Synthesis and Characterization of Octamolybdates containing Co-ordinatively Bound Salicylideneiminato and Methioninato (MetO) Ligands. Crystal Structures of $[NH_3Pr]_2[Mo_8O_{22}(OH)_4(OC_6H_4CH{=}NPr\text{-}2)_2]\cdot 6MeOH$ and $[Hmorph]_4[Mo_8O_{24}(OH)_2(MetO)_2]\cdot 4H_2O$ (morph = morpholine)†

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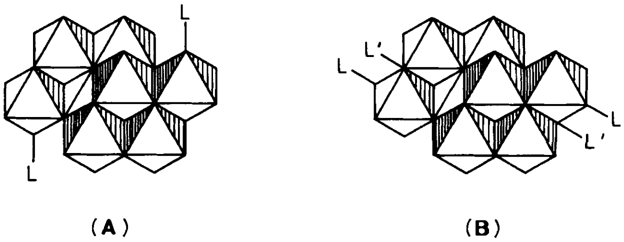
The compound $[MoO_2(sal)_2]$ (Hsal = salicylaldehyde) reacts with n-propylamine in methanol to give $[NH_3Pr]_2[Mo_8O_{22}(OH)_4(OC_6H_4CH{=}NPr\text{-}2)_2]\cdot 6MeOH$ (**1**). The same complex was obtained by the reaction of ammonium paramolybdate with *N*-propylsalicylideneimine. The structure determined by *X*-ray analysis showed that the octamolybdate anion consists of eight condensed octahedra with 16 terminal positions, two of which are occupied by the salicylideneiminato ligands. The reaction of MoO_2Cl_2 with methionine yields the neutral complex $[Mo_8O_{20}(OH)_4(MetO)_4]\cdot$solvent (**2**) (solvent = H_2O or MeOH, MetO = methioninate). If the methanolic solution of (**2**) is neutralized with morpholine (morph) the anionic complex $[Hmorph]_4[Mo_8O_{24}(OH)_2(MetO)_2]\cdot 4H_2O$ (**3**) is obtained. It has been shown by *X*-ray analysis that the structure of (**3**) is analogous to that of (**1**) with two MetO ligands linked to two terminal sites of the Mo_8O_{26} core.

Isopolymolybdates containing organic ligands are becoming interesting as models for a better understanding of the interactions between organic substrates and catalytic metal oxide surfaces,[1–4] and also owing to their photochemical properties in the photo-oxidation processes of organic compounds.[5–8] In the last ten years several octamolybdates containing oxygen- and nitrogen-donating ligands have been prepared and structurally characterized. Most of them have the general formula $[Mo_8O_{26}L_2]^{2n-4}$ (where *n* is the formal charge of L) where only two sites of the Mo_8O_{26} core are occupied by the ligand L [Scheme 1, (**A**)]. The structures of $[NH_3Pr^i]_6[Mo_8O_{26}(OH)_2]\cdot 2H_2O$[9] and $[NH_4]_6[Mo_8O_{26}(O_2CH)_2]\cdot 2H_2O$[10] with oxygen-donating ligands and $[Hpy]_4[Mo_8O_{26}(py)_2]\cdot 2Me_2SO$[11] (py = pyridine) and $K_6[Mo_8O_{26}(NCS)_2]\cdot 6H_2O$[12] with nitrogen-donating ligands are known. The only known exception is the structure of $Na_4[Mo_8O_{24}(OMe)_4]\cdot 8MeOH$ with four co-ordinated methoxo-groups [Scheme 1, (**B**)].[13] Two methoxo-groups are terminal (L) and two bridging (L′), the terminal and bridging groups being *cis* to each other. The terminal methoxo-groups are in stereochemically different positions to those of the ligands L in (**A**). Among different possibilities, these isopolymolybdate anions adopt the γ-$[Mo_8O_{26}]^{4-}$ type structure (proposed as an intermediate in the α- $\rightleftharpoons$ β-$[Mo_8O_{26}]^{4-}$ conversion) but with two additional terminal positions satisfying the six-co-ordination of all molybdenum atoms.[14] However, such a structure was also described as type II with eight condensed octahedra and 16 terminal positions.[15]

The present paper deals with the syntheses of three other examples of substituted octamolybdates: $[NH_3Pr]_2[H_4Mo_8O_{26}(OC_6H_4CH{=}NPr\text{-}2)_2]\cdot 6MeOH$ ($OC_6H_4CH{=}NPr\text{-}2$ = *N*-propylsalicylideneiminate) (**1**), $H_4[Mo_8O_{24}(MetO)_4]\cdot 4H_2O$ (MetO = methioninate) (**2**), and $[Hmorph]_4[H_2Mo_8O_{26}(MetO)_2]\cdot 4H_2O$ (morph = morpholine) (**3**). In an attempt to prepare better crystals of (**2**) by substituting methanol for water as solvent the analogous solvate $H_4[Mo_8O_{24}(MetO)_4]\cdot 8MeOH$ (**2a**) was obtained. The *X*-ray structure analysis of (**1**) and (**3**) shows that in both cases salicylideneiminato- and methioninato-oxygens are the stronger donors so that Mo–O but not Mo–N or Mo–S bonds are formed. Up to now we have not been able to prepare crystals of (**2**) and (**2a**) suitable for structure analysis. The structures of (**1**) and (**3**) are of type (**A**), those of (**2**) and (**2a**) presumably of type (**B**) (Scheme 1).



(**A**) (**B**)

Scheme 1.

