$s = (d/1.882)^{-6} \qquad (4)$$

where *d* is the bond length in Å. These values differ from those calculated using equation (5),[15] where $d_1$ = 1.9144 Å and $B$ =

$$\log s' = (d_1 - d)/B \qquad (5)$$

0.953. The *s* and *s*′ values are given in Table 7. The difference between the Mo–O bond strengths (*s*′) about an oxygen atom with co-ordination number *n* and the nominal value 2 is, as a consequence of the valence rule,[16] the charge on that oxygen atom, *i.e.* c.u. = *s*′ − 2. The charge units (c.u.s) of the oxygen atoms in the $MoNO_5$ octahedra are also given in Table 7. In compound 2, the oxygen atoms O(12) and O(13) and O(25) and O(26), form the strongest Mo–O bonds to Mo(4) and Mo(5) respectively and as a consequence have the smallest c.u. values. Similarly O(3) and O(19) form the strongest of Mo–O bonds in the Mo(1) octahedron in compound **3**. The Mo–N bond strengths *s* are 0.39 and 0.37 for **2** and 0.36 for **3** (Table 7) and are similar to pyridine octamolybdate[6] (*s* = 0.32) and pyrazole octamolybdate[7] (*s* = 0.35), indicating a covalent interaction in

**Table 3** Selected bond lengths (Å) and angles (°) for $[NH_2Me_2]_4[Mo_8O_{26}(Him)_2]\cdot 3H_2O$ **2** with e.s.d.s in parentheses *

