Intercalation of the Oxo-transfer Molybdenum(VI) Complex $[MoO_2\{O_2CC(S)Ph_2\}_2]^{2-}$ into a Zinc(II)–Aluminium(III) Layered Double Hydroxide Host. Catalysis of the Air Oxidation of Thiols†

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The intercalation of bis(2,2-diphenyl-2-sulfidoacetato)dioxomolybdate(VI) $[MoO_2\{O_2CC(S)Ph_2\}_2]^{2-}$ **1** into an hydrotalcite-like zinc(II)–aluminium(III) layered double hydroxide by anion exchange yielded $[Zn_{3-x}Al_x(OH)_6]^{x+}[\{MoO_2[O_2CC(S)Ph_2]_2\}_{\frac{y}{2}}(NO_3)_{x-y}]^{x-}\cdot H_2O$ ($x = 0.75$). Data from powder X-ray diffraction, IR and diffuse reflectance spectroscopy and thermogravimetric analysis confirmed intercalation within a 13 Å-height gallery, indicating that the molybdenum anion probably lies with its *cis*-dioxomolybdenum(VI) plane parallel to the hydroxide layers. Complex **1**, immobilized in the layered double hydroxide, operates as an effective heterogeneous catalyst for the oxidation of thiols (PhSH) by either dioxygen or air as evaluated by gas chromatography. The active oxidant is $[MoO_2\{O_2CC(S)Ph_2\}_2]^{2-}$, while a molybdenum(IV) species acts as the reductant by interaction with dioxygen to regenerate the molybdenum(VI) oxidant. This constitutes the first reported heterogeneous catalyst containing an oxo-transfer $Mo^{VI}O_2$ complex capable of activating dioxygen. Oxidation proceeds in ethanolic solutions without deactivation by water or excess thiol even at relatively high temperatures (up to 80 °C). It is, therefore, concluded that intercalation of $[MoO_2\{O_2CC(S)Ph_2\}_2]^{2-}$ into the layered double hydroxide host inhibits the formation of a catalytically inactive molybdenum(V) species which was previously observed under homogeneous conditions.

Of all elements, the oxygen-atom transfer chemistry of molybdenum is the most extensively investigated and best understood. Comprehensive accounts of molybdenum-mediated oxo-transfer reactions are available.[1] In general, one oxygen atom can be removed from the starting $Mo^{VI}O_2$ complex containing sulfur-donor ligands, but the reactivity of the reduced $Mo^{IV}O$ products reveals some of the complications inherent in molybdenum solution chemistry. Thus, the $Mo^{IV}O$ complex interacts with the unreacted $Mo^{VI}O_2$ complex to form the corresponding oxo-bridged molybdenum(V) dimer according to equation (1).

$$Mo^{VI}O_2 + Mo^{IV}O \longrightarrow OMo^{V}\text{–}O\text{–}Mo^{V}O \qquad (1)$$

Taking into account that the formation of these catalytically inactive molybdenum(V) species occurs irreversibly in most of the studied systems, large multidentate ligands have been devised to prevent this dimerization of the oxo Mo^{VI}–Mo^{IV} monomers. Two sterically bulky ligands figure prominently in the catalytic chemistry of molybdenum complexes, namely the tridentate 2,6-bis(2,2-diphenyl-2-sulfanylethyl)pyridine (H_2L),[2] and the tetradentate hydrotris(3,5-dimethylpyrazol-yl)-borate(1 −).[3] Only the former complex, $[Mo^{VI}O_2L]$, has been demonstrated as being cleanly reduced by arenethiols whose more acidic character has been assumed to promote the protonation and subsequent loss of one of the two terminal oxo ligands.[4] By reoxidizing the $[Mo^{IV}OL]$ product with an oxo-donor compound such as Me_2SO, catalytic cycles were also developed under homogeneous conditions. However, there were found certain limitations for this catalytic system. First, both the oxidized and reduced complexes are neutral charged species only soluble in aprotic organic solvents such as dimethylforme in which only the more acidic arenethiols react at an appreciable rate, *e.g.* the reaction was 63% complete after 62 h. Secondly, one or both complexes are unstable in the presence of an excess of thiol and consequently only a low number of catalytic cycles, *ca.* 4 turnovers in 108 h, could be achieved.

