# Solid state coordination chemistry: two-dimensional oxides constructed from polyoxomolybdate clusters and copper–organoamine subunits

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**Copper–organodiamine substructures are effective bridging groups for polyoxomolybdate anions in the construction of two-dimensional mixed metal networks, of which [{Cu(bpe)}$_4$(α-Mo$_8$O$_{26}$)]·2H$_2$O and [{Cu(pyrd)}$_4$(γ-H$_4$Mo$_8$O$_{26}$)] are representative [bpe = 1,2-bis(4-pyridyl)ethylene; pyrd = pyridazine].**

The structural influence of organic molecules on inorganic oxide microstructures has been demonstrated in four families of materials: zeolites,[1,2] mesoporous phases of the MCM-41 class,[3] biomineralized materials[4] and transition metal–oxide–phosphate compounds or TMPO's.[5,6] We have recently extended this concept to the molybdenum oxides by introducing the organic component as part of a transition metal complex subunit, complex cation or complex coordination polymer.[7–9] A structural characteristic common to several of these organic–inorganic composite materials is the presence of octamolybdate [Mo$_8$O$_{26}$]$^{4-}$ clusters as fundamental building blocks of one-, two- or three-dimensional covalently linked solids. Since the heterometal–organoamine substructure serves to link the molybdate clusters through {Mo–O–M′} bridges, the overall structure of the oxide phase reflects the coordination preferences of the heterometal and the geometry of the ligand, as manifested both by donor group orientation and spacer length and topology. As part of our continuing program in the synthesis and structural characterization of organic–inorganic oxide composite materials, we are exploring the influences of ligand geometries on the inorganic microstructures. In a previous communication,[7] structures incorporating the rigid rodlike ligand 4,4′-bipyridine (4,4′-bpy) were reported. The donor group distance may be readily lengthened by inserting a spacer between pyridine donors, as in 1,2-bis(4-pyridyl)ethylene (bpe), or may be diminished by incorporating the nitrogen donors into the same ring, as in pyridazine (pyrd). This expedient provides two new members of this family of molybdenum oxides, [{Cu(bpe)}$_4$(Mo$_8$O$_{26}$)]·4H$_2$O **1** and [{Cu(pyrd)}$_4$(H$_4$Mo$_8$O$_{26}$)] **2**.

The hydrothermal reaction of Cu(NO$_3$)$_2$·2.5H$_2$O, MoO$_3$, bpe, and water in the mole ratio 1:1.39:1.72:2470 at 200 °C for 25.5 h produced small orange crystals of **1** in 40% yield. Similarly, the reaction of CuSO$_4$·5H$_2$O, MoO$_3$, pyridazine and water in the mole ratio 1:1:1.26:1690 at 200 °C for 48 h yielded black rhombs of **2** in 85% yield. The infrared spectrum of **1** displayed features at 813 and 840 cm$^{-1}$ attributed to $\nu$(Mo–O–Mo) and strong bands at 910 and 922 cm$^{-1}$ associated with $\nu$(Mo=O). In contrast, the infrared spectrum of **2** exhibited a complex pattern of ten bands in the 670–940 cm$^{-1}$ range, including strong bands at 945, 939, 897 and 888 cm$^{-1}$ attributed to $\nu$(Mo=O) for the presence of both Mo(v) and Mo(vi) centers.

The structure of **1**,† illustrated in Fig. 1, consists of α-[Mo$_8$O$_{26}$]$^{4-}$ clusters[10] linked by {Cu(bpe)}$_n^{n+}$ chains into a two-dimensional sheet. Each cluster employs the terminal oxogroups of the two capping tetrahedral {MoO$_4$} units to bridge to the {Cu(bpe)}$_n^{n+}$ chains. Each of these oxo-groups bridges two copper sites, one from each of two parallel polymeric