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Mo(1)–O(1) | 1.702(3) | Mo(3)–O(9) | 1.966(3) | Mo(4)–N(1) | 2.197(4) | Mo(6)–O(24) | 1.699(3) |
| Mo(1)–O(2) | 1.706(3) | Mo(3)–O(8) | 2.282(3) | Mo(4)–O(6) | 2.144(3) | Mo(6)–O(18) | 2.216(3) |
| Mo(1)–O(3) | 2.385(3) | Mo(7)–O(18B) | 2.398(3) | Mo(4)–O(8) | 2.233(3) | Mo(8)–O(18) | 2.257(3) |
| Mo(1)–O(4) | 1.938(3) | Mo(7)–O(16B) | 1.761(3) | Mo(4)–O(9) | 1.896(3) | Mo(8)–O(15) | 1.931(3) |
| Mo(1)–O(5) | 2.224(2) | Mo(7)–O(14) | 1.886(3) | Mo(4)–O(13) | 1.708(3) | Mo(8)–O(20) | 1.707(4) |
| Mo(1)–O(6) | 1.929(3) | Mo(7)–O(18) | 1.942(3) | Mo(4)–O(12) | 1.687(3) | Mo(8)–O(21) | 1.911(3) |
| Mo(2)–O(3) | 1.754(3) | Mo(7)–O(15) | 2.152(3) | Mo(5)–N(3) | 2.219(3) | Mo(8)–O(19) | 1.707(3) |
| Mo(2)–O(5) | 1.930(3) | Mo(7)–O(17) | 1.695(3) | Mo(5)–O(25) | 1.701(3) | Mo(8)–O(16B) | 2.341(3) |
| Mo(2)–O(7) | 1.704(3) | N(1)–C(3) | 1.394(6) | Mo(5)–O(15B) | 2.081(3) | N(3)–C(4) | 1.305(8) |
| Mo(2)–O(6) | 2.136(3) | C(2)–C(3) | 1.360(9) | Mo(5)–O(26) | 1.726(3) | C(4)–N(4) | 1.329(7) |
| Mo(2)–O(8) | 1.885(3) | C(2)–N(2) | 1.374(8) | Mo(5)–O(14B) | 2.265(3) | N(4)–C(5) | 1.367(9) |
| Mo(2)–O(5A) | 2.490(3) | N(2)–C(1) | 1.339(7) | Mo(5)–O(23) | 1.882(3) | C(5)–C(6) | 1.339(9) |
| Mo(3)–O(5A) | 2.235(3) | C(1)–N(1) | 1.307(7) | Mo(6)–O(23) | 1.956(3) | C(6)–N(3) | 1.382(7) |
| Mo(3)–O(4) | 1.941(3) | N(5)–C(7) | 1.471(8) | Mo(6)–O(14B) | 2.376(3) | N(5)–C(8) | 1.482(10) |
| Mo(3)–O(11) | 1.712(3) | C(5)–C(6) | 1.339(9) | Mo(6)–O(22) | 1.715(3) | N(4)–C(5) | 1.366(9) |
| Mo(3)–O(10) | 1.699(3) | C(4)–N(4) | 1.329(7) | Mo(6)–O(21) | 1.936(3) | N(6)–C(9) | 1.450(12) |
| O(3)–Mo(1)–O(4) | 78.6(1) | O(23)–Mo(5)–O(25) | 103.2(2) | O(7)–Mo(2)–O(8) | 105.2(1) | O(22)–Mo(6)–O(23) | 98.4(1) |
| O(3)–Mo(1)–O(2) | 172.7(1) | O(25)–Mo(5)–O(14B) | 166.2(1) | O(6)–Mo(2)–O(7) | 96.9(1) | O(21)–Mo(6)–O(23) | 151.5(1) |
| O(1)–Mo(1)–O(4) | 103.9(1) | O(22)–Mo(5)–O(24) | 104.8(2) | O(5)–Mo(2)–O(8) | 140.5(1) | O(18)–Mo(6)–O(23) | 83.7(1) |
| O(1)–Mo(1)–O(5) | 152.9(1) | O(17)–Mo(7)–O(18) | 101.1(1) | O(3)–Mo(2)–O(6) | 159.2(1) | O(20)–Mo(8)–O(21) | 104.4(2) |
| O(6)–Mo(1)–O(4) | 144.6(1) | O(16)–Mo(7)–O(18) | 98.6(1) | O(7)–Mo(2)–O(5) | 179.4(1) | O(19)–Mo(8)–O(21) | 97.5(2) |
| O(1)–Mo(1)–O(2) | 105.1(2) | O(15)–Mo(7)–O(18) | 73.8(1) | O(6)–Mo(2)–O(8) | 76.4(1) | O(19)–Mo(8)–O(20) | 104.8(2) |
| O(11)–Mo(3)–O(8) | 164.1(1) | O(15)–Mo(7)–O(16) | 158.0(1) | O(9)–Mo(4)–O(1) | 160.9(1) | O(18)–Mo(8)–O(21) | 73.3(1) |
| O(9)–Mo(3)–O(4) | 150.9(1) | O(14)–Mo(7)–O(17) | 104.3(1) | O(8)–Mo(4)–N(1) | 84.3(1) | O(15)–Mo(8)–O(19) | 97.5(2) |
| O(8)–Mo(3)–O(9) | 74.4(1) | O(14)–Mo(7)–O(16) | 101.2(1) | O(6)–Mo(4)–O(13) | 159.3(1) | O(18)–Mo(8)–O(20) | 155.5(2) |
| O(4)–Mo(3)–O(8) | 82.6(1) | C(1)–N(1)–C(3) | 106.6(4) | O(6)–Mo(4)–O(8) | 69.5(1) | N(1)–C(1)–N(2) | 110.8(5) |
| O(9)–Mo(3)–O(11) | 95.9(1) | N(2)–C(2)–C(3) | 106.1(5) | O(13)–Mo(4)–N(1) | 84.5(1) | N(4)–C(5)–C(6) | 105.7(6) |
| O(10)–Mo(3)–O(11) | 104.9(2) | C(7)–N(5)–C(8) | 113.0(5) | O(8)–Mo(4)–O(9) | 76.9(1) | C(9)–N(6)–C(10) | 113.0(6) |
| O(23)–Mo(5)–N(3) | 163.4(1) | N(3)–C(4)–N(4) | 111.3(5) | O(23)–Mo(6)–O(24) | 97.9(1) | N(3)–C(6)–C(5) | 109.7(5) |
| O(25)–Mo(5)–N(3) | 88.5(2) | C(4)–N(4)–C(5) | 107.9(5) | O(21)–Mo(6)–O(24) | 100.8(2) | C(11)–N(7)–C(12) | 114.9(6) |
| O(23)–Mo(5)–O(26) | 102.6(1) | | | O(22)–Mo(6)–O(24) | 104.8(2) | | |

* For the octahedra of Mo(1)–Mo(4), O(*n*A) is at $1 - x, 1 - y, -z$ and for Mo(5)–Mo(8), O(*n*B) is at $-x, -y, -z$.

