On the atomic environment and the mode of action of the catalytic centre in an intercalated oxo–molybdenum complex $[MoO_2\{O_2CC(S)Ph_2\}_2]^{2-}$ for oxygen-transfer reactions

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The title anion accommodated as a pillar in the interlamellar space of a $Zn(^{II})Al^{III}$ double hydroxide (hydrotalcite-like) host is shown by X-ray absorption spectroscopy, supplemented by other studies, to possess three terminal Mo=O groups, in contrast to the two that exist in the dispersed, catalytically active anion.

It is acknowledged that in oxidations catalysed by molybdenum-based enzymes, the $Mo^{IV}O$ species generated after loss of oxygen from the parent $Mo^{VI}O_2$ complex tends to form the catalytically inactive molybdenum(v) oxo dinuclear species ($Mo^{VI}O_2 + Mo^{IV}O \longrightarrow OMo^{V}–O–Mo^{V}O$) thereby suppressing the further oxidation of the organic substrate.[1–3] Some of us have previously shown[4,5] that one effective way in which the activity of oxomolybdenum model enzymes—catalysts that, for example, cleanly oxidise thiols (PhSH) by either dioxygen or air—may be sustained is to insert the sterically and bulky protective complex into the interlamellar spaces of synthetic layered double hydroxides. Typically, cationic $Zn^{II}Al^{III}$ sheet hydroxides,[6] of composition $[Zn_{3-x}Al_x(OH)_6]^{x+}[NO_3]^{x-}\cdot H_2O$ that readily assimilate other anionic entities in place of nitrate, are used for this purpose. Whilst the intercalated anionic oxomolybdenum complex {*i.e.* $[Mo^{VI}O_2\{O_2CC(S)Ph_2\}_2]^{2-}$ **1**} becomes freely accessible to the reactants, as is the case in interlamellar catalysis generally,[7,8] the 'pillaring' complex itself is sterically prevented from binuclear combination because of appreciable interaction between it and the host layered hydroxide. This strategy, which in essence converts **1** from a homogeneous to a uniform[9,10] heterogeneous catalyst, is successful. But what is the precise structure of the resulting catalytically active 'pillar'?

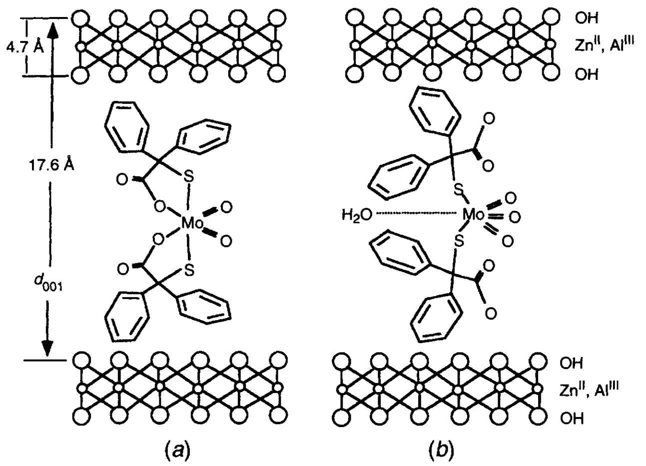

Fig. 1 (*a*) Structure of the intercalated title anion **1** based on d_{001}-spacings and other indirect arguments given in ref. 5. (*b*) The structure deduced from EXAFS [see Fig. 2 (*b*), (*c*)]. The coordination numbers (*N*), bond distances (*R*) in Å, and the Debye–Waller factors ($2\sigma^2$) are respectively: for the Mo=O atom pair, 3.0, 1.74, 0.006; for the Mo–O atom pair, 1.0, 2.46, 0.011; and for the Mo–S atom pair, 2.0, 2.43, 0.017.

This question cannot be answered by conventional X-ray crystallography because the intercalated complex yields a solid that lacks adequate long-range three-dimensional order. A

$$[Mo^{IV}O_2\{O_2CC(S)Ph_2\}_2]^{2-} + 2H_2O \xrightarrow{\text{Zn–Al hydroxide}} [Mo^{VI}O_3\{O_2CC(S)Ph_2\}_2(H_2O)]^{4-} + 2H^+$$