The hydrogen-atom positions in all such anions could not be deduced exactly, but for charge neutrality the protons must be attached to the Mo_8O_{26} groups. Since all terminal Mo–O bond lengths are about 1.70 Å. corresponding to Mo=O double bonds, it seems most probable that once the positions L (and L′) have been occupied by the ligands OR the protons are bonded to the doubly bridging atoms O(8), O(9) [if not occupied by L′], and O(10). Such Mo–OH bonding with corresponding lengthening of the molybdenum–oxygen bond was found, for example, in the structures of $[NH_3Pr^i]_6[Mo_8O_{26}(OH)_2]\cdot 2H_2O$[9] and $[NBu^n{}_4]_3[Mo_4O_{12}(OH)(O_2CH_2)]$.[16] Consequently, the compounds described here are best formulated as: $[NH_3Pr]_2[Mo_8O_{22}(OH)_4(OC_6H_4CH{=}NPr\text{-}2)_2]\cdot 6MeOH$ (**1**), $[Mo_8O_{20}(OH)_4(MetO)_4]\cdot 4H_2O$ (**2**), $[Hmorph]_4[Mo_8O_{24}(OH)_2(MetO)_2]\cdot 4H_2O$ (**3**) and the methanol solvate (**2a**) analogously to (**2**).

Experimental

Materials.—The compounds MoO_2Cl_2 and $[MoO_2(sal)_2]$ (Hsal = salicylaldehyde) were prepared by methods described

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

in the literature.[17,18] All other reagents commercially available were of reagent grade.

Apparatus.—Infrared spectra were recorded in the range of 4 000—200 cm^{-1} on a Perkin-Elmer 580B spectrophotometer using KBr pellets. Powder diffraction diagrams were obtained using a General Electric XRD-5 diffractometer.

Preparation of the Compounds.—$[NH_3Pr]_2[Mo_8O_{22}(OH)_4(OC_6H_4CH{=}NPr\text{-}2)_2]\cdot6MeOH$ (**1**). To a methanolic suspension (50 cm^3) of $[MoO_2(sal)_2]$ (1.25 g, 3.38 mmol) was added n-propylamine (0.82 cm^3, 10 mmol) and the mixture heated under reflux for 30 min. After standing for 10 d at room temperature the pale yellow crystalline product (0.43 g, 55.8%) was filtered off and washed with methanol (Found: C, 21.25; H, 3.95; Mo, 42.20; N, 3.00. $C_{32}H_{72}Mo_8N_4O_{34}$ requires C, 21.05; H, 4.00; Mo, 42.05; N, 3.05%). I.r. spectrum: 3 520m br, 3 180m, 3 058w, 2 978m, 2 940vw, 2 882vw, 1 662vs, 1 608vs, 1 550m, 1 505w, 1 478vs, 1 458vw, 1 396w, 1 365vw, 1 340w, *1 285vs*, *1 238m*, 1 215m, 1 165s, 1 152s, 1 120vw, 1 063vw, 1 045w, 1 020vw, 945vs, 908vs, 885(sh), 850vs, 792(sh), 758vw, 690vs, 623m, 582m, 557m, 526vw, 490vw, 450w, 412w, 380m, and 340w cm^{-1}. Alternatively the same compound was obtained when a freshly prepared methanolic solution (15 cm^3) of *N*-propylsalicylideneimine (3.68 g, 22.5 mmol) was added to a water solution (20 cm^3) of ammonium paramolybdate, $[NH_4]_6[Mo_7O_{24}]\cdot4H_2O$, (1.58 g, 1.28 mmol), the resulting solution acidified by concentrated HCl (1.25 cm^3) and heated as mentioned above. Methanol (*ca.* 10 cm^3) was added to the resulting oily residue and after standing overnight pale yellow *crystals were* obtained. They were filtered off, washed with water–methanol (1:1) and dried *in vacuo* (1.8 g, 88.2%) (Found: C, 21.15; H, 4.15; Mo, 42.25; N, 3.20%).

$[Mo_8O_{20}(OH)_4(MetO)_4]\cdot4H_2O$ (**2**). To a water solution (30 cm^3) of MoO_2Cl_2 (1.2 g, 6 mmol) a water solution (20 cm^3) of methionine (1.8 g, 12 mmol) was added dropwise at room temperature. The white precipitate (0.56 g, 40.9%) was washed with distilled water and ethanol (Found: C, 13.30; H, 2.65; Mo, 42.00; N, 2.95; S, 7.20. $C_{20}H_{52}Mo_8N_4O_{36}S_4$ requires C, 13.20; H, 2.90; Mo, 42.15; N, 3.10; S, 7.05%). I.r. spectrum: 3 450m br, 3 145vw, 3 070vw, 2 925vw, 1 735vw, 1 612vs, 1 508s, 1 440vw, 1 430s, 1 360m, 1 338m, 1 320 (sh), 1 282vw, 1 252w, 1 196w, 1 180 (sh), 1 150m, 1 105vw, 1 073vw, 1 020 (sh), 1 003vw, 970 (sh), 950vs, 918vs, 898 (sh), 767m, 675vw, 670vw, 550vs br, 420vw, 385vw, and 355m br cm^{-1}.