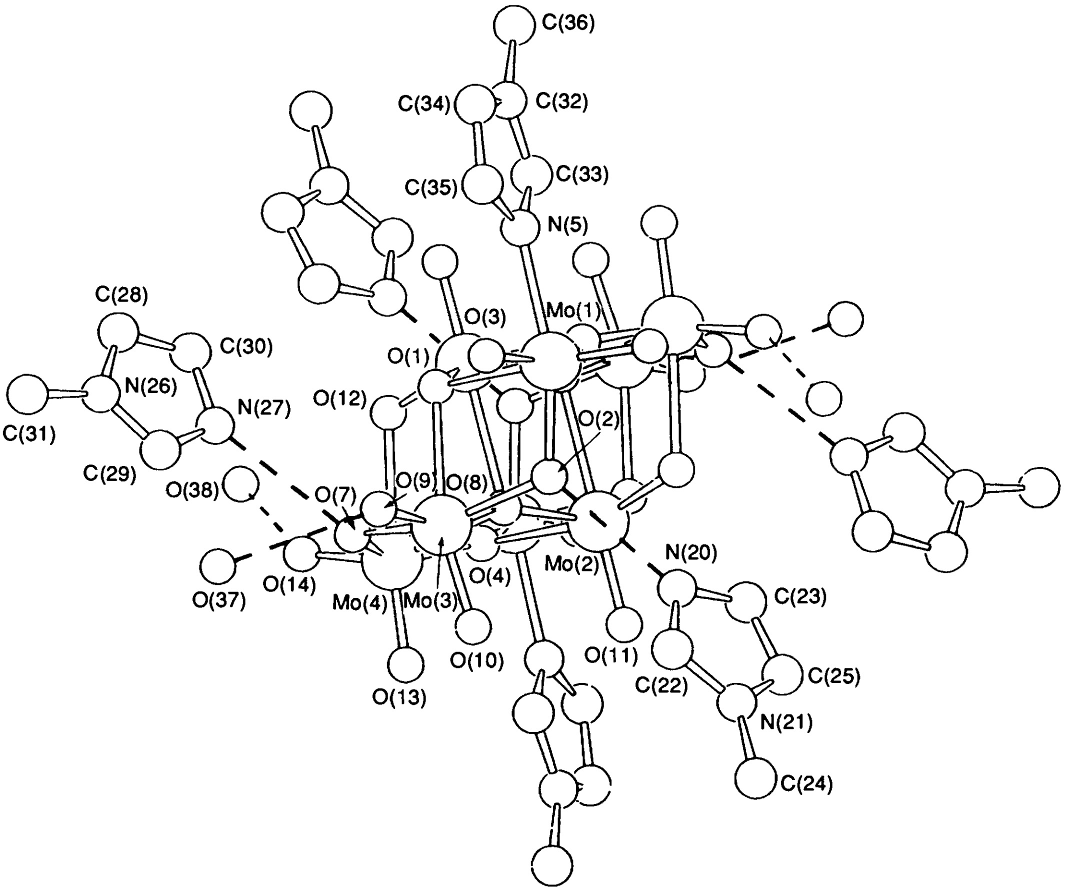


Fig. 2 Perspective view of 3 showing the atom labelling scheme. Hydrogen atoms are omitted for clarity

**Table 4** Fractional atomic coordinates with e.s.d.s. in parentheses for $[1\text{-Hmim}]_4[Mo_8O_{26}(1\text{-mim})_2]\cdot 2H_2O$ **3**

