Synthesis, Characterisation and Crystal Structure of Molybdenum and Molybdenum–Copper Hydroxy-rich Schiff-base Complexes†

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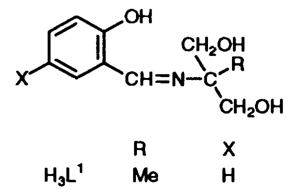
The reaction of hydroxy-rich Schiff bases [$H_3L = XC_6H_3(OH)CH{=}NC(R)(CH_2OH)_2$ where X = H, 5-Cl or 5-Br and R = Me or Et] with [$MoO_2(acac)_2$] (acac = acetylacetonate) gave mononuclear complexes [$MoO_2(HL)(MeOH)$]. The complexes were characterised by spectroscopic methods and by a single-crystal structure determination. Reaction of the mononuclear complexes with $Ph_2PCH_2PPh_2$ in methanol or acetonitrile led to five-co-ordinate polymeric compounds of the type [$MoO(L)$]$_n$ in which the fifth position of the distorted square pyramid is occupied by the oxygen atom of a CH_2O^- moiety of a neighbouring repeat unit. The complex [$MoO_2(HL^3)(MeOH)$] [H_3L^3 = 2-(5-chlorosalicylideneamino)-1,3-dihydroxy-2-methylpropane] reacted with $Cu(O_2CMe)_2$ in methanol–acetonitrile to yield the mixed-metal cluster [$Cu_2Mo_2O_4L^3_2(OMe)_2$] with a $Cu_2Mo_2O_4$ cubane-like core. Reflux of this complex with an excess of 2,2′-bipyridine in acetonitrile yielded pale blue-green crystals of the tetranuclear cluster [$CuMo_3O_8(HL^3)_2(bipy)_2$] the structure of which has been determined by X-ray crystallography. The molybdenum part may be described in terms of three oxo-bridged centres, one tetraoxomolybdate [MoO_4]$^{2-}$ and two six-co-ordinated MoO_2(Schiff base) moieties. The magnetic properties of this compound have been studied in the temperature range 5–300 K.

Molybdenum(VI) and copper(II) Schiff-base complexes represent an important and interesting class of co-ordination compounds which have played a significant role in the domain of model systems of biological interest. It is well known [1–3] that catalytic reactions of the molybdeno-oxotransferases involve oxidation states Mo^{VI}, Mo^{V} and Mo^{IV} during the process of electron transfer to or from the redox centres. Simple molybdenum(VI) compounds contain the *cis*-MoO_2^{2+} group. Bi-, tri- and tetra-dentate Schiff base–MoO_2^{2+} complexes, in which the monomeric form [MoO_2L]·A (L = dianionic Schiff base, A = monodentate ligand) is dominant, have been reported[4–7]. Also the co-ordination chemistry of polymolybdates with organic molecules is of interest in the development of models for the interaction of organic substrates with catalytic oxide surfaces.[8–10] Furthermore, the antagonistic function of the molybdenum ion with regard to copper in humans and animals[11] has raised interest in the interaction of copper ions with ligated molybdenum species. Most of the Mo–Cu mixed-metal complexes reported till now[12,13] employ mainly [MoS_4]$^{2-}$ as the source of the molybdenum component. We have extended this chemistry to the Schiff-base ligands which form complexes with oxygen rich co-ordination environments.[14] The compound reported here is the first example including a [MoO_4]$^{2-}$ group, which is the major source of molybdenum in biological systems and the product of the hydrolysis of MoO_2^{2+} species at pH 7, interacting with copper(II) ions. This may be considered as a new insight into the metabolic disturbances and diseases in humans and animals caused by a deficiency or excess of molybdenum and copper trace elements.[11] In the course of this research, the chemistry of MoO_2(Schiff base)(MeOH) compounds interacting with copper(II) ions has been studied.[14]



	R	X
H_3L^1	Me	H
H_3L^2	Et	H
H_3L^3	Me	Cl
H_3L^4	Me	Br
H_3L^5	Et	Cl
H_3L^6	Et	Br

In this report we present the chemistry of Mo^{VI} with hydroxy-rich Schiff bases, their reactivity with $Ph_2PCH_2PPh_2$ (dppm) and the chemistry of a new Mo^{VI}–Cu^{II} cluster having a Mo:Cu ratio of 3:1. The molecular and crystal structures of the mononuclear [$MoO_2(HL^3)(MeOH)$] **1b** and the mixed-metal tetranuclear [$CuMo_3O_8(HL^3)_2(bipy)_2$] **2a** (bipy = 2,2′-bipyridine) compounds are also reported.

Experimental

Materials.—The chemicals for the synthesis of the compounds were used without further purification. Acetonitrile was distilled from calcium hydride and MeOH from magnesium

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† *Supplementary data available* (No. SUP 57095, 5 pp.): magnetic susceptibility data. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, issue 1, pp. xxv–xxx.

Non-SI units employed: G = 10^{-4} T, $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}.

and were stored over 3 Å molecular sieves. Diethyl ether (anhydrous grade) and absolute ethanol were used without further purification. Salicylaldehyde, 5-chloro- and 5-bromosalicylaldehyde, 2-amino-2-methylpropane-1,3-diol, 2-amino-2-ethylpropane-1,3-diol and $[MoO_2(acac)_2]$ (acac = acetylacetonate) were obtained from Aldrich and $Cu(O_2CMe)_2{\cdot}H_2O$ from Merck. All chemicals and solvents were reagent grade. The complexes $[Cu_2Mo_2O_4L^3{}_2(OMe)_2]$ or $[Cu_2Mo_2O_4L^4{}_2(OMe)_2]$ were prepared as described previously.[14]

Physical Measurements.—Infrared spectra (200–4000 cm^{-1}) were recorded on a Perkin-Elmer 467 spectrometer with samples prepared as KBr pellets, UV/VIS spectra on a Perkin-Elmer Lambda-5 dual-beam spectrophotometer, ^1H NMR spectra on Bruker 360 pulse and 90 pulse Fourier-transform spectrometers with $SiMe_4$ as internal standard. Solution and solid-state EPR spectra were recorded on a Bruker ESR 300 spectrometer equipped with a Varian variable-temperature controller; diphenylpicrylhydrazyl (dpph) was used as an external standard. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 240B elemental analyser, while Cu and Mo were determined by atomic absorption spectroscopy on a Perkin-Elmer 1100B spectrophotometer. Room-temperature magnetic measurements were carried out by Faraday's method using mercury tetrathiocyanatocobaltate(II) as a calibrant. Variable-temperature magnetic measurements were carried out on a polycrystalline sample (0.0582 g) of complex **2a** using a quantum design Squid susceptometer and 30 points were collected in the range 5.00–300 K. The applied magnetic field was 1000 G. The correction for the diamagnetism of the complex was estimated from Pascal constants as -392×10^{-6} cm^3 mol^{-1}; a value of 60×10^{-6} cm^3 mol^{-1} was used for the temperature-independent paramagnetism of the copper(II) ion. The magnetism of the sample was found to be field independent. Electrical conductance measurements were carried out with a WTW model LF 530 conductivity outfit and a type C cell, which had a cell constant of 0.996. This represents a mean value calibrated at 25 °C with potassium chloride. All temperatures were controlled with an accuracy of ±0.1 °C using a Haake thermoelectric circulating system. Cyclic voltammetry studies were completed on a G. Bank Electronic, type Wenking PCA 72L electrochemical analyser. A three-electrode cell was employed with a planar Beckman platinum electrode as the working electrode, a platinum wire as the counter electrode and a calomel electrode saturated with NaCl(SSCE) as the reference. The supporting electrolyte, KCl, was obtained from Merck. Oxygen was removed by purging the solutions with pure nitrogen which had been previously saturated with solvent vapour. All electrochemical measurements were performed at 25.0 ± 0.2 °C. The temperature was controlled by means of a thermostatically controlled water-bath.