$[Mo_8O_{20}(OH)_4(MetO)_4]\cdot8MeOH$ (**2a**). To a methanolic solution (25 cm^3) of MoO_2Cl_2 (1 g, 5 mmol) was added methionine (1.5 g, 10 mmol) at room temperature. The pale yellow solution was warmed at 60 °C for 2 h. Slow cooling gave a white precipitate (0.5 g, 39.7%) (Found: C, 16.85; H, 2.95; Mo, 38.10; N, 2.80; S, 7.00. $C_{28}H_{76}Mo_8N_4O_{40}S_4$ requires C, 16.80; H, 3.80; Mo, 38.30; N, 2.80; S, 6.40%). I.r. spectrum: 3 430m br, 3 115vw, 3 040vw, 2 920w, 2 825vw, 2 610vw, 1 735vw, 1 620vs, 1 598vs, 1 505s, 1 432s, 1 425s, 1 342m, 1 318vw, 1 282vw, 1 245w, 1 190m, 1 150w br, 1 068w, 995s, 942vs, 905vs, 880m, 755vs, 670 (sh), 622w, 570m, 515m, 495w, 380w, and 320m cm^{-1}.

$[HMorph]_4[Mo_8O_{24}(OH)_2(MetO)_2]\cdot4H_2O$ (**3**). A solution of MoO_2Cl_2 (1 g, 5 mmol) and methionine (0.19 g, 1.27 mmol) in methanol (40 cm^3) was neutralized by a methanolic solution of morpholine (10%) to the pH 6. The white precipitate (1.0 g, 83.3%) was filtered off and washed with methanol. Crystals suitable for *X*-ray work were obtained by recrystallization from water (Found: C, 16.30; H, 3.45; Mo, 40.45; N, 4.50; S, 3.10. $C_{26}H_{70}Mo_8N_6O_{38}S_2$ requires C, 16.40; H, 3.70; Mo, 40.25; N, 4.40; S, 3.35%). I.r. spectrum: 3 450m br, 2 955w, 2 920w, 2 730w, 2 625vw, 2 100m, 1 655m, 1 620s br, 1 584vs, 1 518m, 1 448w, 1 417vs, 1 345vs, 1 315 (sh), 1 280s, 1 240vw, 1 225m, 1 165m, 1 105m, 1 082m, 1 045m, 1 012 (sh), 1 002w, 932s, 875m, 825 (sh), 782m, 758w, 720vw, 710w, 688m, 678vw, 652w, 555s, 502m, 440s, 380s, and 330s cm^{-1}.

X-Ray Structure Determination.—Data collection was carried out on a Philips PW 1100 diffractometer with a graphite monochromator and Cu-K_α radiation for compound (**1**) and Mo-K_α radiation for (**3**). Crystal fragments of maximum dimensions 0.2 mm were selected and used for intensity measurements. The lattice parameters were determined from 16 reflections in the range $10 < \theta < 12°$ for (**1**) and from 19 reflections in the range $5 < \theta < 12°$ for (**3**).

Crystal data. $C_{32}H_{72}Mo_8N_4O_{34}$, (**1**), M = 1 824.48, triclinic, space group $P\bar{1}$, a = 12.497(2), b = 12.269(3), c = 10.483(3) Å, α = 85.83(1), β = 99.17(1), γ = 96.25(2)°, U = 1 574.8 Å^3, D_m = 1.94 g cm^{-3} (pycnometrically), Z = 1, D_c = 1.924 g cm^{-3}, $F(000)$ = 900, λ(Cu-K_α) = 1.541 78 Å, μ(Cu-K_α) = 140.1 cm^{-1}.

$C_{26}H_{70}Mo_8N_6O_{38}S_2$, (**3**). M = 1 906.52, triclinic, space group $P\bar{1}$, a = 12.144(2), b = 12.062(3), c = 10.217(3) Å, α = 90.48(3), β = 94.91(4), γ = 109.90(2)°, U = 1 400.9 Å^3, D_m = 2.13 g cm^{-3} (pycnometrically), Z = 1, D_c = 2.260 g cm^{-3}, $F(000)$ = 940, λ(Mo-K_α) = 0.710 69 Å, μ(Mo-K_α) = 18.8 cm^{-1}.

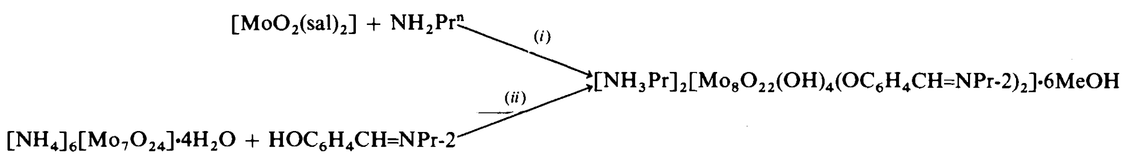
Intensities were measured using the ω—2θ scan method with a scan speed of 0.04° s^{-1} and scan width 1.60°, between 3 and 70°, yielding 5 099 independent reflections for compound (**1**), 4 889 of which were above background $[I > 3\sigma(I)]$, and between 2 and 28° θ yielding 5 484 independent reflections for (**3**), 4 914 of which were above background $[I > 3\sigma(I)]$. Because of crystal decomposition the intensity data for (**3**) were collected from two different crystals mounted in a capillary tube. Three standard reflections were measured every 2 h and their changes used to bring the reflections to a common scale. The data were rescaled, and corrected for Lorentz and polarization factors but not for absorption. Solution of the structures was achieved by the heavy-atom method through Patterson and Fourier maps. Refinement of the scale factors, positional and anisotropic thermal parameters for non-hydrogen atoms converged to give a final conventional agreement index R of 0.052 (R' = 0.059) for (**1**) and 0.072 (R' = 0.071) for (**3**). The structures were refined by a block-matrix least-squares procedure, minimizing the function $\Sigma w(|F_o| - |F_c|)^2$ with $w = 1/[\sigma^2(F_o) + 0.005\ 514|F_o|^2]$ for (**1**) and $w = 1/[\sigma^2(F_o) + 0.010\ 542|F_o|^2]$ for (**3**). Hydrogen-atom positions were not discernible from electron-density difference maps; those belonging to the cations and organic ligands were generated at geometrically fixed positions.