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Mo(1) | 0.841 36(3) | 0.318 52(6) | 0.660 54(3) |
| Mo(2) | 0.735 63(3) | 0.091 97(5) | 0.477 96(3) |
| Mo(3) | 0.688 22(3) | 0.257 87(6) | 0.621 55(3) |
| Mo(4) | 0.611 27(3) | 0.273 30(7) | 0.484 22(3) |
| O(1) | 0.754 4(2) | 0.414 3(4) | 0.600 4(2) |
| O(2) | 0.775 7(3) | 0.192 5(5) | 0.649 2(2) |
| O(3) | 0.826 9(3) | 0.393 8(6) | 0.721 8(3) |
| O(4) | 0.652 4(2) | 0.193 6(5) | 0.427 0(2) |
| N(5) | 0.896 2(3) | 0.498 2(7) | 0.654 1(3) |
| O(7) | 0.623 8(2) | 0.344 2(5) | 0.563 5(2) |
| O(8) | 0.707 8(2) | 0.208 7(4) | 0.532 9(2) |
| O(9) | 0.679 0(3) | 0.343 3(5) | 0.682 1(2) |
| O(10) | 0.652 6(3) | 0.112 9(5) | 0.627 6(3) |
| O(11) | 0.696 8(3) | −0.047 7(5) | 0.486 1(3) |
| O(12) | 0.687 4(3) | 0.437 2(5) | 0.482 6(3) |
| O(13) | 0.565 3(3) | 0.145 7(7) | 0.494 1(3) |
| O(14) | 0.559 2(3) | 0.377 4(7) | 0.443 2(3) |
| O(19) | 0.906 8(3) | 0.228 6(7) | 0.686 5(3) |
| N(20) | 0.780 5(4) | 0.933 9(6) | 0.642 5(3) |
| N(21) | 0.757 0(3) | 0.748 4(6) | 0.671 3(3) |
| C(22) | 0.755 5(5) | 0.874 3(7) | 0.682 9(4) |
| C(23) | 0.798 9(5) | 0.845 8(9) | 0.604 9(4) |
| C(24) | 0.735 7(5) | 0.647 3(8) | 0.708 2(4) |
| C(25) | 0.783 7(5) | 0.728 7(8) | 0.624 9(4) |
| N(26) | 0.581 6(4) | 0.769 4(8) | 0.613 0(4) |
| N(27) | 0.613 1(5) | 0.609 4(8) | 0.568 5(5) |
| C(28) | 0.614 9(5) | 0.817 6(9) | 0.573 9(5) |
| C(29) | 0.581 3(5) | 0.642 5(10) | 0.609 0(6) |
| C(30) | 0.634 4(6) | 0.716 7(12) | 0.545 6(6) |
| C(31) | 0.553 8(7) | 0.847 2(15) | 0.653 6(6) |
| N(32) | 0.951 2(3) | 0.652 7(8) | 0.625 9(3) |
| C(33) | 0.920 4(4) | 0.543 5(9) | 0.610 9(4) |
| C(34) | 0.946 3(5) | 0.682 4(10) | 0.682 7(4) |
| C(35) | 0.911 7(5) | 0.586 9(9) | 0.700 3(4) |
| C(36) | 0.985 7(6) | 0.728 2(12) | 0.588 2(6) |
| O(37) | 0.578 0(9) | 0.453 5(20) | 0.728 6(9) |
| O(38) | 0.538 5(10) | 0.517 9(18) | 0.334 5(10) |

all these cases, while for $K_6[Mo_8O_{26}(NCS)_2]\cdot 6H_2O$[17] the *s* value of 0.46 indicates an electrostatic component in the Mo–N bonding.

The cation of $[NH_2Me_2]_4[Mo_8O_{26}(Him)_2]\cdot 3H_2O$ **2** is formed in acid medium by dmf hydrolysis, in accordance with equation (6), this reaction is probably catalysed by $MoO_3$.

$$Me_2NCOH + H_3O^+ \longrightarrow [NH_2Me_2]^+ + HCO_2H \quad (6)$$

The $[NH_2Me_2]^+$ cation is more abundant than the imidazolium cation and therefore acts as the counterion in the isopolymolybdate obtained.

The four $[NH_2Me_2]^+$ cations are bonded to oxygen atoms of the $[Mo_8O_{26}(Him)_2]^{4-}$ anion by hydrogen bonds (Table 8) with distances in the range 2.97–3.27 Å. There are also some relatively short C–H···O (3.25–3.47 Å) hydrogen contacts between the oxygen atoms of the anions and the carbon atoms of the cations which cannot be considered to be hydrogen bonds, but they do indicate some degree of polarization and the role of this type of interaction in the octamolybdates of organic bases has been examined previously.[18] For compound **2**, there are also intermolecular hydrogen bonds between N(2) and O(22) [3.203(5) Å, symmetry relation $x + \frac{1}{2}, -y - \frac{1}{2}, z - \frac{1}{2}$], N(2) and O(26) [3.117(5) Å, $x + \frac{1}{2}, -y - \frac{1}{2}, z - \frac{1}{2}$] and N(4) and O(11) [2.741(5) Å, $x + \frac{1}{2}, -y - \frac{1}{2}, z - \frac{1}{2}$], and two water molecules are bonded to oxygen atoms of the polyanion by hydrogen bonds, *i.e.* O(W3)···O(19) [2.729(7) Å, $x + 1, y, z + 1$] and O(W2)···O(10) [3.027(6) Å, $x, y, z + \frac{1}{2}$]. The latter water molecule is also hydrogen-bonded to the nitrogen atom of $[NH_2Me_2]^+$ [O(W2)···N(5) 3.134(7) Å, $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$] and one water molecule is also bonded to another [O(W3)···O(W1) 2.731(8) Å, $x + 1, y, z$].