Preparation of the Compounds.—The Schiff-bases were synthesised by condensation of salicylaldehyde, 5-bromo- or 5-chloro-salicylaldehyde with 2-amino-2-methyl- or 2-amino-2-ethyl-propane-1,3-diol.

$[MoO_2(HL^1)(MeOH)]$ **1a**. Salicylaldehyde (1.1 cm^3, 10 mmol) was added to a solution of 2-amino-2-methylpropane-1,3-diol (10 mmol, 1.05 g) in MeOH (100 cm^3). The resulting mixture was refluxed for 1 h, generating a pale yellow solution. When the solution was cooled to room temperature $[MoO_2(acac)_2]$ (3.26 g, 10 mmol) was added with stirring. This pale yellow solution was refluxed for 2 h. After the reaction mixture was cooled to room temperature it was exposed to air and left slowly to evaporate. A yellow crystalline solid was deposited in a couple of days, yield 70% (Found: C, 39.20; H, 4.60; Mo, 26.10; N, 3.80. Calc. for $C_{12}H_{17}MoNO_6$: C, 39.25; H, 4.65; Mo, 26.15; N, 3.80%). IR(KBr pellet, cm^{-1}): ν(O–H) 3400s (br), 3310vs; ν(C=N) 1625vs; ν(C=O) 1550s; ν_{asym}(Mo=O) 930vs; ν_{sym}(Mo=O) 890vs. UV/VIS [in dimethylformamide (dmf)]: 349nm (3080 dm^3 mol^{-1} cm^{-1}).

$[MoO_2(HL^3)(MeOH)]$ **1b**. The procedure was identical to that described above, except that 5-chlorosalicylaldehyde was used instead of salicylaldehyde. Yield 80% (Found: C, 35.65; H, 4.00; Mo, 24.50; N, 3.50. Calc. for $C_{12}H_{16}ClMoNO_6$: C, 35.75; H, 3.95; Mo, 23.85; N, 3.45%). IR(KBr pellet, cm^{-1}): ν(O–H) 3400s (br); 3320vs; ν(C=N) 1625vs; ν(C=O) 1550s; ν_{asym}(Mo=O) 935vs; ν_{sym}(Mo=O) 900vs. UV/VIS (dmf): 357 nm (3320 dm^3 mol^{-1} cm^{-1}).

$[MoO_2(HL^4)(MeOH)]$ **1c**. The procedure was identical to that described above, except that 5-bromosalicylaldehyde was used instead of salicylaldehyde. Yield 70% (Found: C, 32.00; H, 3.50; Mo, 21.00; N, 3.20. Calc. for $C_{12}H_{16}BrMoNO_6$: C, 32.20; H, 3.60; Mo, 21.45; N, 3.15%): IR(KBr pellet, cm^{-1}): ν(O–H) 3400s (br), 3320vs; ν(C=N) 1625vs; ν(C=O) 1540s; ν_{asym}(Mo=O) 930vs; ν_{sym}(Mo=O) 895vs. UV/VIS (dmf): 349 nm (3100 dm^3 mol^{-1} cm^{-1}).

$[MoO_2(HL^2)(MeOH)]$ **1d**. The procedure was identical to that described above, except that 2-amino-2-ethylpropane-1,3-diol was used instead of 2-amino-2-methylpropane-1,3-diol. Yield 80% (Found: C, 40.90; H, 4.90; Mo, 25.00; N, 3.60; Calc. for $C_{13}H_{19}MoNO_6$: C, 40.95; H, 5.00; Mo, 25.20; N, 3.65%). IR(KBr pellet, cm^{-1}): ν(O–H) 3400s (br), 3310vs; ν(C=N) 1620vs; ν(C=O) 1550s; ν_{asym}(Mo=O) 935vs; ν_{sym}(Mo=O) 900vs. UV/VIS (dmf): 346 nm (3510 dm^3 mol^{-1} cm^{-1}).

$[MoO_2(HL^5)(MeOH)]$ **1e**. The procedure was identical to that described above, except that 2-amino-2-ethylpropane-1,3-diol was used instead of 2-amino-2-methylpropane-1,3-diol and 5-chlorosalicylaldehyde instead of salicylaldehyde. Yield 65% (Found: C, 37.50; H, 4.40; Mo, 23.00; N, 3.30. Calc. for $C_{13}H_{18}ClMoNO_6$: C, 37.55; H, 4.35; Mo, 23.10; N, 3.35%). IR(KBr pellet, cm^{-1}): ν(O–H) 3430s (br), 3320vs; ν(C=N) 1630vs; ν(C=O) 1550s; ν_{asym}(Mo=O) 930vs; ν_{sym}(Mo=O) 895vs. UV/VIS (dmf): 355 nm (3070 dm^3 mol^{-1} cm^{-1}).

$[MoO_2(HL^6)(MeOH)]$ **1f**. The procedure was identical to that described above, except that 5-bromosalicylaldehyde was used instead of salicylaldehyde and 2-amino-2-ethylpropane-1,3-diol instead of 2-amino-2-methylpropane-1,3-diol. Yield 55% (Found: C, 33.80; H, 3.80; Mo, 20.60; N, 3.75. Calc. for $C_{13}H_{18}BrMoNO_6$: C, 33.85; H, 3.90; Mo, 20.80; N, 3.65%). IR(KBr pellet, cm^{-1}): ν(O–H) 3400s (br), 3350vs; ν(C=N) 1625vs; ν(C=O) 1540s; ν_{asym}(Mo=O) 930vs; ν_{sym}(Mo=O) 895vs. UV/VIS (dmf): 357 nm (2910 dm^3 mol^{-1} cm^{-1}).