The atomic scattering factors and anomalous dispersion corrections for all non-hydrogen atoms were taken from the literature.[19,20] Calculations were made on the UNIVAC 1110 computer of the University Computing Centre in Zagreb using the SHELX program system.[21] Final atomic co-ordinates for the compounds are listed in Tables 1 and 2.

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

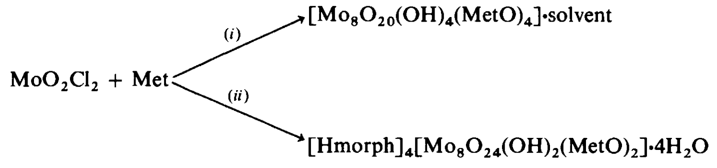
Results and Discussion

All our attempts to prepare $[MoO_2(OC_6H_4CH{=}NPr\text{-}2)_2]$ as described in the literature by treating $[MoO_2(sal)_2]$ with n-propylamine or ammonium paramolybdate with *N*-propylsalicylideneimine were unsuccessful.[18] Instead we always obtained a pale yellow crystalline product (**1**) soluble in hot methanol as shown in Scheme 2. The reaction of MoO_2Cl_2 with methionine in water yielded a white crystalline precipitate (**2**) insoluble in common organic solvents (Scheme 3).



(1)

Scheme 2. (*i*) Solvent = MeOH; (*ii*) solvent = water–methanol



(2)

(3)

Scheme 3. (*i*) Solvent = water or MeOH; (*ii*) solvent = MeOH, morpholine was added to pH 6

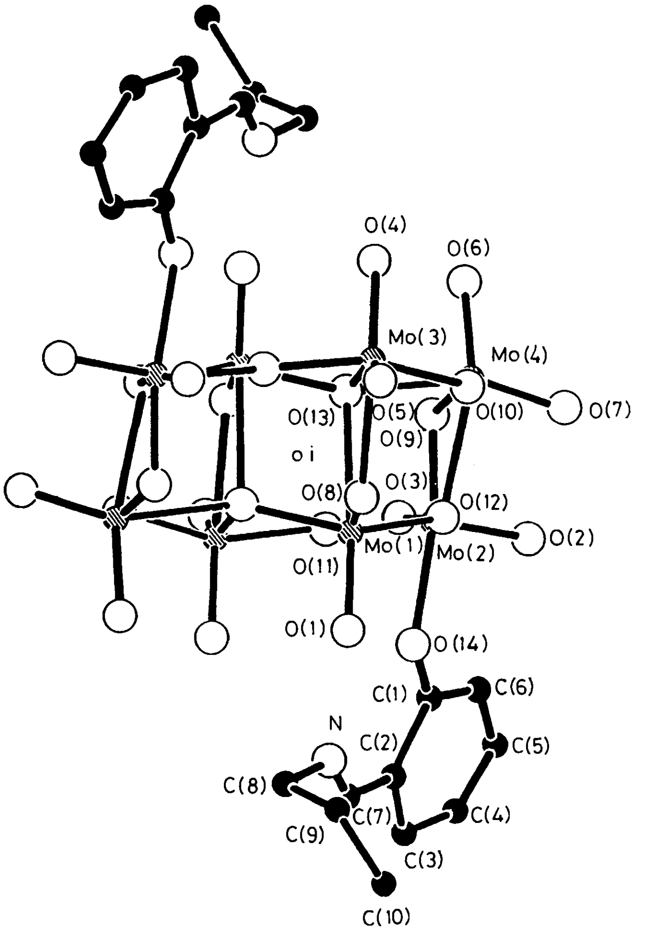


Figure 1. Structure of the anion of compound (1), [Mo$_8$O$_{22}$(OH)$_4$-(OC$_6$H$_4$CH=NPr-2)$_2$]$^{2-}$, viewed along the *c* axis, with the atom labelling scheme

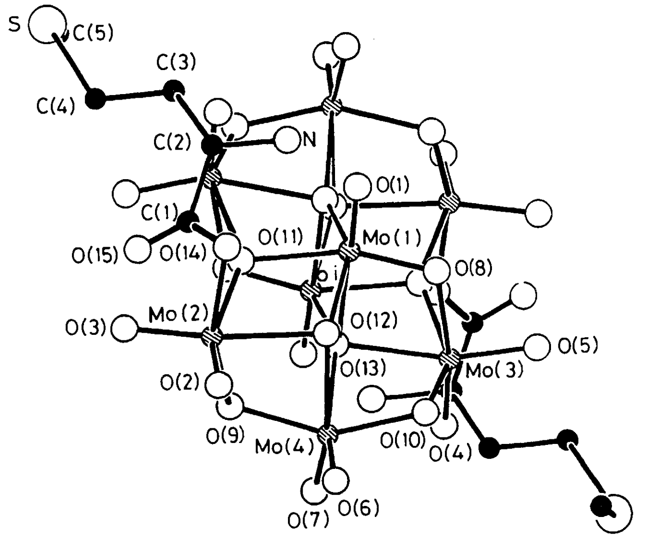


Figure 2. Structure of the anion of compound (3), [Mo$_8$O$_{24}$(OH)$_2$-(MetO)$_2$]$^{4-}$, viewed along the *c* axis, with the atom labelling scheme

The product was a tetrahydrate, but if water was replaced by methanol as a solvent the corresponding solvate (**2a**) was formed. Neutralization of the methanolic solution with morpholine led to the formation of a white crystalline product (**3**).