In $[1\text{-Hmim}]_4[Mo_8O_{26}(1\text{-mim})_2]\cdot 2H_2O$ **3** there are four $[1\text{-Hmim}]^+$ cations bonded to oxygen atoms of $[Mo_8O_{26}(1\text{-mim})_2]^{4-}$ by hydrogen bonds (2.76–2.69 Å). The two water molecules are hydrogen-bonded to oxygen atoms of the isopolymolybdate anion [O(37)–H···O(9) 2.864(7) and O(38)–H···O(14) 2.865(4) Å]. These water molecules are in the same asymmetric unit.

**Table 5** Selected bond lengths (Å) and angles (°) for $[1\text{-Hmim}]_4[Mo_8O_{26}(1\text{-mim})_2]\cdot 2H_2O$ **3** with e.s.d.s. in parentheses *

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Mo(1)–O(1) | 2.294(5) | Mo(3)–O(10) | 1.707(5) | Mo(2)–O(4) | 2.182(5) | Mo(4)–O(14) | 1.688(7) |
| Mo(1)–O(2) | 1.896(5) | C(22)–N(20) | 1.333(11) | Mo(2)–O(8) | 1.947(5) | C(28)–N(26) | 1.368(14) |
| Mo(1)–O(3) | 1.711(6) | C(23)–N(20) | 1.380(11) | Mo(2)–O(11) | 1.702(5) | C(29)–N(26) | 1.319(13) |
| Mo(1)–O(19) | 1.682(7) | C(22)–N(21) | 1.335(10) | Mo(2)–O(1A) | 1.882(5) | C(31)–N(26) | 1.466(14) |
| Mo(1)–O(4A) | 2.072(6) | C(24)–N(21) | 1.490(10) | Mo(2)–O(8A) | 2.438(5) | C(29)–N(27) | 1.324(15) |
| Mo(1)–N(5) | 2.227(7) | C(25)–N(21) | 1.344(11) | Mo(2)–O(12A) | 1.727(6) | C(30)–N(27) | 1.358(15) |
| Mo(3)–O(1) | 2.280(5) | C(25)–C(23) | 1.365(12) | Mo(4)–O(4) | 1.937(5) | C(30)–C(28) | 1.352(15) |
| Mo(3)–O(2) | 1.964(5) | C(33)–N(5) | 1.316(11) | Mo(4)–O(7) | 1.946(5) | C(34)–N(32) | 1.382(12) |
| Mo(3)–O(7) | 1.925(5) | C(35)–N(5) | 1.396(11) | Mo(4)–O(8) | 2.231(5) | C(36)–N(32) | 1.490(12) |
| Mo(3)–O(8) | 2.251(5) | C(33)–N(32) | 1.317(11) | Mo(4)–O(12) | 2.364(5) | C(35)–C(34) | 1.355(14) |
| Mo(3)–O(9) | 1.712(5) | | | Mo(4)–O(13) | 1.696(6) | | |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| O(2)–Mo(1)–O(1) | 74.7(2) | O(13)–Mo(4)–O(4) | 97.3(2) | O(8)–Mo(2)–O(4) | 73.9(2) | O(10)–Mo(3)–O(8) | 93.1(2) |
| O(3)–Mo(1)–O(1) | 92.0(2) | O(13)–Mo(4)–O(7) | 97.4(3) | O(11)–Mo(2)–O(4) | 96.4(2) | O(10)–Mo(3)–O(9) | 104.6(3) |
| O(3)–Mo(1)–O(2) | 99.4(2) | O(13)–Mo(4)–O(8) | 101.5(3) | O(11)–Mo(2)–O(8) | 103.2(2) | O(13)–Mo(4)–O(12) | 171.1(3) |
| N(5)–Mo(1)–O(1) | 88.1(2) | O(14)–Mo(4)–O(4) | 103.4(3) | O(2)–Mo(3)–O(1) | 73.8(2) | O(14)–Mo(4)–O(7) | 103.1(3) |
| N(5)–Mo(1)–O(2) | 162.7(2) | O(14)–Mo(4)–O(8) | 154.4(3) | O(7)–Mo(3)–O(1) | 84.4(2) | O(14)–Mo(4)–O(12) | 84.5(3) |
| N(5)–Mo(1)–O(3) | 82.5(3) | O(14)–Mo(4)–O(13) | 104.1(4) | O(7)–Mo(3)–O(2) | 151.1(2) | C(35)–N(5)–C(33) | 106.5(7) |
| O(19)–Mo(1)–O(1) | 163.7(3) | C(23)–N(20)–C(22) | 110.8(7) | O(8)–Mo(3)–O(1) | 73.3(2) | C(24)–N(21)–C(22) | 123.2(7) |
| O(19)–Mo(1)–O(2) | 101.7(3) | C(25)–N(21)–C(22) | 110.2(7) | O(8)–Mo(3)–O(2) | 82.1(2) | C(25)–N(21)–C(24) | 126.5(7) |
| O(19)–Mo(1)–O(3) | 104.2(3) | N(21)–C(22)–N(20) | 106.2(7) | O(8)–Mo(3)–O(7) | 73.4(2) | C(25)–C(23)–N(20) | 104.5(7) |
| O(19)–Mo(1)–N(5) | 94.4(3) | C(23)–C(25)–N(21) | 108.3(7) | O(9)–Mo(3)–O(1) | 90.0(2) | C(31)–N(26)–C(28) | 125.0(10) |
| O(7)–Mo(4)–O(4) | 145.4(2) | C(31)–N(26)–C(29) | 126.7(11) | O(9)–Mo(3)–O(2) | 100.7(3) | C(30)–N(27)–C(29) | 109.8(9) |
| O(8)–Mo(4)–O(4) | 72.9(2) | C(30)–C(28)–N(26) | 107.7(9) | O(9)–Mo(3)–O(7) | 98.0(2) | N(27)–C(29)–N(26) | 108.2(10) |
| O(8)–Mo(4)–O(7) | 73.5(2) | C(28)–C(30)–N(27) | 105.9(10) | O(9)–Mo(3)–O(8) | 161.7(2) | C(34)–N(32)–C(33) | 107.8(8) |
| O(12)–Mo(4)–O(4) | 82.8(2) | C(36)–N(32)–C(33) | 125.5(9) | O(10)–Mo(3)–O(1) | 163.0(2) | C(36)–N(32)–C(34) | 126.7(8) |
| O(12)–Mo(4)–O(7) | 78.1(2) | N(32)–C(33)–N(5) | 111.3(8) | O(10)–Mo(3)–O(2) | 94.7(3) | C(35)–C(34)–N(32) | 106.7(8) |
| O(12)–Mo(4)–O(8) | 70.0(2) | C(34)–C(35)–N(5) | 107.7(9) | O(10)–Mo(3)–O(7) | 101.7(3) | | |