$[CuMo_3O_8(HL^3)_2(bipy)_2]$ **2a**. The complex $[Cu_2Mo_2O_4L^3{}_2(OMe)_2]$ (0.927 g, 1 mmol) was refluxed with an excess (10 mmol) of bipy in acetonitrile. The deep green solution slowly turned light blue. After about 2 h the reaction mixture was filtered to remove a very small amount of a white precipitate and left at ambient temperature slowly to evaporate. Light blue-green crystals were deposited in 1 week. Yield 25% (Found: C, 39.50; H, 3.40; Cu, 4.65; Mo, 22.20; N, 6.70. Calc. $C_{42}H_{40}Cl_2CuMo_3N_6O_{14}{\cdot}H_2O{\cdot}0.5CH_3CN$: C, 39.30; H, 3.25; Cu, 4.85; Mo, 21.95; N, 6.95%). IR(KBr pellet, cm^{-1}): ν(O–H) 3400s (br), 3310vs; ν(C=N) 1630vs; ν(C=O) 1545s; ν_{asym}(Mo=O) 920vs; ν_{sym}(Mo=O) 890vs; ν(Mo=O) of $MoO_4{}^{2-}$ 860vs, 825vs, 805vs and 775vs. UV/VIS(Nujol mull): 680 and 720 (sh) nm.

$[CuMo_3O_8(HL^4)_2(bipy)_2]$ **2b**. The procedure was identical to that described above, except that $[Cu_2Mo_2O_4L^4{}_2(OMe)_2]$ was used instead. The pale blue-green microcrystalline product was deposited in a couple of days. Yield 30% (Found: C, 37.00; H, 3.20; Cu, 4.35; Mo, 20.10; N, 6.80. Calc. for $C_{42}H_{40}Br_2CuMo_3N_6O_{14}{\cdot}H_2O$: C, 36.55; H, 3.05; Cu, 4.60; Mo, 20.85, N, 6.90%). IR(KBr pellet, cm^{-1}): ν(O–H) 3400m (br), 3310vs; ν(C=N) 1630vs; ν(C=O) 1545s; ν_{asym}(Mo=O) 920vs; ν_{sym}(Mo=O) 890vs; ν(Mo=O) of $MoO_4{}^{2-}$ 860vs, 825vs, 805vs and 775vs cm^{-1}. UV/VIS(Nujol mull): 680 and 720 (sh) nm.

$[MoO(L^1)]$ **4a**. The complex $[MoO_2(HL^1)(MeOH)]$ (0.18 g, 5 mmol) was dissolved in MeOH or MeCN (100 cm^3). Excess of dppm or PBu_3 (20 mmol) was added under nitrogen and the reaction mixture was refluxed for 1 h. The pale yellow solution turned slowly dark red-brown and a red-brownish microcrystalline solid was isolated upon cooling to room temperature. Yield

60% (Found: C, 41.05; H, 3.80; Mo, 29.40; N, 4.30. Calc. for $C_{11}H_{12}MoNO_4$: C, 41.50; H, 3.75; Mo, 30.20; N, 4.40%). IR(KBr pellet or Nujol mull, cm^{-1}): ν(C=N) 1615vs; ν(C=O) 1555s; ν(C–O) 1110vs; ν(Mo=O) 943vs. UV/VIS (Nujol mull): 405 and 505 (sh) nm.

$[MoO(L^3)]$ **4b**. The procedure was identical to that described above, except that $[MoO_2(HL^3)(MeOH)]$ was used. Yield 50% (Found: C, 37.65; H, 3.00; Mo, 26.50; N, 4.00. Calc. for $C_{11}H_{11}ClMoNO_4$: C, 37.45; H, 3.10; Mo, 27.25; N, 3.95%). IR (KBr pellet or Nujol mull, cm^{-1}): ν(C=N) 1615vs; ν(C=O) 1540s; ν(C–O) 1120vs; ν(Mo=O) 948vs. UV/VIS (Nujol mull) 410 and 510 (sh) nm.

$[MoO(L^2)]$ **4c**. The procedure was identical to that described above, expect that $[MoO_2(HL^2)(MeOH)]$ was used. Yield 50% (Found: C, 43.20; H, 4.10; Mo, 29.00; N, 4.25. Calc. for $C_{12}H_{14}MoNO_4$: C, 43.35; H, 4.25; Mo, 28.90; N, 4.20%). IR (KBr pellet or Nujol mull, cm^{-1}): ν(C=N) 1615vs; ν(C=O) 1550s; ν(C–O) 1100vs; ν(Mo=O) 945vs. UV/VIS (Nujol mull): 405 and 505 (sh) nm.

$[MoO(L^5)]$ **4d**. The procedure was identical to that described above, except that $[MoO_2(HL^5)(MeOH)]$ was used instead. Yield 55% (Found: C, 39.50; H, 3.40; Mo, 25.80; N, 3.70. Calc. for $C_{12}H_{13}ClMoNO_4$: C, 39.30; H, 3.55; Mo, 26.20; N, 3.80%). IR (KBr pellet or Nujol mull, cm^{-1}): ν(C=N) 1615vs; ν(C=O) 1540s; ν(C–O) 1100vs; ν(Mo=O) 948vs. UV/VIS (Nujol mull): 410 and 510 (sh) nm.

Crystallography.—A pale yellow parallelepiped crystal of $[MoO_2(HL^3)(MeOH)]$ **1b** with approximate dimensions 0.25 × 0.34 × 0.42 mm was mounted in a glass capillary. Complete crystal data and parameters for data collection are in Table 1. The space group was determined by preliminary Weissenberg and precession photographs. Unit-cell dimensions were derived from a least-squares refinement of the setting angles of 25 automatically centred reflections in the range $11 < 2\theta < 24°$ on a Syntex $P2_1$ diffractometer with Nb-filtered Mo-Kα radiation (λ = 0.710 73 Å). Three standard reflections measured every 97, showed < 3.0% intensity fluctuation. Lorentz polarisation and ψ-scan absorption correction were applied. Scattering factors were taken from ref. 15.

For complex **2a** a pale blue-green prismatic crystal with approximate dimensions 0.40 × 0.30 × 0.10 mm was mounted in a glass capillary. Complete crystal data and parameters for data collection are in Table 1. Unit-cell dimensions were derived from a least-squares refinement of the setting angles of 25 automatically centred reflections in the range $22 < 2\theta < 30°$ on a CAD4-F diffractometer with Nb-filtered Mo-Kα (0.710 69 Å) radiation. Two standard reflections (2, −2, −10 and 7, 5, 7) were collected 151 times. The diffraction standard interval time was 3600 and no decay of the standard intensities was observed. Lorentz polarization and ψ-scan absorption corrections were applied. Scattering factors were taken from ref. 15.

Solution and refinement of the structures. Symmetry-equivalent data for complex of **1b** were averaged with $R = 0.0316$ to give 2629 independent reflections from a total of 3091 collected. The structure was solved by direct methods using the program SHELX 86[16] and by full-matrix least-squares techniques with SHELX 76[17a] using only 2342 reflections with $F > 2\sigma(F_o)$ and refining 254 parameters. All hydrogen atoms were located from difference maps and their positions refined isotropically. All non-hydrogen atoms were refined anisotropically. The final values for R and R' (unit weights) for all data were 0.0301 and 0.0319 respectively. The maximum and minimum residual peaks in the final difference map were 0.21 and −0.22 e $Å^{-3}$. The largest shift/e.s.d. in the final cycle was 0.06. The fractional atomic coordinates of the non-H atoms are listed in Table 2, selected bond lengths and angles in Table 3.