The i.r. spectra of all the complexes, hydrates and alcoholates, exhibit absorbances in the 700—950 cm^{-1} region characteristic of the presence of both terminal and bridging oxo groups, as well as a band at 1 662 cm^{-1} for (**1**) which could be assigned to the non-co-ordinated C=N group of the salicylideneiminate ligand, and at about 1 400 and 1 600 and 3 100 cm^{-1} for (**2**) and (**2a**) corresponding to the COO and N–H stretch of the co-ordinated methionine. The elemental analysis data suggested a stoicheiometry of the octamolybdates with two co-ordinated salicylideneiminato [in (**1**)] and either two [in (**3**)] or four [in (**2**) and (**2a**)] co-ordinated methioninato ligands. The i.r. spectrum as well as the *X*-ray powder diffraction diagram of (**2**) was identical to those of the molybdenum complex described earlier as Mo$_2$O$_7$H$_3$(MetO),[22] confirming that the neutral complexes (**2**) and (**2a**) contain four methionines attached to the octamolybdate units. They do not crystallize well as does the anionic complex (**3**).

The structures of compounds (**1**) and (**3**) are shown in Figures 1 and 2 respectively. Selected bond lengths and angles are listed in Table 3. In both structures, with salicylideneimine and methionine, the polymolybdate anions consist of eight centrosymmetrically condensed edge-sharing octahedra. They belong to the proposed γ-[Mo$_8$O$_{26}$]$^{4-}$ type but with two additional terminal positions, thus satisfying the octahedral co-ordination of all eight molybdenum atoms.[14] Ideally such an arrangement might be considered as comprising cubic close-

Table 1. Fractional atomic co-ordinates (× 10^4, × 10^5 for Mo) for $[NH_3Pr]_2[Mo_8O_{22}(OH)_4(OC_6H_4CH{=}NPr\text{-}2)_2]\cdot 6MeOH$ (**1**) with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
Mo(1)	60 157(4)	10 535(4)	3 522(1)
Mo(2)	56 978(4)	21 838(4)	−26 905(5)
Mo(3)	35 886(4)	7 515(4)	16 459(5)
Mo(4)	36 381(4)	21 944(4)	−10 848(5)
O(1)	7 367(5)	1 398(6)	773(7)
O(2)	5 685(7)	3 573(6)	−2 935(8)
O(3)	5 708(6)	1 692(6)	−4 167(7)
O(4)	2 208(6)	454(6)	1 325(8)
O(5)	3 860(7)	960(6)	3 246(8)
O(6)	2 296(6)	1 766(7)	−1 511(8)
O(7)	3 747(7)	3 590(6)	−1 331(8)
O(8)	5 498(5)	1 113(5)	1 795(7)
O(9)	4 159(5)	1 788(5)	−2 603(7)
O(10)	3 711(5)	2 188(5)	807(7)
O(11)	6 021(5)	726(5)	−1 628(6)
O(12)	5 555(5)	2 334(5)	−580(6)
O(13)	4 076(5)	538(5)	−289(6)
O(14)	7 415(4)	2 380(4)	−2 167(5)
C(1)	8 124(6)	2 759(6)	−2 927(8)
C(2)	9 248(6)	2 573(7)	−2 603(9)
C(3)	9 982(7)	2 956(7)	−3 421(10)
C(4)	9 693(9)	3 555(9)	−4 565(10)
C(5)	8 627(9)	3 787(9)	−4 863(11)
C(6)	7 851(7)	3 386(8)	−4 087(10)
C(7)	9 674(6)	1 989(7)	−1 415(10)
C(8)	9 686(7)	1 113(8)	755(10)
C(9)	9 876(9)	1 888(10)	1 793(11)
C(10)	10 770(10)	2 822(11)	1 601(16)
N(1)	9 162(6)	1 621(5)	−481(8)
O(15)	3 686(5)	−43(5)	5 800(6)
O(16)	4 846(6)	6 132(5)	8 185(7)
O(17)	2 642(14)	3 860(18)	5 775(27)
C(14)	4 389(14)	6 352(13)	6 839(16)
C(15)	2 641(8)	−742(8)	5 750(11)
C(16)	3 181(17)	3 752(20)	4 757(32)
C(11)	1 549(12)	5 144(14)	−1 415(13)
C(12)	1 779(9)	5 566(10)	−73(12)
C(13)	2 652(8)	5 040(8)	803(10)
N(2)	3 772(6)	5 351(5)	421(7)