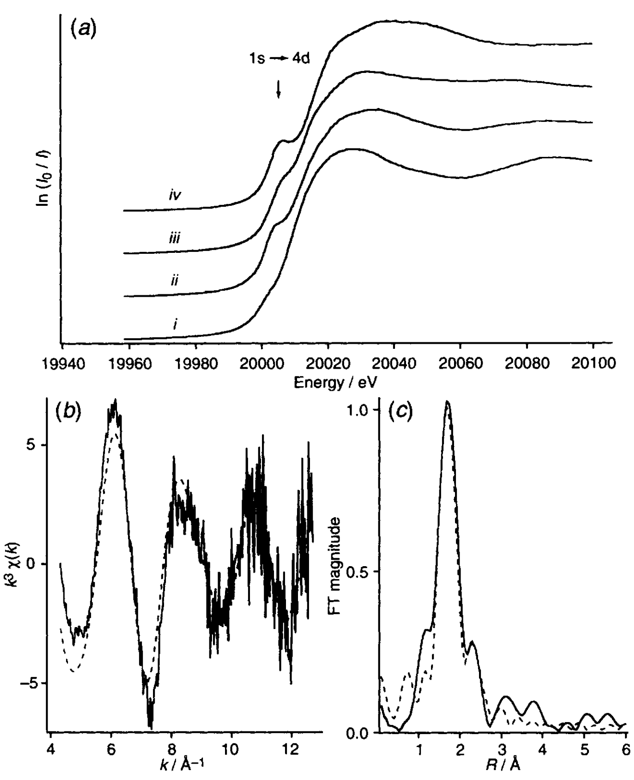

Fig. 2 (*a*) Mo K-edge XANES spectra of (*i*) $[NBu^n_4]Na\ [Mo^{VI}\{O_2CC(S)Ph_2\}_3]$; (*ii*) $[NBu^n_4]\ [Mo^{V}O\{O_2CC(S)Ph_2\}_2]$; (*iii*) $[NH_4]_2[Mo^{VI}\{O_2\{O_2CC(S)Ph_2\}_2]$; (*iv*) anion **1** intercalated into Zn–Al hydrotalcite (see text). (*b*) Mo K-edge EXAFS and (*c*) the associated Fourier transforms of the $[NH_4]_2[Mo^{VI}O_2\{O_2CC(S)Ph_2\}_2]$ intercalated material. The solid and the dashed lines represent the experimental and calculated data, respectively. [XRA data recorded at station 9.2 of the SRS Daresbury Laboratory (typical current 150–250 mA, 2.0 GeV energy). This station was equipped with an Si(220) monochromator, ion chambers and a fluorescence detector for measuring XRA spectra. A typical *k*-range of 3–13 $Å^{-1}$ was used for the analysis using the suite of programs EXCALIB, EXBROOK and EXCURV92.]

plausible model has, however, been hitherto proposed [Fig. 1(*a*)] based on evidence accumulated from X-ray powder diffraction patterns, as well as from IR and diffuse reflectance spectroscopy. But X-ray absorption spectroscopy (XRA) provides a direct means of answering the question; and the structure that emerges (see below) is that shown in Fig. 1(*b*).

Full details of the structural analysis and the ratiocinative arguments upon which Fig. 1(*b*) is based will be reported elsewhere. Briefly, some of the interlamellar nitrate ions of the synthetic Zn,Al layered hydrotalcite-like host were replaced by complex **1** thereby yielding a material $\{[\mathrm{Zn}_{3-x}\mathrm{Al}_x(\mathrm{OH})_6]^{x+}$-$[\mathrm{NO}_3]^-_{x-y}\mathbf{1}_{y/2}\}\mathrm{H_2O}(x = 0.25)$, that is indefinitely stable in air. Its $\{00l\}$ X-ray reflections are shifted, compared to those of the parent hydrotalcite nitrate, to an extent that signifies an interlamellar expansion (d_{001}) to 17.6 Å. Although solid-state ^{13}C (CPMAS) NMR, XPS and UV–VIS spectroscopy provide powerful corroborative evidence, the key information pointing to the structure in Fig. 1(*b*) comes from XRA measurements on the active, intercalated catalyst and on the following comparator materials: $[\mathrm{NH_4}]_2[\mathrm{Mo^{VI}O_2}\{\mathrm{O_2CC(S)Ph_2}\}_2]$, $[\mathrm{NBu^n_4}][\mathrm{Mo^VO}$-$\{\mathrm{O_2CC(S)Ph_2}\}]$ and $[\mathrm{NBu^n_4}]\mathrm{Na}[\mathrm{Mo^{IV}}\{\mathrm{O_2CC(S)Ph_2}\}_3]$.

Fig. 2(*a*) shows the respective X-ray absorption near-edge (XANES) structures, and Fig. 2(*b*) and (*c*) the experimental and fitted extended X-ray absorption fine-structures (EXAFS) for the intercalated complex **1** using the structural parameters summarised (Fig. 1). It is significant that the characteristic low-energy feature [in XANES, Fig. 2(*a*)] amounting almost to a resolved separate peak is exactly what one would expect[11–13] from an increasing number of Mo=O bonds. This peak is attributable to a bound-state transition, which is primarily of 1s → 4d character. Further support for the proposed structure [Fig. 1(*b*)] comes from a bond valence sum analysis[14] which gives acceptable values for the oxidation state of the central molybdenum.

The chemico-catalytic consequences of the intercalated complex **1**, with its $\mathrm{MoO_3S_2(H_2O)}$ active site, prompts us to propose that disassociation of coordinated carboxylate groups in the $\mathrm{Mo^{VI}O_2}$ complex is the first step which induces sufficient positive charge on the $\mathrm{Mo^{VI}}$ centre to allow an oxygen atom transfer from a contiguous molecule of water with no change in the oxidation state of Mo.

Such a reaction must be reversible since UV–VIS spectra of solutions containing pure $[\mathrm{NH_4}]_2[\mathrm{Mo^{VI}O_2}\{\mathrm{O_2CO(S)Ph_2}\}_2]$ and the extracted complex, back-exchanged by shaking with an alcoholic solution of ammonium nitrate, are found to be identical.

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