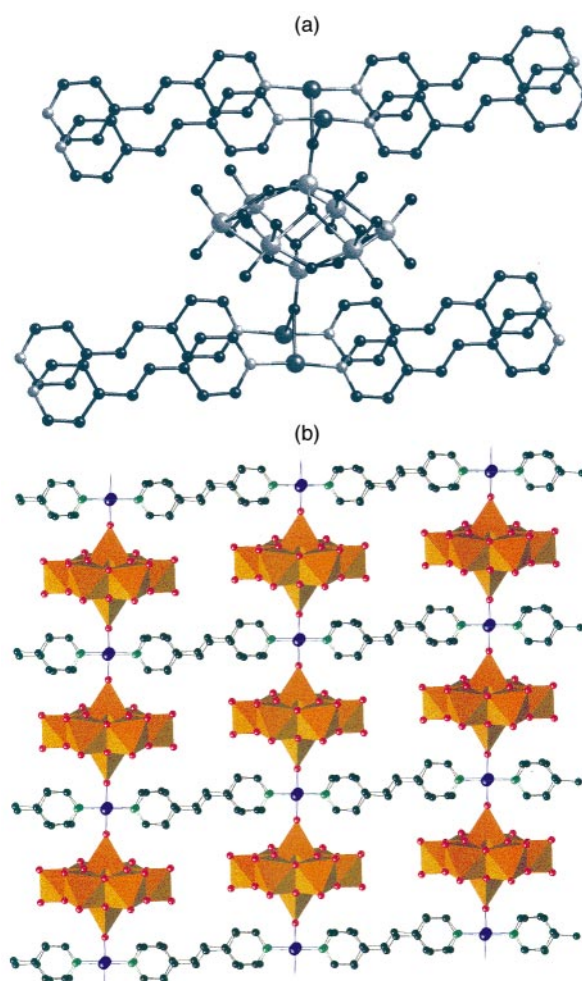**Fig 1** (a) A view of the {α-Mo$_8$O$_{26}$}$^{4-}$ unit linked to four adjacent {Cu(bpe)}$^+$ chains in **1**. Copper atoms are large dark spheres; molybdenum atoms are large lighter spheres. (b) A view of the [{Cu(bpe)}$_2$(Mo$_8$O$_{26}$)]$^{2-}$ sheets. Molybdenum polyhedra are shown in yellow; copper are large blue spheres; nitrogen atoms are small green spheres; oxygen atoms are red spheres. Selected bond lengths (Å): Cu1–N, 1.88(1) and 1.90(1); Cu2–N, 1.920(9) and 1.93(1); Cu2–O, 2.442(8) and 2.461(8); tetrahedral Mo-site Mo–O, 1.77(1) (average); octahedral Mo-sites Mo–O, 1.70(1) (average) × 2, 1.91(1) (average) × 2, 2.44 (average) × 2, (H$_4$Mo$_8$O$_{26}$).

chains propagating between pairs of clusters. This arrangement results in a {Cu$_2$O$_2$} rhomb linking pairs of clusters.