The structure of complex **2a** was solved by direct methods using the program SHELX 86. The refinement was carried out using the program CRYSTALS.[17b] The alcohol group and the methyl group bonded to the tertiary carbon C(208) were found to be disordered with occupancy factors of 0.25 and 0.75. The acetonitrile solvent was disordered around the origin over two positions with a total occupancy of 0.5. Its coordinates were refined using slack constraints: C–C 1.45(3) and C–N 1.20(3) Å. The hydrogen atoms of the aromatic groups and of the secondary carbon atoms were placed in their expected positions after each refinement cycle. The hydrogen atoms of the non-disordered methyl and alcohol groups were obtained from Fourier difference maps and their coordinates refined using slack constraints: C–H 1.08(3) Å and 109(3)° angles around the carbon atom. The hydrogen atoms of the disordered acetonitrile, alcohol and methyl groups of occupancy 0.25 were not found. With anisotropic thermal parameters for all non-hydrogen atoms except the acetonitrile atoms, the final R = 0.0336 and R' = 0.0364 (w = 1) Maximum and minimum electron density peaks 0.63 and −0.95 e $Å^{-3}$. The fractional atomic coordinates of the non-H atoms are listed in Table 4, selected bond lengths and angles in Table 5.

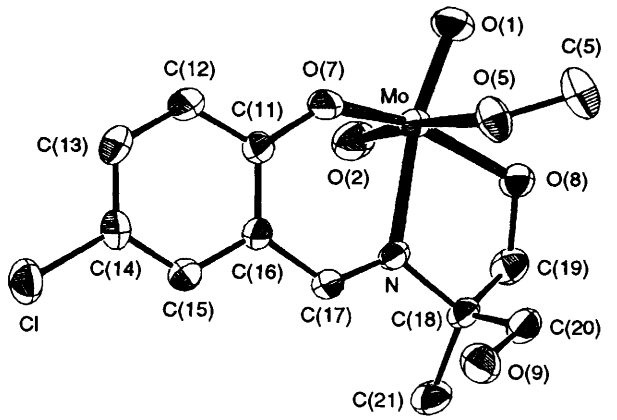


Fig. 1 An ORTEP view of complex **1b** showing the atom labelling scheme

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

Results and Discussion

Synthesis.—The synthesis of the molybdenum compounds reported here can be achieved *via* the pseudo-template reaction of $[Mo^{VI}O_2(acac)_2]$ with salicylaldehyde, 5-bromo- or 5-chloro-salicylaldehyde and 2-amino-2-methyl- or 2-amino-2-ethyl-propane-1,3-diol, in methanol. The reactions involve deprotonation of the ligand by the $[MoO_2(acac)_2]$ without using a base, *e.g.*, equation (1). The molybdenum compounds

$$XC_6H_3(OH)CHO + H_2NC(R)(CH_2OH)_2 + [MoO_2(acac)_2] \xrightarrow{MeOH} [MoO_2\{XC_6H_3(O)CH{=}NC(R)(CH_2O)(CH_2OH)\}(MeOH)] \quad (1)$$

are yellow crystalline solids which appear to be air and moisture stable. They are soluble in Me_2SO, dmf, and hot MeCN but insoluble in CH_2Cl_2 and water. None is an electrolyte in Me_2SO or dmf.

Reaction of $[MoO_2(HL^3)(MeOH)][H_3L^3$ = 2-(5- chloro-salicylideneamino)-1,3-dihydroxy-2-methylpropane] with $Cu(O_2CMe)_2$ in methanol–acetonitrile (1:1) yields the mixed-metal cluster $[Cu_2Mo_2O_4L^3{}_2(OMe)_2]$ **3** with a $Mo_2Cu_2O_4$ cubane-like core.[14b] The unco-ordinated CH_2OH group and MeOH are deprotonated without using a base, equation (2). Reflux of **3** with an excess of bipyridine in acetonitrile yields pale blue-green crystals of the tetranuclear cluster $[CuMo_3O_8(HL^3)_2(bipy)_2]$ **2a**. This procedure was successful

Table 1 Summary of crystal data

	1b	**2a**
Colour	Yellow	Pale blue-green
Formula	$C_{12}H_{16}ClMoNO_6$	$C_{42}H_{40}Cl_2CuMo_3N_6O_{14}\cdot H_2O\cdot 0.5CH_3CN$
M	401.6	1313.62
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
a/Å	8.666(1)	13.381(3)
b/Å	9.274(1)	14.355(3)
c/Å	18.818(2)	14.463(2)
α/°	–	77.82(2)
β/°	89.77(1)	68.00(2)
γ/°		73.72(2)
U/Å^3	1512.28(1)	2455(17)
D_c/Mg m^{-3}	1.764	1.76
D_m/Mg m^{-3}	1.75	1.74
Z	4	2
μ/cm^{-1}	10.04	13.4
Minimum, maximum absorption corrections	1.00, 1.13	0.83, 1.20
h, *k*, *l* ranges	0–10, 0–11, −22 to 22	−15 to 15, −17 to 17, 0–17
2θ/°	50.0	50.0
F(000)	1808	1312
No. refined parameters	254	678
Unique reflections	2629	9050
Reflections used in refinement	2342 $[F_o^2 > 2\sigma(F_o^2)]$	6117 $[F_o^2 > 3\sigma(F_o^2)]$
R_{int}	0.0216	0.0151
Extinction coefficient	–	5.815 (0.005)
R	0.0194	0.0336
R′ *	0.0221	0.0364

* $R' = [\Sigma w(\Delta F)^2/\Sigma w F_o^2]^{\frac{1}{2}}$.

Table 2 Fractional atomic coordinates for complex **1b**

Atom	*X/a*	*Y/b*	*Z/c*
Mo	0.7384(0)	0.3949(0)	0.3560(0)
O(1)	0.5851(2)	0.3041(2)	0.3203(1)
O(2)	0.7766(2)	0.3116(2)	0.4341(1)
O(5)	0.7152(2)	0.5382(2)	0.2508(1)
C(5)	0.7045(5)	0.4739(4)	0.1820(2)
O(7)	0.6362(2)	0.5665(2)	0.3919(1)
C(11)	0.6746(3)	0.6690(3)	0.4386(1)
C(12)	0.5567(3)	0.7342(3)	0.4780(1)
C(13)	0.5887(3)	0.8421(3)	0.5253(1)
C(14)	0.7395(3)	0.8899(3)	0.5335(1)
Cl	0.7788(1)	1.0290(1)	0.5928(0)
C(15)	0.8587(3)	0.8261(3)	0.4962(1)
C(16)	0.8283(3)	0.7133(3)	0.4486(1)
C(17)	0.9584(3)	0.6486(3)	0.4114(1)
N	0.9495(2)	0.5378(2)	0.3712(1)
C(18)	1.0901(3)	0.4824(3)	0.3347(1)
C(19)	1.0538(3)	0.3242(3)	0.3196(2)
C(20)	1.1095(3)	0.5640(3)	0.2646(1)
C(21)	1.2368(3)	0.4955(4)	0.3789(2)
O(8)	0.8967(2)	0.3086(2)	0.2973(1)
O(9)	1.1306(2)	0.7132(2)	0.2773(1)

