# Organic–inorganic composite oxide phases: one-dimensional molybdenum oxide chains entrained within a three-dimensional coordination complex cationic framework in [{$Cu_2$(triazolate)$_2$($H_2O$)$_2$}$Mo_4O_{13}$]

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**The hydrothermal reaction of $MoO_3$, $CuSO_4{\cdot}5H_2O$, 1,2,4-triazole and $H_2O$ produces a 50% yield of [{$Cu_2$(triazolate)$_2$($H_2O$)$_2$}$Mo_4O_{13}$], a material constructed from $\{Mo_4O_{13}\}_n^{2n-}$ chains entrained within the three dimensional framework provided by the {$Cu_2$(triazolate)$_2$($H_2O$)$_2$}$_n^{2n+}$ polymeric complex.**

Inorganic oxides constitute a vast family of materials which are ubiquitous as both naturally occurring and synthetic materials[1] and are endowed with a range of physical properties giving rise to applications in areas as diverse as heavy construction, sorption, catalysis, biomineralization and microelectronics.[2,3] The recent elaboration of the chemistries of zeolites,[4] mesoporous materials of the MCM-41 class,[5] biomineralized materials,[6] and organically templated transition metal phosphates[7] has led to an appreciation of the dramatic influence of organic components on the microstructures of inorganic oxides.

We have recently described a fifth major class in which organic materials exert a significant structural role in controlling the architecture of the inorganic oxide: the organically templated molybdenum oxides.[8–13] A subclass of these new materials was inspired by the diversity of topologies adopted by metal–dipodal organonitrogen ligand complexes,[14] whose variability of channel dimensions suggested that metal oxide anionic units could be incorporated into the void space of the cationic skeleton. This strategy has provided a variety of novel molybdenum oxides coexisting with mononuclear, binuclear, trinuclear, and one- and two-dimensional coordination complex cations, of which [{Cu(4,4′-bpy)}$_4$$Mo_{15}O_{47}$],[8] [Cu(4,4′-bipyridylamine)$_{0.5}$$MoO_4$], and [Cu{1,2-*trans*-(4-pyridyl)ethene}-$MoO_4$][15] are representative examples. However, in no instance of a dipodal ligand was a three-dimensional cationic framework observed for the molybdate family of composites, despite introduction of $M^{II}$ sites with octahedral coordination preferences. Recent studies on crystal engineering of three-dimensional frameworks[16] suggested that tripodal or higher denticity ligands with appropriate donor group orientation may favor three-dimensional architectures, although the coordination preferences of the $M^{II}$ site and interactions with the oxide substructure may also influence the structure. Inspired by these results, 1,2,4-triazole was introduced as the organic component for a copper molybdate phase. The expectation of a three-dimensional cationic framework was realized in the isolation of [{$Cu_2$(triazolate)$_2$($H_2O$)$_2$}$Mo_4O_{13}$] **1**.

The hydrothermal reaction of $MoO_3$, $CuSO_4{\cdot}5H_2O$, 1,2,4-triazole and $H_2O$ in the mole ratio 1 : 1 : 1 : 1817 for 72 h at 200 °C yielded blue crystals of **1** as a monophasic material in *ca*. 50% yield. The IR spectrum of **1** exhibited a strong band at 954 $cm^{-1}$ ascribed to $\nu$(Mo=O) and a series of bands in the 720–920 $cm^{-1}$ region characteristic of $\nu$(Mo–O–Mo).

As shown in Fig. 1, the structure† of **1**$^+$ consists of one-dimensional $\{Mo_4O_{13}\}_n^{2n-}$ chains entrained within the three-dimensional framework of the {$Cu_2$(triazolate)$_2$($H_2O$)$_2$}$_n^{2n+}$ polymeric coordination cation. There are two unique copper sites in the cationic framework. One site Cu(A) is effectively square pyramidal $\{CuN_4O\}$ through ligation to four triazolate nitrogen donors, one from each of four triazolate ligands and to a terminal oxo-group of the molybdate chain. The second site Cu(B) is octahedral $\{CuN_2O_4\}$, exhibiting coordination to two *trans* disposed triazolate nitrogen donors, two aquo ligands, and two terminal oxo-groups of the molybdate chains. The organic moiety adopts the anionic triazolate form in a three connect ligation mode. The resulting cationic framework is constructed from undulating chains of Cu(A) sites bridged through the 1,2-nitrogen donors of the triazolate ligands and linked to adjacent chains through the Cu(B) centers which coordinate to the remaining 4-nitrogen donors of the triazolate ligands (Fig. 2). This connectivity pattern produces a honeycomb network when viewed along the crystallographic *c* axis. Furthermore, the disposition of bridging triazolate ligands about a chain results in linkage to four adjacent parallel chains (Fig. 1) giving rise to large tunnels which are occupied by the molybdate chains.

The undulating molybdate chain, Fig. 3, is constructed from edge-sharing molybdenum octahedra and tetrahedra. It is noteworthy that the polyhedral connectivity within these $\{Mo_4O_{13}\}_n^{2n-}$ chains is distinct from that reported for other one-dimensional molybdenum oxides: $K_2Mo_3O_{10}$, $(NH_4)_2Mo_3O_{10}$, $(H_3NCH_2CH_2NH_3)Mo_3O_{10}$, $[H_3N(CH_2)_6NH_3]$-$Mo_3O_{10}$, $Na(NH_4)Mo_3O_{10}$ and [{Cu(4,4′-bpy)}$_4$$Mo_{15}O_{47}$].[8] The chain structure conforms to the constraints imposed by the copper–triazolate framework and the coordination requirements of the $Cu^{II}$ sites of the framework.