Table 2. Fractional atomic co-ordinates (× 10^4, × 10^5 for Mo) for $[Hmorph]_4[Mo_8O_{24}(OH)_2(MetO)_2]\cdot 4H_2O$ (**3**) with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Mo(1)	47 332(4)	2 455(5)	65 745(5)
Mo(2)	58 897(5)	−17 035(5)	78 763(6)
Mo(3)	67 221(5)	23 291(5)	48 129(6)
Mo(4)	77 360(5)	6 250(5)	66 233(6)
O(1)	3 667(4)	127(5)	7 616(5)
O(2)	6 705(5)	−1 378(5)	9 355(5)
O(3)	5 580(5)	−3 177(5)	7 614(6)
O(4)	7 807(5)	2 488(5)	3 801(6)
O(5)	6 642(5)	3 709(5)	5 020(6)
O(6)	8 690(5)	631(5)	5 482(6)
O(7)	8 570(5)	932(5)	8 089(6)
O(8)	5 203(4)	1 751(4)	6 238(5)
O(9)	7 086(4)	−1 122(4)	6 740(5)
O(10)	7 565(4)	2 145(4)	6 415(5)
O(11)	4 629(4)	−1 552(4)	6 416(5)
O(12)	6 048(4)	198(4)	7 688(4)
O(13)	6 196(4)	379(4)	5 089(5)
O(14)	4 403(4)	−1 823(5)	8 890(5)
O(15)	4 289(5)	−3 255(5)	10 292(6)
C(1)	3 921(6)	−2 536(6)	9 767(7)
C(2)	2 740(6)	−2 457(6)	10 063(7)
N	2 777(5)	−1 224(5)	9 844(7)
C(3)	1 729(6)	−3 323(7)	9 158(8)
C(4)	1 701(8)	−4 582(7)	9 136(10)
S	393(2)	−5 638(2)	8 323(3)
C(5)	614(11)	−5 458(10)	6 618(12)
N(1)	−609(4)	982(5)	1 196(6)
C(6)	−477(7)	928(5)	2 615(9)
C(7)	249(7)	2 084(9)	3 270(8)
O(16)	1 422(6)	2 516(9)	2 725(7)
C(8)	1 266(7)	2 541(7)	1 239(8)
C(9)	513(7)	1 364(7)	692(8)
N(2)	7 607(5)	6 967(6)	4 484(7)
C(10)	6 366(8)	6 459(6)	4 444(10)
C(11)	5 846(8)	6 105(9)	3 065(11)
O(17)	6 194(7)	7 153(9)	2 241(8)
C(12)	7 451(9)	7 714(7)	2 321(11)
C(13)	7 939(9)	7 998(9)	3 716(11)
O(18)	6 277(5)	5 769(9)	−93(7)
O(19)	2 287(14)	4 952(9)	2 800(11)

packed oxygen atoms with molybdenum atoms occupying octahedral sites. Alternatively, the octamolybdate octahedra with 16 terminal positions belong to type II[15] first observed in the crystal structure of $[NH_3Pr^i]_6[Mo_8O_{26}(OH)_2]\cdot 2H_2O$.[9] Of the 16 terminal positions, 14 are occupied by oxo-oxygen and two by salicylideneiminato- or methioninato-oxygen atoms. In compound (**1**) the Mo=O bond lengths range from 1.690(8) to 1.709(7) Å, those in (**3**) from 1.698(5) to 1.715(6) Å. These values agree very well with those found in most structures with molybdenum–oxygen double bonds.[23,24] Of the remaining 12 oxygen atoms, six [O(8), O(9), O(10), and their centrosymmetric pairs] bridge two Mo atoms, four [O(11), O(12), and their centrosymmetric pairs] bridge three Mo atoms, while two [O(13) and centrosymmetric O(13′)] bridge four Mo atoms. As a consequence of such bridging systems within the octamolybdates, the Mo–O distances are significantly different: in the single bridges Mo–O–Mo they vary from 1.746(8) to 2.361(6) Å in (**1**) and from 1.755(5) to 2.368(5) Å in (**3**), in the triply-bridging Mo_3O core from 1.884(6) to 2.360(6) Å in (**1**) and from 1.879(5) to 2.308(5) Å in (**3**), and finally in the Mo_4O core from 1.949(6) to 2.437(6) Å in (**1**) and from 1.950(5) to 2.399(5) Å in (**3**). The most significant lengthenings of the Mo–O bonds occur in the case of Mo(1)–O(13) [2.437(6) in (**1**) and 2.399(5) Å in (**3**)], Mo(2)–O(12) [2.270(7) and 2.247(5) Å], Mo(3)–O(8) [2.361(6) and 2.368(5) Å] and Mo(3)–O(13) [2.249(7) and 2.245(5) Å], Mo(4)–O(12) [2.360(6) and 2.308(5) Å] and Mo(4)–O(13) [2.231(6) and 2.271(5) Å] and are due to the *trans* influence of the terminal oxo-oxygen atoms. The bond lengths Mo–OR between molybdenum and oxygen atoms from salicylideneiminato and methioninato ligands are equal [2.120(5) and 2.121(6) Å] and correspond to a Mo–O single bond.[23] Thus the surroundings of the molybdenum atoms are different: Mo(1), one terminal oxo, O_t; one μ-O, two μ_3-O, and two μ_4-O; Mo(2), three O_t (one from the ligand), one μ-O, and two μ_3-O; Mo(3) and Mo(4), each two O_t, two μ-O, one μ_3-O, and one μ_4-O atom. The bond lengths and angles in the salicylideneiminato and methioninato ligands have the expected values.