* The atoms O(*n*A) are related to O(*n*) by the symmetry operation $1.5 - x, 0.5 - y, 1 - z$.

**Table 6** Degree of distortion of $MoO_6$ and $MoNO_5$ octahedra for **2** and **3**

(*a*) $[NH_2Me_2]_4[Mo_8O_{26}(Him)_2]\cdot 3H_2O$ **2**

| Distortion ( $\times 10^4$) | Mo(1) | Mo(2) | Mo(3) | Mo(4) | Mo(5) | Mo(6) | Mo(7) | Mo(8) |
|---|---|---|---|---|---|---|---|---|
| $\Delta l$ | 161 | 179 | 132 | 130 | 128 | 154 | 147 | 155 |
| $\Delta e$ | 36 | 34 | 15 | 22 | 27 | 17 | 26 | 29 |
| $\Delta\alpha$ | 209 | 204 | 147 | 120 | 131 | 148 | 192 | 207 |

(*b*) $[1\text{-Hmim}]_4\,[Mo_8O_{26}(1\text{-min})_2]\cdot 2H_2O$ **3**

| Distortion ( $\times 10^4$) | Mo(1) | Mo(2) | Mo(3) | Mo(4) |
|---|---|---|---|---|
| $\Delta l$ | 143 | 171 | 134 | 162 |
| $\Delta e$ | 36 | 63 | 17 | 30 |
| $\Delta\alpha$ | 121 | 264 | 150 | 199 |