Table 3 Selected bond distances (Å) and angles (°) of complex **1b**

Mo–O(1)	1.712(2)	Mo–O(7)	1.942(2)
Mo–O(2)	1.694(2)	Mo–O(8)	1.931(2)
Mo–O(5)	2.393(2)	Mo–N	2.278(2)
O(2)–Mo–O(1)	105.7(1)	N–Mo–O(5)	81.4(1)
O(5)–Mo–O(1)	83.2(1)	N–Mo–O(7)	81.0(1)
O(5)–Mo–O(2)	171.1(1)	O(8)–Mo–O(1)	97.1(1)
O(7)–Mo–O(1)	100.7(1)	O(8)–Mo–O(2)	99.5(1)
O(7)–Mo–O(2)	99.4(1)	O(8)–Mo–O(5)	79.6(1)
O(7)–Mo–O(5)	78.1(1)	O(8)–Mo–O(7)	149.4(1)
N–Mo–O(1)	163.8(1)	O(8)–Mo–N	75.2(1)
N–Mo–O(2)	89.8(1)		

only with the 5-Cl and 5-Br derivatives. Compounds **2a** and **2b** are 1:1 electrolytes in water and slightly soluble in dmf or Me_2SO solvent.

$$2[MoO_2(HL^3)(MeOH)] + 2Cu(O_2CMe)_2 \xrightarrow{MeOH} [Cu_2Mo_2O_4L^3{}_2(OMe)_2] + 4MeCO_2H \quad (2)$$

Structure of $[MoO_2(HL^3)(MeOH)]$ **1b**.—In this molecule the Schiff base acts as a dianionic tridentate ligand. An ORTEP[18] diagram of **1b** is given in Fig. 1, fractional atomic coordinates in Table 2, and selected bond distances and angles in Table 3. The molybdenum atom is six-co-ordinate and can be described as having a distorted-octahedral geometry. The Mo–O distances are influenced by the different types of oxygen atoms. The Mo=O bond distances [1.694(2)–1.712(2) Å] and angle 105.7(1)° as well as the Mo–O distances of the Schiff-base alkoxy oxygen [1.931(2) Å] and of the phenolate oxygen [1.942(2) Å] of the *cis*-MoO_2 group are within the usual ranges observed for monomeric analogues.[1,4] The two oxygens of the Schiff-base ligand occupy the *trans* positions in the equatorial plane with a O(7)–Mo–O(8) angle of 149.4(1)°. The nitrogen atom of the Schiff base is *trans* to the double-bonded O(1) at a distance Mo–N 2.278(2) Å which is longer than those observed[4] for other molybdenum(VI) complexes with nitrogen-donor ligands(average 2.10 Å), but it is within the range (2.28–2.50 Å) when the nitrogen is *trans* to a double-bonded oxygen. The sixth position of the distorted octahedron is occupied by a methanolic oxygen *trans* to the double-bonded oxygen O(2) with Mo–O 2.393(2) Å and O(5)–Mo–O(2) angle 171.1(1)° which is the largest among the three *trans* angles. It is noticeable that the sums of the *trans* Mo–X (X = O or N) distances are very similar (3.873, 3.990, 4.087 Å).

Structure of $[CuMo_3O_8(HL^3)_2(bipy)_2]$ **2a**.—A brief description of the crystal structure has been reported.[14c] The structure confirms the presence of a trinuclear unit $[Mo_3O_8]^{2-}$ co-

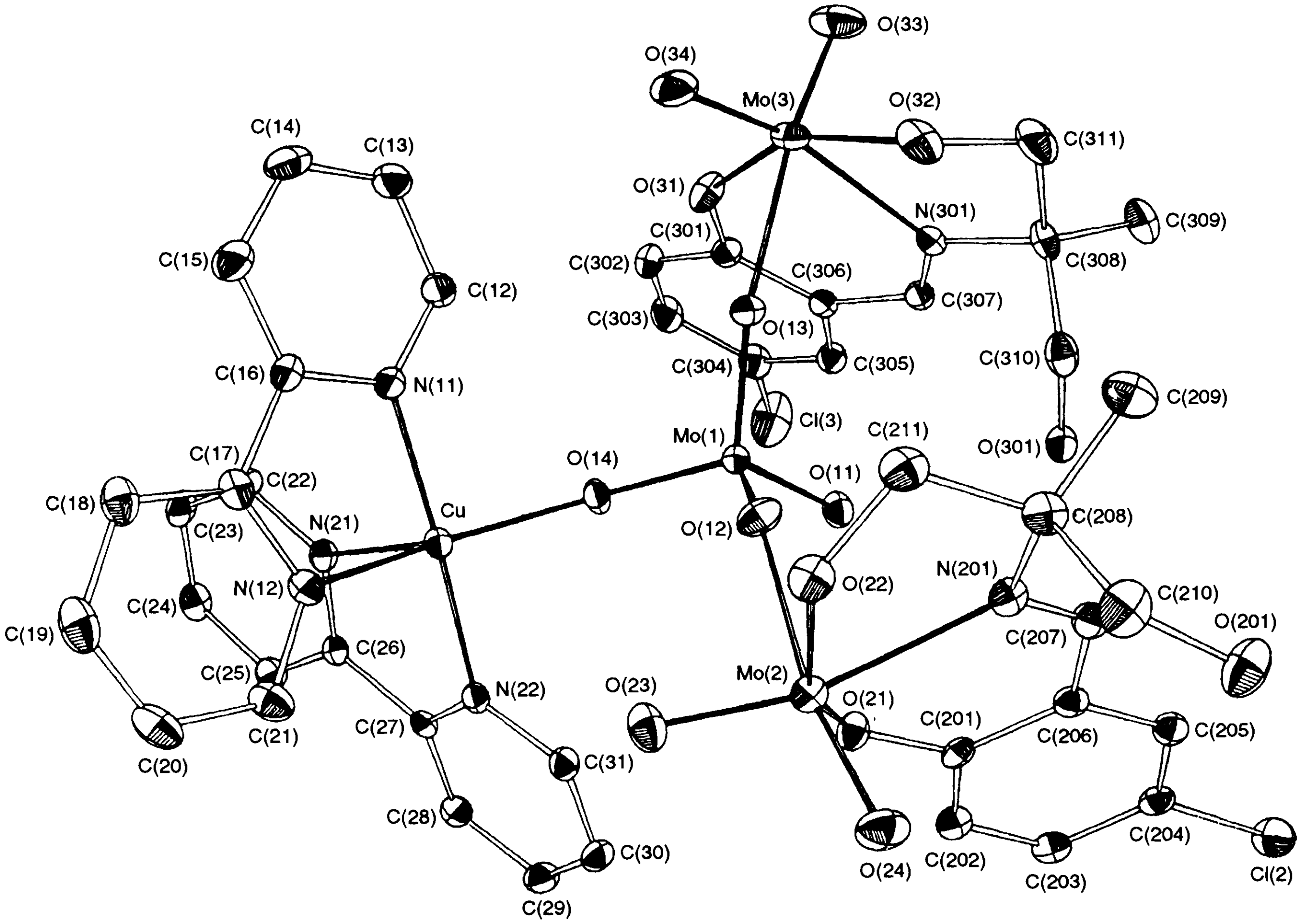


Fig. 2 An ORTEP view of complex **2a** with 50% thermal ellipsoids, showing the atom labelling scheme