The relative values of the Mo–OR bond strengths $s_{Mo-O} = (d_{Mo-O}/1.882)^{-6.0}$, where *d* is the bond length in Å,[25] are the

Table 3. Selected bond lengths (Å) and angles (°) in compounds (**1**) and (**3**) with e.s.d.s in parentheses

	(**1**)	(**3**)		(**1**)	(**3**)
Mo(1)–O(1)	1.691(6)	1.715(6)	Mo(3)–O(4)	1.709(7)	1.704(6)
Mo(1)–O(8)	1.746(8)	1.755(5)	Mo(3)–O(5)	1.690(8)	1.713(6)
Mo(1)–O(11)	2.144(7)	2.132(5)	Mo(3)–O(8)	2.361(6)	2.368(5)
Mo(1)–O(12)	1.884(6)	1.897(5)	Mo(3)–O(10)	1.914(6)	1.910(5)
Mo(1)–O(13)	2.437(6)	2.399(5)	Mo(3)–O(13)	2.249(7)	2.245(5)
Mo(1)–O(13′)	1.949(6)	1.950(5)	Mo(3)–O(11′)	1.930(6)	1.931(4)
Mo(2)–O(2)	1.706(7)	1.699(5)	Mo(4)–O(6)	1.701(7)	1.712(6)
Mo(2)–O(3)	1.704(8)	1.701(6)	Mo(4)–O(7)	1.707(7)	1.698(5)
Mo(2)–O(9)	1.946(6)	1.887(5)	Mo(4)–O(9)	1.929(8)	1.992(5)
Mo(2)–O(11)	2.080(6)	2.099(5)	Mo(4)–O(10)	1.970(7)	1.926(5)
Mo(2)–O(12)	2.270(7)	2.247(5)	Mo(4)–O(12)	2.360(6)	2.308(5)
Mo(2)–O(14)	2.120(5)	2.121(6)	Mo(4)–O(13)	2.231(6)	2.271(5)

Salicylideneiminate ligand		Salicylideneiminate ligand		Methioninate ligand		Methioninate ligand	
C(1)–O(14)	1.310(10)	N(1)–C(8)	1.482(12)	C(1)–O(14)	1.283(9)	C(2)–C(3)	1.540(9)
C(2)–O(7)	1.446(13)	C(8)–C(9)	1.471(16)	C(1)–O(15)	1.213(10)	C(3)–C(4)	1.508(13)
C(7)–N(1)	1.282(13)	C(9)–C(10)	1.537(17)	C(1)–C(2)	1.525(11)	C(4)–S	1.793(8)
				C(2)–N	1.491(10)	S–C(5)	1.789(12)

	(**1**)	(**3**)		(**1**)	(**3**)
O(1)–Mo(1)–O(8)	103.5(3)	102.3(3)	O(2)–Mo(2)–O(3)	106.4(4)	104.7(3)
O(1)–Mo(1)–O(11)	98.2(3)	100.2(2)	O(2)–Mo(2)–O(9)	99.1(3)	100.2(2)
O(1)–Mo(1)–O(12)	102.3(3)	104.5(2)	O(2)–Mo(2)–O(11)	155.4(3)	154.8(2)
O(1)–Mo(1)–O(13)	178.9(3)	178.8(2)	O(2)–Mo(2)–O(12)	89.2(3)	90.5(2)
O(1)–Mo(1)–O(13′)	102.3(2)	102.2(2)	O(2)–Mo(2)–O(14)	90.2(3)	87.5(2)
O(8)–Mo(1)–O(11)	158.0(3)	157.4(2)	O(3)–Mo(2)–O(9)	97.3(3)	99.6(3)
O(8)–Mo(1)–O(12)	101.8(3)	100.1(2)	O(3)–Mo(2)–O(11)	95.8(3)	95.7(2)
O(8)–Mo(1)–O(13)	77.5(3)	78.4(2)	O(3)–Mo(2)–O(12)	163.9(3)	164.8(2)
O(8)–Mo(1)–O(13′)	98.3(3)	98.6(2)	O(3)–Mo(2)–O(14)	95.6(3)	97.1(3)
O(11)–Mo(1)–O(12)	76.1(3)	76.2(2)	O(9)–Mo(2)–O(11)	88.2(3)	90.7(2)
O(11)–Mo(1)–O(13)	80.7(2)	79.1(2)	O(9)–Mo(2)–O(12)	75.7(3)	76.4(2)
O(11)–Mo(1)–O(13′)	73.6(2)	74.4(2)	O(9)–Mo(2)–O(14)	161.4(2)	159.2(2)
O(12)–Mo(1)–O(13)	77.9(2)	76.3(2)	O(11)–Mo(2)–O(12)	69.7(2)	69.9(2)
O(12)–Mo(1)–O(13′)	142.8(3)	143.1(2)	O(11)–Mo(2)–O(14)	77.1(2)	75.3(2)
O(13)–Mo(1)–O(13′)	76.7(4)	76.7(2)	O(12)–Mo(2)–O(14)	88.3(2)	84.3(2)
O(4)–Mo(3)–O(5)	105.1(4)	105.6(3)	O(6)–Mo(4)–O(7)	106.4(4)	105.2(3)
O(4)–Mo(3)–O(8)	172.3(3)	169.7(2)	O(6)–Mo(4)–O(9)	98.3(3)	95.8(2)
O(4)–Mo(3)–O(10)	99.3(3)	98.0(3)	O(6)–Mo(4)–O(10)	99.8(3)	102.0(3)
O(4)–Mo(3)–O(11′)	97.5(3)	99.2(3)	O(6)–Mo(4)–O(12)	165.8(3)	162.1(2)
O(4)–Mo(3)–O(13)	101.4(3)	99.0(2)	O(6)–Mo(4)–O(13)	94.0(3)	93.7(2)
O(5)–Mo(3)–O(8)	82.6(3)	84.7(2)	O(7)–Mo(4)–O(9)	100.4(3)	97.8(2)
O(5)–Mo(3)–O(10)	105.0(3)	103.0(3)	O(7)–Mo(4)–O(10)	95.5(3)	97.6(3)
O(5)–Mo(3)–O(13)	153.2(3)	155.4(2)	O(7)–Mo(4)–O(12)	87.4(3)	90.5(2)
O(5)–Mo(3)–O(11′)	101.1(3)	102.7(3)	O(7)–Mo(4)–O(13)	158.7(3)	160.3(2)
O(8)–Mo(3)–O(10)	78.9(3)	78.6(2)	O(9)–Mo(4)–O(10)	151.5(3)	152.4(2)
O(8)–Mo(3)–O(13)	70.8(2)	70.7(2)	O(9)–Mo(4)–O(12)	73.9(2)	73.1(2)
O(8)–Mo(3)–O(11′)	80.2(2)	78.9(2)	O(9)–Mo(4)–O(13)	83.7(3)	85.2(2)
O(10)–Mo(3)–O(13)	73.9(3)	73.8(2)	O(10)–Mo(4)–O(12)	83.5(3)	84.1(2)
O(10)–Mo(3)–O(11′)	143.9(3)	143.8(3)	O(10)–Mo(4)–O(13)	73.3(3)	72.9(2)
O(13)–Mo(3)–O(11′)	71.6(2)	72.1(2)	O(12)–Mo(4)–O(13)	73.5(2)	71.9(2)