The interlamellar region between the [{Cu(bpe)}$_2$(Mo$_8$O$_{26}$)]$_n^{2n-}$ sheets is occupied by space filling and charge-compensating {Cu(bpe)}$^+$ chains, running parallel to the chains of the layer networks. The result is the common pattern of alternating oxide anion layers and "organic" cation layers.[11]
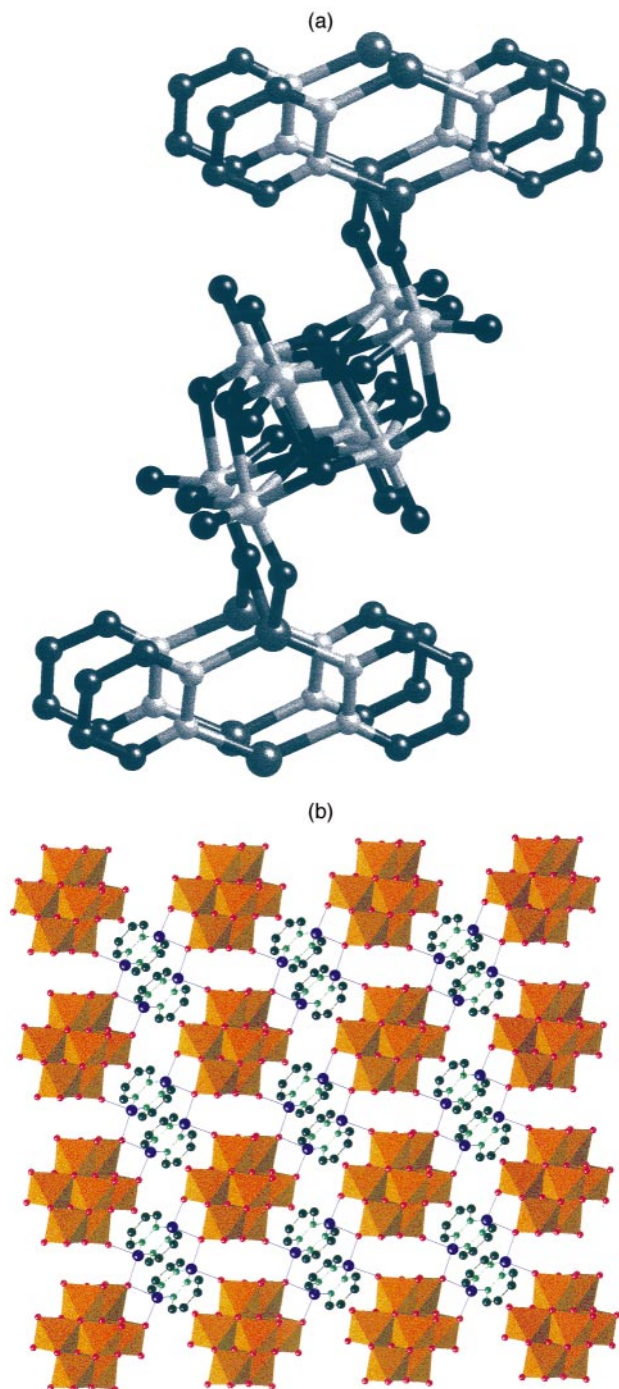
**Fig. 2** (a) A view of the [{Cu(pyrd)}₄(H₄Mo₈O₂₆)] unit of **2**. Copper atoms are large dark spheres; molybdenum atoms are large lighter spheres. (b) The packing of chains in the *ac* plane, color coded as for Fig. 1(b). Selected bond lengths (Å): Cu(1)–N, 1.990(7) and 2.002(6); Cu(1)–O, 2.146(6) and 2.171(6); Cu(2)–N, 1.989(7) and 1.968(7); Cu(2)–O, 2.056(6) and 2.268(6); octahedral Mo-sites: Mo1–O1, 1.697(8); Mo1–O2, 1.758(5); Mo1–O9, 1.957(5); Mo1–O5, 1.962(8); Mo–O10, 2.141(5) and 2.404(5); Mo2–O7, 1.700(6); Mo2–O12, 1.718(8); Mo2–O8, 1.904(5); Mo2–O5, 2.025(5); Mo2–O10, 2.277(5); Mo2–O9, 2.411(5); Mo(3)–O3, 1.713(6); Mo3–O13, 1.729(5); Mo3–O6, 1.912(8); Mo3–O9, 1.996(5); Mo3–O5, 2.325(5); Mo3–O10, 2.354; Mo4–O11, 1.751(5); Mo4–O1, 1.709(6); Mo4–O8, 1.923(6); Mo4–O6, 1.928(8); Mo4–O2, 2.225(5). The average valence sum for the Mo-sites is *ca.* 5.5, while those for the γ-Mo₈O₂₆⁴⁻ cluster of ref. 13 are +6.0.

The structure contrasts dramatically with that of the analogous 4,4′-bpy solid, [{Cu(4,4′-bpy)}₄(Mo₈O₂₆)].[7] This latter material displays δ-[Mo₈O₂₆]⁴⁻ clusters entrained in a matrix of {Cu(4,4′-bpy)}ₙⁿ⁺ polymer chains, disposed in layers of parallel chains with perpendicular chains intervening between layers and molybdate clusters.