Table 4 Fractional atomic coordinates for complex **2a**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Mo(1)	0.252 64(4)	0.223 69(3)	0.260 79(3)	C(28)	0.045 5(5)	−0.032 4(4)	0.637 6(4)
O(11)	0.336 0(3)	0.114 2(3)	0.221 4(3)	C(29)	0.154 1(5)	−0.060 7(4)	0.635 1(4)
O(12)	0.319 8(3)	0.281 2(3)	0.307 5(3)	C(30)	0.221 5(5)	0.003 7(5)	0.591 2(4)
O(13)	0.222 9(3)	0.301 2(3)	0.159 7(3)	C(31)	0.180 4(4)	0.094 4(4)	0.550 9(4)
O(14)	0.128 1(3)	0.200 5(3)	0.353 4(3)	N(22)	0.074 8(3)	0.123 9(3)	0.553 3(3)
Cu	0.018 21(5)	0.246 63(4)	0.476 76(5)	Mo(2)	0.424 49(4)	0.260 85(3)	0.403 23(4)
N(11)	−0.050 6(3)	0.365 6(3)	0.405 4(3)	O(21)	0.441 6(3)	0.125 3(3)	0.384 1(3)
C(12)	−0.052 9(5)	0.372 6(4)	0.312 5(4)	C(201)	0.528 4(4)	0.059 3(4)	0.336 2(4)
C(13)	−0.111 5(5)	0.453 7(5)	0.271 3(5)	C(202)	0.532 7(5)	−0.038 7(4)	0.373 0(4)
C(14)	−0.171 1(6)	0.529 5(5)	0.327 2(5)	C(203)	0.619 8(5)	−0.110 9(4)	0.328 1(4)
C(15)	−0.169 6(5)	0.522 6(4)	0.423 1(5)	C(204)	0.703 0(5)	−0.084 8(4)	0.242 9(4)
C(16)	−0.108 6(4)	0.440 2(4)	0.461 0(4)	C(205)	0.700 6(5)	0.010 2(4)	0.202 7(4)
C(17)	−0.098 7(5)	0.425 0(4)	0.561 9(4)	C(206)	0.613 4(4)	0.084 6(4)	0.248 7(4)
C(18)	−0.152 5(5)	0.493 1(4)	0.629 9(5)	C(207)	0.618 1(5)	0.184 5(4)	0.205 4(4)
C(19)	−0.136 2(6)	0.471 8(5)	0.721 1(5)	N(201)	0.555 3(4)	0.259 8(3)	0.246 5(3)
C(20)	−0.069 8(6)	0.384 8(5)	0.743 0(5)	C(208)	0.576 8(5)	0.358 9(4)	0.202 2(5)
C(21)	−0.018 3(6)	0.320 0(5)	0.672 2(4)	C(209)	0.608 7(7)	0.378 2(5)	0.088 6(5)
N(12)	−0.033 1(4)	0.340 1(3)	0.582 9(3)	C(210)	0.667 4(6)	0.370 7(5)	0.237 6(5)
N(21)	−0.125 1(3)	0.182 9(3)	0.539 3(3)	O(201)	0.766 5(5)	0.300 6(4)	0.206 6(5)
C(22)	−0.226 3(4)	0.220 4(4)	0.534 6(4)	O(251)	0.697(2)	0.326(2)	0.029(2)
C(23)	−0.312 1(4)	0.173 8(5)	0.584 2(5)	C(211)	0.467 1(5)	0.428 2(4)	0.251 2(5)
C(24)	−0.293 4(5)	0.086 5(4)	0.640 4(4)	O(22)	0.423 0(3)	0.395 7(3)	0.353 7(3)
C(25)	−0.189 5(5)	0.046 6(4)	0.647 4(4)	Cl(2)	0.816 6(2)	−0.175 8(1)	0.189 5(1)
C(26)	−0.106 5(4)	0.097 5(3)	0.594 9(4)	O(23)	0.304 4(4)	0.274 0(3)	0.502 8(3)
C(27)	0.007 5(4)	0.060 7(4)	0.596 8(3)	O(24)	0.525 1(4)	0.234 1(3)	0.455 2(3)

ordinatively bound to a $[Cu(bipy)]^{2+}$ ion. An ORTEP diagram is given in Fig. 2, fractional atomic coordinates in Table 3, and selected bond distances and angles in Table 5. The molybdenum part of the structure may be described in terms of three oxo-bridged centres, alternating one tetraoxomolybdate $[MoO_4]^{2-}$ and two six-co-ordinated MoO_2(Schiff base) moieties. The two oxo-groups of the capping $[MoO_4]^{2-}$ unit interact with the Schiff base-co-ordinated Mo atoms at an average distance of

Table 5 Selected bond lengths (Å) and angles (°) of complex **2a**

Mo(1)–O(11)	1.720(4)	Mo(2)–O(12)	2.239(4)
Mo(1)–O(12)	1.748(4)	Mo(2)–O(21)	1.961(4)
Mo(1)–O(13)	1.742(4)	Mo(2)–O(22)	1.915(4)
Mo(1)–O(14)	1.770(3)	Mo(2)–O(23)	1.704(4)
Cu–N(22)	1.990(4)	Mo(2)–O(24)	1.695(4)
Cu–N(21)	2.161(4)	Mo(2)–N(201)	2.287(5)
Cu–O(14)	1.942(3)	Cu–N(11)	1.978(4)
Cu–N(12)	2.047(4)		
O(13)–Mo(1)–O(11)	109.7(2)	O(12)–Mo(1)–O(11)	110.5(2)
O(12)–Mo(1)–O(13)	107.8(2)	O(14)–Mo(1)–O(11)	108.3(2)
O(14)–Mo(1)–O(13)	109.2(2)	O(14)–Mo(1)–O(12)	111.3(2)
O(22)–Mo(2)–O(21)	152.1(2)	O(23)–Mo(2)–N(201)	165.2(2)
O(24)–Mo(2)–O(12)	168.0(2)	O(24)–Mo(2)–O(23)	104.5(2)
N(21)–Cu–O(14)	116.2(2)	N(21)–Cu–N(12)	95.7(2)
N(22)–Cu–N(11)	175.0(2)		

Parameters for Mo(3) are similar to those for Mo(2).