* Primed atoms are related by the symmetry element $1 - x, -y, -z$ for compound (**1**) and $1 - x, -y, 1 - z$ for compound (3).

same 0.49 for both structures. This is very close to 0.51, the value found for the structure of $[NH_4]_6[Mo_8O_{26}(O_2CH)_2]\cdot 2H_2O$,[10] but considerably smaller than 0.76 found for $[NH_3Pr^i]_6[Mo_8O_{26}(OH)_2]\cdot 2H_2O$[9] and 0.92 for $Na_4[Mo_8O_{24}(OMe)_4]\cdot 8MeOH$[13] [taking into account only the Mo–OMe terminal bond length], although all oxygen-bound ligands in these structures carry the same formal negative charge. Such different values of *s* most probably indicate different amounts of electrostatic charge concentrated at the ligand oxygen atoms.[11] Nevertheless, the weak Mo–OR interactions are compensated within Mo(2) octahedra in both structures by some other strong Mo–O bonds so that the sums of the bond strengths Σs_{Mo-O}, corresponding to the bond orders of molybdenum in the MoO_6 octahedra, amount to 5.80 and 6.02 (in valence units) for the structures of (**1**) and (**3**) respectively.

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References

1 E. M. McCarron III and A. W. Sleight, *Polyhedron*, 1986, **5**, 129 and refs. therein.

2 T-C. Hsieh, S. N. Shaikh, and J. Zubieta, *Inorg. Chem.*, 1987, **26**, 4079.
3 S. Liu, S. N. Shaikh, and J. Zubieta, *Inorg. Chem.*, 1987, **26**, 4303.
4 S. Liu, S. N. Shaikh, and J. Zubieta, *Inorg. Chem.*, 1988, **27**, 3064.
5 P. K. Bharadwaj, Y. Ohashi, Y. Sasada, Y. Sasaki, and T. Yamase, *Acta Crystallogr., Sect. C*, 1984, **40**, 48.
6 T. Yamase, *J. Chem. Soc., Dalton Trans.*, 1985, 2585.
7 T. Yamase, *Polyhedron*, 1986, **5**, 79.
8 M. M. Williamson, D. A. Bouchard, and C. L. Hill, *Inorg. Chem.*, 1987, **26**, 1436.
9 M. Isobe, F. Marumo, T. Yamase, and T. Ikawa, *Acta Crystallogr., Sect. B*, 1978, **34**, 2728.
10 R. D. Adams, W. G. Klemperer, and R-S. Liu, *J. Chem. Soc., Chem. Commun.*, 1979, 256.
11 E. M. McCarron III, J. F. Whitney, and D. B. Chase, *Inorg. Chem.*, 1984, **23**, 3275.
12 B. Kamenar, M. Penavić, and B. Marković, *Acta Crystallogr., Sect. C*, 1988, **44**, 1521.
13 E. M. McCarron III and R. L. Harlow I, *J. Am. Chem. Soc.*, 1983, **105**, 6179.
14 W. G. Klemperer and W. Shum, *J. Am. Chem. Soc.*, 1976, **98**, 8291.
15 A. J. Wilson, V. McKee, B. R. Penfold, and C. J. Wilkins, *Acta Crystallogr., Sect. C*, 1984, **40**, 2027.
16 V. W. Day, M. F. Fredrich, W. G. Klemperer, and R-S. Liu, *J. Am. Chem. Soc.*, 1979, **101**, 491.
17 R. L. Graham and L. G. Helper, *J. Phys. Chem.*, 1959, **63**, 723.
18 K. Yamanouchi and S. Yamada, *Inorg. Chim. Acta*, 1974, **9**, 83.
19 J. A. Ibers and W. C. Hamilton (eds.), 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.
20 T. Cromer and D. Liberman, *J. Chem. Phys.*, 1970, **53**, 1891.
21 G. M. Sheldrick, SHELX 76 Program for Crystal Structure Determination and Refinement, University of Cambridge, 1976.
22 H. Eguchi, T. Takeuchi, A. Ouchi, and A. Furnhashi, *Bull. Chem. Soc. Jpn.*, 1969, **42**, 3585.
23 F. A. Schröder, *Acta Crystallogr., Sect. B*, 1975, **31**, 2294.
24 F. A. Schröder, *Z. Naturforsch., Teil B*, 1975, **30**, 638.
25 J. C. J. Bart and V. Ragaini, *Inorg. Chim. Acta*, 1979, **36**, 261 and refs. therein.

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