The title compound demonstrates that the structural variability of the cationic scaffolding constructed from appropriately linked transition metal sites extends to 3-D coordination polymers as well as 1-D and 2-D types, with tunable void volumes, providing a domain for the formation of low dimensional metal oxides. The synthetic approach appears to provide a facile method for modification of the structures of metal oxides, employing a ‘ship in the bottle’ approach, and

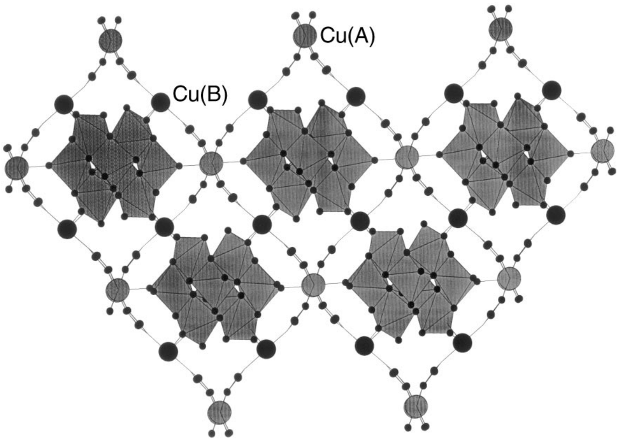

**Fig. 1** A view parallel to the crystallographic *b* axis and to the molybdenum oxide chain of the structure of **1**. The molybdate chain is depicted in polyhedral form. The large lighter spheres are the Cu(A) sites, the smaller darker spheres are the Cu(B) sites.

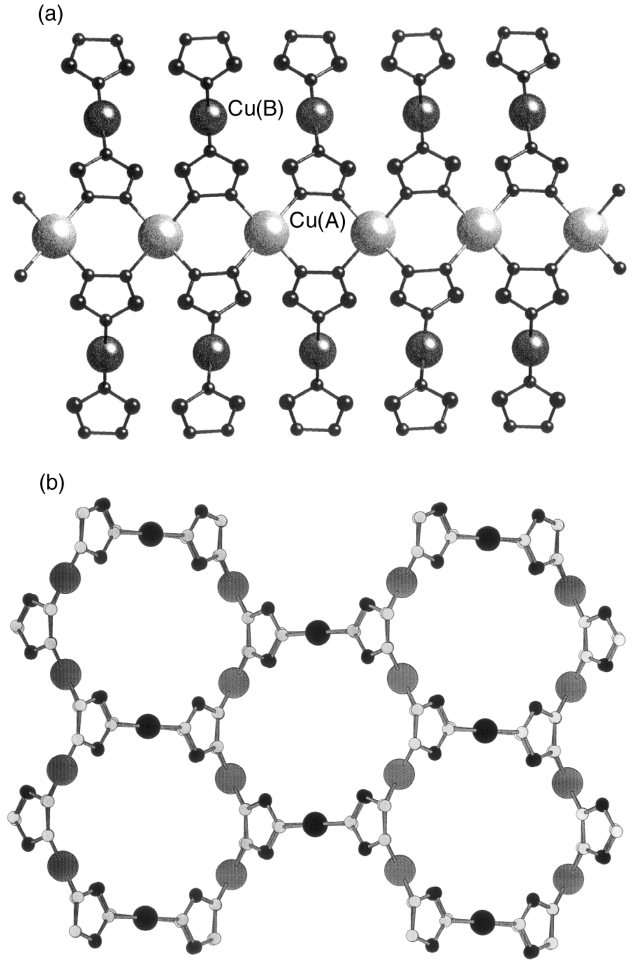

**Fig. 2** (a) A view parallel to the crystallographic *a* axis of the chain formed by triazolate bridged Cu(A) sites (large, lighter spheres) and the linkage through Cu(B) centers (large, darker spheres) to adjacent chains. (b) The honeycomb pattern of the $\{Cu_2(triazolate)_2(H_2O)_2\}_n{}^{2n+}$ framework when viewed parallel to the crystallographic *c* axis. The bonding of the copper sites to the oxide substructure has been omitted for clarity. Selected bond lengths (Å): Cu(A)–N(×4) 1.993(5), Cu(A)–O(10) 2.343(4), Cu(B)–N(×2) 1.947(5), Cu(B)–O 2.000(5)(×2) 2.328(4)(×2).

ultimately for tuning of electronic, magnetic and optical properties of these phases.

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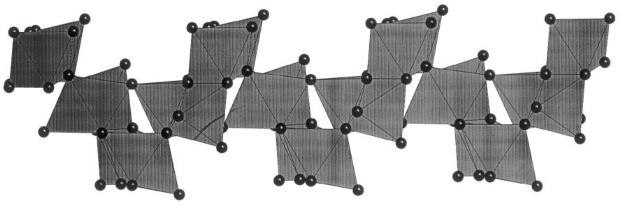

**Fig. 3** A polyhedral view of the molybdenum oxide $\{Mo_4O_{13}\}_n{}^{2n-}$ chain

## Notes and References

† *Crystal data* for $C_4H_8Cu_2Mo_4N_6O_{15}$ **1**: $M$ = 891.00, monoclinic, space group $P2_1/n$, $a$ = 13.6939(3), $b$ = 7.7967(1), $c$ = 17.2311(4) Å, $\beta$ = 89.8570(9)°, $V$ = 1839.71(6) Å$^3$, $Z$ = 4, $D_c$ = 3.206 g cm$^{-3}$, $T$ = 243(2) K, $\mu$ = 5.004 cm$^{-1}$, $F(000)$ = 1680; solution and refinement based on 4364 reflections converged at $R1$ = 0.0356 and $wR2$ = 0.0772. CCDC 182/958.

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