The incorporation of pyridazine in place of bpe has dramatic

consequences on both the inorganic microstructure and the properties of the material [{Cu(pyrd)}₄(H₄Mo₈O₂₆)] **2** shown in Fig. 2.‡ In this instance, the clusters adopt the γ-molybdate structure with six six-coordinate and two five-coordinate Mo sites. Each molybdate cluster bonds to four {Cu₂(pyrd)₂} units, which are present in the form of tetranuclear {Cu₄O₆(pyrd)₄} clusters. The copper clusters consist of pairs of oxo-bridged copper tetrahedra which are linked through four pyridazine ligands, in such a fashion as to generate a Cu₄ box of dimensions 3.25 × 3.02 Å with π-stacked pyridazine rings. Each {Cu₄O₆-(pyrd)₄} cluster links a molybdate cluster to three neighboring molybdate units. The resultant two-dimensional structure may be described in terms of the corner-sharing of polyhedra from two distinct cluster types.

The crystals of **2** are black, indicative of mixed valence. Valence sum calculations[12] confirm that the average oxidation state of the Mo sites is +5.5, rather than +6 for the fully oxidized form.[13] Similarly, valence sum calculations on the Cu sites provide an average oxidation state of +1.0, suggesting that the components of **2** may be described as [Cu₄(pyrd)₄]⁴⁺ and [H₄Mo₈O₂₆]⁴⁻. Charge compensation is achieved by protonation of the triply-bridging and quadruply-bridging oxo-groups, which exhibit valence sums of 1.00 to 1.50 in the absence of protonation. The occurrence of a reduced form for any isomeric type of an octamolybdate cluster is unexpected since reduced clusters are observed exclusively for "naked" polyanion aggregates which are constructed from polyhedra with one terminal oxo-group, classified as type I.[14] While the "naked" γ-{Mo₈O₂₆}ⁿ⁻ cluster is a type II polyanion, and consequently exhibits irreversible reduction, the molybdenum oxide component of solid phase **2** exhibits covalent bonding to the copper sites through six terminal oxo-groups, rendering the cluster, in a sense, type I. Alternatively, the reduced form of the cluster may be considered to be stabilized by covalent linkage to the cationic copper–pyridazine clusters which provide charge delocalization. It is also noteworthy that the valence sum calculations indicate that the four additional cluster electrons of the {H₄Mo₈O₂₆}⁴⁻ units are not localized on specific sites but rather delocalized throughout the cluster. Magnetic susceptibility studies of **2** indicate that the material is effectively diamagnetic at room temperature, with a transition below 14 K to a ferromagnetic or canted antiferromagnetic state.

The isolation of the title compounds demonstrates that discrete clusters may be exploited as building blocks in the synthesis of two-dimensional networks.[15] The exploitation of hydrothermal conditions requires a shift in paradigm from the thermodynamic to the kinetic, such that equilibrium phases are replaced by structurally more complex metastable phases.[16] The structure-directing role of the organic component is manifest in the copper coordination complex cationic components which interact with the anionic molybdate clusters in a geometric correspondence which produces the architecture of the network. While it may be premature to classify such synthesis as "designed", it should be noted that preformed clusters or conditions favoring cluster aggregation are required for the preparation of such materials.

## Acknowledgements

## Notes and references

† Crystal data for C₂₄H₂₄Cu₂Mo₄N₄O₁₅ (**1**): *M* = 1758.05, triclinic, *P*1̄, *a* = 10.5793(1), *b* = 13.1590(2), *c* = 13.5431(3) Å, *a* = 106.86(2), *β* = 100.885(1) *γ* = 96.035(1)°, *U* = 1639.25(5) Å³, *Z* = 2, *D*꜀ = 2.268 g cm⁻³, *T* = 293(2) K, *μ* = 4.812 mm⁻¹; structure solution and refinement based on 7038 reflections converged at *R*1 = 0.0722, *wR*2 = 0.1294.
‡ Crystal data for C₁₆H₂₀Cu₄Mo₈N₈O₂₆ (**2**): *M* = 1119.31, triclinic, *P*1̄, *a* = 9.8995(4), *b* = 9.9102(3), *c* = 10.6930(4) Å, *a* = 89.093(1), *β* = 72.909(1), *γ* = 72.650(1)°, *U* = 954.13(6) Å³, *Z* = 1, *D*꜀ = 3.060 g cm⁻³, *T* = 293(2) K, *μ* = 2.833 mm⁻¹; structure solution and refinement based on 4237 reflections converged at *R*1 = 0.0579, *wR*2 = 0.1517. CCDC reference number 186/1200.

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