**Table 7** Bond lengths (*d*) and bond strengths (*s* and *s'*) of Mo–O and Mo–N bonds and c.u. values for oxygen atoms in the $MoNO_5$ octahedra of the octamolybdate compounds **2** and **3**

| | *d*/Å | *s* | *s'* | c.u. |
|---|---|---|---|---|
| (*a*) $[NH_2Me_2]_4[Mo_8O_{26}(Him)]\cdot 3H_2O$ **2** | | | | |
| Mo(4)–O(6) | 2.144 | 0.46 | 0.57 | −1.43 |
| Mo(4)–O(8) | 2.233 | 0.36 | 0.46 | −1.54 |
| Mo(4)–O(9) | 1.896 | 0.96 | 1.04 | −0.96 |
| Mo(4)–O(13) | 1.708 | 1.79 | 1.64 | −0.36 |
| Mo(4)–O(12) | 1.687 | 1.93 | 1.73 | −0.27 |
| Mo(4)–N(1A) | 2.197 | 0.39 | 0.50 | |
| $\Sigma s$ | | 5.88 | 5.94 | |
| Mo(5)–O(25) | 1.701 | 1.83 | 1.67 | −0.33 |
| Mo(5)–O(15A) | 2.081 | 0.55 | 0.67 | −1.33 |
| Mo(5)–O(26) | 1.726 | 1.68 | 1.76 | −0.24 |
| Mo(5)–O(14A) | 2.265 | 0.33 | 0.43 | −1.57 |
| Mo(5)–O(23) | 1.882 | 1.00 | 1.08 | −0.92 |
| Mo(5)–N(3) | 2.219 | 0.37 | 0.48 | |
| $\Sigma s$ | | 5.76 | 6.09 | |
| (*b*) $[1\text{-Hmim}]_4[Mo_8O_{26}(1\text{-mim})_2]\cdot 2H_2O$ **3** | | | | |
| Mo(1)–O(1) | 2.294 | 0.30 | 0.40 | −1.60 |
| Mo(1)–O(3) | 1.711 | 1.77 | 1.62 | −0.37 |
| Mo(1)–O(2) | 1.896 | 0.96 | 1.04 | −0.96 |
| Mo(1)–O(19) | 1.682 | 1.96 | 1.75 | −0.25 |
| Mo(1)–O(4A) | 2.072 | 0.56 | 0.68 | −1.32 |
| Mo(1)–N(5) | 2.227 | 0.36 | 0.47 | −1.53 |
| $\Sigma s$ | | 5.91 | 5.97 | |

**Table 8** Interatomic contacts (Å) involving hydrogen bonds for $[NH_2Me_2]_4[Mo_8O_{26}(Him)_2]\cdot 3H_2O$ **2**

| | |
|---|---|
| $N(6)\cdots O(3^{I})$ | 2.855(6) |
| $N(6)\cdots O(9^{II})$ | 2.886(6) |
| $N(5)\cdots O(25^{I})$ | 2.923(7) |
| $N(5)\cdots O(20^{III})$ | 3.224(6) |
| $N(6)\cdots (22^{IV})$ | 3.040(6) |
| $N(7)\cdots O(20^{V})$ | 3.229(7) |
| $N(7)\cdots O(16^{VI})$ | 2.943(7) |
| $N(8)\cdots O(17^{IV})$ | 2.868(6) |
| $C(12)\cdots O(2^{I})$ | 3.272(8) |
| $C(7)\cdots O(25^{I})$ | 3.192(7) |

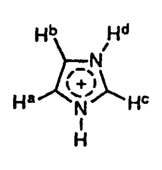
* Atoms related by the symmetry operations: I $x - \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; II $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; III $-x - \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; IV $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; V $-x, -y, -z + 1$; VI $x, y, z + 1$.

The values found for all the hydrogen bonds are similar to those described in the literature for other organic isopolymolybdates.[3,4,7,18] However, while the angles C(1)–N(1)–C(3) and N(1)–C(1)–N(2) of the co-ordinated imidazole in the first asymmetric unit of $[NH_2Me_2]_4[Mo_8O_{26}(Him)_2]$ **2** [106.6(4)° and 110.8(5)°, respectively] are the same as in the pyrazole octamolybdate,[7] those in the second asymmetric unit of the same compound [C(4)–N(3)–C(6) and N(3)–C(4)–N(4)] are 105.4(5) and 111.3(5)°, respectively. These values together with the other imidazole angles indicate that in second unit the imidazole ring is less regular than in first. For compound **3**, the angles C(35)–N(5)–C(33) and N(5)–C(35)–C(34) are 106.5(7) and 107.7(9)°, respectively, and therefore are more regular than in **2**. In both octamolybdates, all the imidazole rings are essentially planar, with negligible deviation from the best least-squares plane.