2.22 Å. The third oxo group of the tripodal $[MoO_4]^{2-}$ tetrahedron bridges the $[Mo_3O_8]^{2-}$ unit to the $[Cu(bipy)_2]^{2+}$ ion, possessing one site in the equatorial plane of the trigonal-bipyramidal Cu^{2+} co-ordination environment. The Mo–O (alkoxy) 1.915 Å, Mo–O (phenoxy) 1.971 Å (average) and Mo–N 2.229 Å (average) distances of the Schiff base are consistent with the Mo–O and Mo–N distances of the monomer analogue (see below). It is noteworthy that the sum of the *trans* Mo–O distances of the $MoO_2(HL^3)$ units are almost identical (3.876–3.998, mean 3.933 Å). While the octahedrons around each Mo(Schiff base) unit show a strong *cis* distortion, the lack of any elongation or depression along one of the axes of the octahedron is strong evidence that Mo keeps a d^0 configuration and a VI oxidation state. The phenolate and the co-ordinated aliphatic oxygens occupy *trans* positions of the octahedron with O(22)–Mo(2)–O(21) and O(31)–Mo(3)–O(32) angles of 152.1(2) and 153.5(2)° respectively. The O(14) bridging the molybdenum and copper units forms an angle of 140.6(2)° while the angles involving the oxygens connecting Mo(1) with Mo(2) and Mo(3) are 145.5(2) and 161.2(2)° respectively. The $[MoO_4]^{2-}$ moiety shows an almost ideal tetrahedral geometry with the O(*i*)–Mo(1)–O(*j*) angles varying from 107.8 to 111.3°, average 109.4°. The copper unit shows a distorted trigonal-bipyramidal geometry in which each bipy molecule occupies one axial and one equatorial position. The axial distances Cu–N(22) 1.990 and Cu–N(11) 1.978 Å are shorter than those in the equatorial plane, Cu–N(21) 2.161, Cu–N(12) 2.047 Å, showing a Jahn–Teller distortion.[19] The angle between the two bipy planes is 95.7° which is smaller (97–124°) than those observed in a series of $[Cu(bipy)_2Cl]^+$ complexes with similar geometry.[19,20] This angular distortion by 24° from the idealised trigonal-bipyramidal geometry results in the appearance of two peaks separated by *ca* 500 cm^{-1} in the electronic spectrum.

The co-ordination mode of the Schiff base is also quite interesting. In the starting material $[MoO_2(HL^3)(MeOH)]$ it acts as a tridentate ligand, possessing three sites in the equatorial plane of the molybdenum octahedron. In compound **3** the Schiff base is transferred from the molybdenum to copper and acts as a tetradentate ligand with two oxygens and one nitrogen bound to Cu^{2+}, occupying the three sites in the basal plane of the square pyramid, and one oxygen bound to Mo^{VI} (Fig. 3), while in compound **2a** the Schiff base returns to Mo acting again as a tridentate ligand and possessing three sites in the equatorial plane of the molybdenum octahedron.

Spectroscopic and Magnetic Properties.—The $[MoO_2(Schiff\ base)(MeOH)]$ complexes exhibit two ν(O=Mo=O) vibrations at about 930 (ν_{asym}) and 880–890 cm^{-1} (ν_{sym}) confirming the presence of a *cis*-MoO_2 structure; in the case of a *trans*-MoO_2 group only one band is expected. Dioxomolybdenum(VI) prefers the *cis*-MoO_2 structure for maximum utilisation of the $Mo(d_\pi)$–$O(p_\pi)$ orbitals for chemical bonding. The corresponding $[Cu_2Mo_2O_4(Schiff\ base)_2(OMe)_2]$ complexes show three ν(O=Mo=O) vibrations in the regions 940–950, 910–920 and 885–890 cm^{-1}. The IR spectra of the compounds **2a** and **2b** display a complex pattern of bands in the range 770–920 cm^{-1} attributable to Mo–O modes. The bands at 920 and 890 cm^{-1} may be assigned to the *cis*-MoO_2 moieties of the molybdenum atoms bound to the Schiff-base ligand (see below), while those at 775, 805 and 825 and that at 860 cm^{-1} may be attributed to the bridging and terminal Mo=O group of the MoO_4 moiety,[21] respectively. These assignments show a linear relation with the bond lengths observed for complex **2a**.

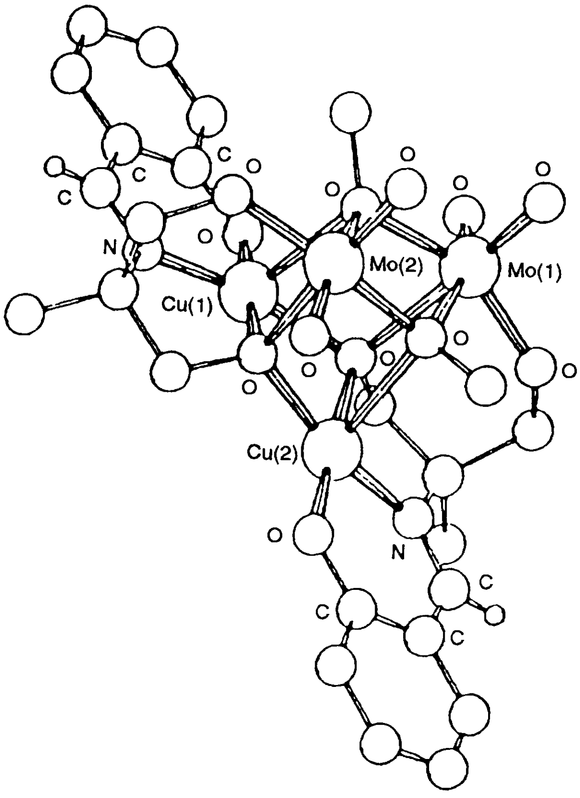


Fig. 3 An ORTEP view of $[Cu_2Mo_2O_4L^3{}_2(OMe)_2]$ **3**,[14b] showing the co-ordination mode of the Schiff base

In the region 3000–3400 cm^{-1} the monomeric complexes show two broad bands due to the ν(O–H) of the co-ordinated methanol and the unco-ordinated CH_2OH group of the ligand. The ν(C=N) and ν(C=O) bands of the Schiff bases appear at about 1630 and 1530 cm^{-1} respectively, characteristic of the five-membered ring Mo–O(7)–C(11)–C(16)–C(17)–N (Fig. 1). For the $[Cu_2Mo_2O_4(Schiff\ base)_2(OMe)_2]$ complexes, Δν = ν(C=N) − ν(C=O) is 20–30 cm^{-1} smaller, reflecting the substitution of Mo by Cu. For compounds **2a** and **2b** the ν(C=N) and ν(C=O) bands are observed at frequencies expected for the MoO_2(Schiff base) species.