The yellow form of compound **3** has the same molecular structure as the white but much thermal motion. The colour may be due to the presence of defects in the crystal.

The infrared spectra of compounds **2** and **3** show a band at 3440 cm$^{-1}$ corresponding to the stretching vibrations of the OH groups of the water molecules involved in hydrogen bonding.[19] The deformation vibrations of the water molecules[19] are observed at 1626 cm$^{-1}$. For compound **2** there is a complex series of absorptions between 2800 and 2000 cm$^{-1}$ which are attributed to the N–H stretching vibrations of the ammonium groups[20] $[NH_2Me_2]^+$. The infrared spectra of the white and yellow forms of **3** are similar, although the yellow form shows broader bands. It is important to emphasize that all the compounds studied show absorptions at frequencies corresponding to the imidazole ring stretching vibrations (1540–1390 cm$^{-1}$), which are different to those of free imidazole indicating the existence of a donor–acceptor bond[21] between imidazole and molybdenum. This has been confirmed by the X-ray structure determination of compounds **2** and **3** (*vide supra*). Out-of-plane hydrogen bending together with the molybdenum–oxygen stretching and bending vibrations of the isopolymolybdate anion occur between 940 and 830 cm$^{-1}$.[4,7,18]

The $^1H$ NMR spectrum of compound **1** shows two singlets at δ 7.42 and 8.58 which are assigned to H$^a$ and H$^b$ (7.42) and H$^c$ (8.58) in agreement with the proton integration curves. These



resonances correspond to the imidazolium cation.[22] Thus, the peak at δ 5.00 is attributed to H$^d$. The $^{13}C$ NMR spectrum shows resonances at δ 120.18 (C$^b$) and 134.84 (C$^c$), characteristic of the imidazolium cation.[22,23] The $^1H$ spectrum of **3** shows singlets at δ 6.87 (H$^b$), 6.99 (H$^a$) and 7.99 (H$^c$), typical of the 1-methylimidazolium cation and the methyl resonance is observed at δ 3.34.[21] The $^{13}C$ NMR spectrum displays resonances at δ 122.09 (C$^a$), 123.20 (C$^b$) and 136.67 (C$^c$) and the methyl group is observed at δ 34.6. Finally, the $^1H$ spectrum of **4** shows singlet resonances at δ 6.68 (H$^a$ and H$^b$), 4.38 (H$^d$) and 2.04 (Me). The $^{13}C$ NMR spectrum shows singlets at δ 119.46 (s, C$^a$ and C$^b$), 143.91 (s C$^c$) and 11.92 (Me).

The thermogravimetric curve for **1** comprises two steps. In the first there is a loss of weight between 240 and 270 °C, corresponding to two imidazole molecules (calc., 8.53; found, 8.40%). The final product is obtained at 400 °C and is identified as $MoO_3$ (calc., 72.15; found, 72.41%). The thermogravimetric and differential scanning calorimetric curves show four stages in the thermal decomposition of **2**. At 135 °C the compound loses the three water molecules (theoretical loss, 3.46; experimental loss, 3.68%) with an endothermic effect. The first decomposition step is followed by an endothermic process between 200 and 260 °C which corresponds to the loss of two $NHMe_2$ molecules (calc., 5.79; found, 5.61) overlapped with the following exothermic stage (260–350 °C), which corresponds to the loss of imidazole. At 540 °C a residual constant weight equal to that expected for $MoO_3$ is obtained (calc., 73.90; found, 73.40), which was confirmed by X-ray powder diffraction. The thermogravimetric and calorimetric curves of **3** show that decomposition occurs in four steps. The first and second steps are endothermic and correspond to loss of water and imidazole molecules while the last two are exothermic. At 400 °C a residual constant weight is obtained, equal to that expected for $MoO_3$ (calc., 67.09; found, 66.95%), also confirmed by X-ray powder diffraction. The final residue $MoO_3$ has been observed for other isopolymolybdates of organic bases.[7,18,24,25]

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