The room-temperature powder and the low-temperature (95 K) dimethyl sulfoxide glass X-band EPR spectrum of complex **2a** is typical of a copper(II) ion with no interaction with the $[MoO_4]^{2-}$ moiety. The EPR powder spectrum shows only a broad band with $g = 2.12$, while the glass spectrum at 95 K shows four copper hyperfine components ($I = \frac{3}{2}$) in the low-field $g_\parallel$ signal, with $g_\parallel = 2.26$, $g_\perp = 2.06$ and $A_\parallel = 165.4 \times 10^{-4}\ cm^{-1}$ [Fig. 4(*a*)]. The *g* values are consistent with axial symmetry.[19] The EPR spectra clearly show that the unpaired electron is located on Cu^{II} and the oxidation states for copper and molybdenum are 2+ and 6+ respectively. No superhyperfine structure due to copper–nitrogen interaction has been detected.

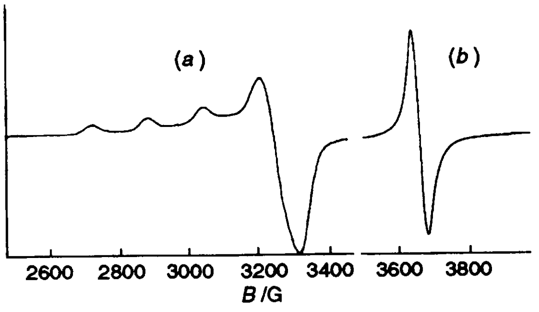


Fig. 4 X-Band EPR spectra at 77 K of (a) complex **2a** in a Me_2SO glass, (*b*) **4a** diluted in ZnO

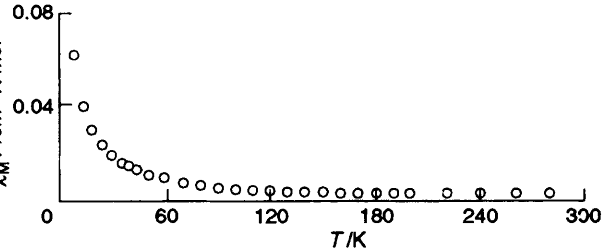


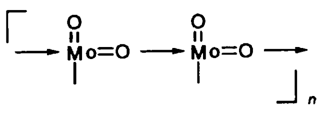
Fig. 5 Temperature dependence (300–5 K) of χT for complex **2a**

All the monomeric $[MoO_2(HL)(MeOH)]$ complexes are diamagnetic. The magnetic behaviour of **2a** in the form of a plot of $\chi_m T$ *vs.* T, χ_m being the magnetic susceptibility per copper(II) ion, is shown in Fig. 5. At room temperature $\chi_m T = 0.375$ cm^3 K mol^{-1} and $\mu_{eff} = 2.184\ \mu_B$, while at 5.00 K, $\chi_m T = 0.464$ cm^3 K mol^{-1} and $\mu_{eff} = 2.179\ \mu_B$. The interpretation of the magnetic behaviour in the temperature range 5.00–300.00 K is straightforward. Each cluster is composed of one Cu^{II} and three Mo^{VI}. However, the three Mo^{VI} are diamagnetic: hence, the only paramagnetic centre in the cluster is the Cu^{II}. All the values of magnetic susceptibility follow the Curie–Weiss law showing an idealised (for $S = \frac{1}{2}$) behaviour. The magnetic properties are consistent with the EPR data.

Cyclic voltammetry of compounds **2a** and **2b** in water shows a reversible wave at $E_{\frac{1}{2}} = -209$ mV. For *cis*-dioxomolybdenum(VI) complexes with Schiff-base ligands in various solvents except water, irreversible redox behaviour at E_{p_c} around -1.2 V is observed.[22–24] This potential is out of the water range (-0.7 to $+0.4$ V), so the reversible wave at $E_{\frac{1}{2}} = -209$ mV might arise from the copper, *i.e.* $[Cu(bipy)_2]^{2+} \longrightarrow [Cu(bipy)_2]^+$. The cathodic potential indicates that the copper(II) oxidation state is stabilised by the bipy ligands.

Reactivity of $[MoO_2$(Schiff base)(MeOH)] *Complexes with dppm.*—The reaction of the monomeric complexes with dppm in methanol or acetonitrile leads to five-co-ordinate complexes of the type MoO(Schiff base) in which the fifth position of a distorted square pyramid is occupied by the oxygen atom of the CH_2O^- moiety of the neighbouring repeat units.

Oxygen-transfer reactions have been reported by Topich and Lyon.[25] According to their results this type of reaction leads to the formation of an oxomolybdenum(IV) complex with a $4d_{xy}^2$ electron configuration. Boyd and Spence[7] have synthesised Mo^{IV}O(Schiff base) from $Mo^{VI}O_2$(Schiff base)L′ complexes (L′ = solvent molecule) using $PEtPh_2$ as the reducing agent, but only μ-oxo-dimolybdenum(V) dimers Mo_2O_3(Schiff base)$_2$ were obtained from some MoO_2(Schiff base) complexes. Chakravorty and co-workers[22] have assigned the presence of only a single stretch at 930 cm^{-1} and a broad band at 800 cm^{-1} for MoO_2(Schiff base) complexes to the formation of a polymer. The polymerisation most likely takes place *via* linkages of the type I. Recently Holm and co-workers[26] have reported the structures of two dimers $[Mo_2O_3L''_2(dmf)_2]$ [L″ = 2-(3-*tert*-butylsalicylideneamino)benzenethiolate(2−)] and $[Mo_2O_3L'''_2(dmf)_2]$ [L‴ = 2-(3-ethoxysalicylideneamino)benzenethiolate(2−)] as products of the reaction of $[Mo^{VI}O_2L'']$ or $[MoO_2L''']$ with $PMePh_2$ as well as the structure of mononuclear [MoO(L″)(bipy)]. All these complexes are diamagnetic, while the compounds of general formula [MoO(Schiff base)]$_n$ in this work show $\mu_{eff} = 1.6$–$1.7\ \mu_B$ which is consistent with the presence of one unpaired electron per molybdenum ion. The powder EPR spectra are characterised by a single broad signal [Fig. 4(*b*)] with $g = 1.900$, consistent with an oxidation state of 5+ for the central atom.[23] The paramagnetism of these compounds may be explained if we accept a monomeric form. Further support for this is that all these complexes exhibit only one ν(Mo=O) band at 940–950 cm^{-1} consistent with a five-co-ordinate geometry.[7]



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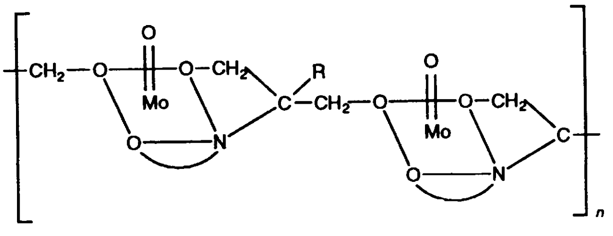

II

The absence of any band at 800 cm^{-1} characteristic for a Mo=O→Mo bridge and the presence of a new strong band at 1100 cm^{-1}, assigned to the aliphatic C–O group bound to Mo, leads to the assignment of a polymeric structure II. The most characteristic feature for the deprotonation of the CH_2OH group is the absence of any ν(O–H) in the region 3100–3400 cm^{-1}.

Acknowledgements

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