We have previously synthesized the anionic $[Mo^{VI}O_2\{O_2CC(S)Ph_2\}_2]^{2-}$ **1** complex,[5] [$O_2CC(S)Ph_2{}^{2-}$ being the sterically hindered dianionic 2,2-diphenyl-2-sulfidoacetate ligand]. It is the first dioxomolybdenum(VI) compound showing a definite capacity to oxidize aliphatic thiols. However, the comproportionation reaction between **1** and its reduced $Mo^{IV}O$ complex leads to the formation of the monomeric molybdenum(V) complex $[Mo^{V}O\{O_2CC(S)Ph_2\}_2]^-$ **2** at acidic pH.[6] Such a particular feature also implies an important limitation to the catalytic activity of **1**. In fact, contrary to all $Mo^{IV}O$ complexes tested so far, complex **2** shows no reducing capacity on common oxidants such as dialkyl *S*-oxides, amine *N*-oxides and dioxygen.

To prevent the formation of catalytically inactive dimeric or monomeric molybdenum(V) species as well as to make possible the use of protic solvents including water, we herein propose and demonstrate the potential of a novel strategy which is applicable to complexes with an anionic character. It consists in their intercalation within a layered double hydroxide (l.d.h.) system. Layered double hydroxides consist of positively charged brucite-like layers separated by charge-balancing hydrated gallery anions.[7] A broad range of compositions of the type $[M^{2+}{}_{3-x}M^{3+}{}_x(OH)_6][A^{n-}]_{x/n}\cdot yH_2O$ ($x = 0.51$–1.00) are

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† *Non-SI unit employed:* atm = 101 325 Pa.

possible, wherein the M^{2+} and M^{3+} occupy octahedral positions in the hydroxide layers and A^{n-} is an exchangeable gallery anion.[8] Recent advances in the pillaring of l.d.h.s by polyoxometalate anions have demonstrated that these microporous materials exhibit large gallery heights suitable for the catalytic oxidation of organic compounds.[9] Their preparation, properties and applications have been reviewed recently.[10]

Most of the polyoxometalates intercalated in l.d.h.s have been prepared by ion-exchange methods. Specifically, well ordered zinc(II)–aluminium(III) l.d.h.s that incorporate $V_{10}O_{28}{}^{6-}$ or α-1,2,3-$[SiV_3W_9O_{40}]^{7-}$ polyoxometalates have been obtained by ion-exchange reactions of simple l.d.h. (A = Cl^- or $NO_3{}^-$) precursors.[11] However, exchange reactions can be slow, particularly with large anions, and other procedures such as the reconstitution of mixed metal-oxide solids, are also known. Thus, the intercalation of the cobalt(II) phthalocyaninetetrasulfonate anion $[CoL']^{4-}$, into a magnesium(II)–aluminium(III) l.d.h. was carried out by reaction of $Mg_{0.63}Al_{0.25}\square_{0.12}O$ (□ = vacancy), prepared by the thermal decomposition of $[Mg_5Al_2(OH)_{14}]CO_3{\cdot}xH_2O$ at 500 °C, with the $[CoL']^{4-}$ ion in aqueous solution.[12] In catalysing the air oxidation of thiols at alkaline pH (9.25), this intercalated cobalt(II) complex was twice as active as the homogeneous complex under equivalent reaction conditions.

To our knowledge, interlayered systems containing oxo-transfer molybdenum complexes have not been previously reported and herein we describe the synthesis of the l.d.h. $[Zn_{2.25}Al_{0.75}(OH)_6]^{0.75+}[\{MoO_2[O_2CC(S)Ph_2]_2\}_{\frac{y}{2}}\text{-}(NO_3)_{0.75-y}]^{0.75-}{\cdot}H_2O$ [l.d.h. (A = **1**, $NO_3{}^-$)] as well as its action as a heterogeneous catalyst in the oxidation of thiophenol by dioxygen.

Results and Discussion

Characterization of the Hydrotalcite-like Compounds.—The X-ray powder diffraction pattern for the l.d.h. (A = $NO_3{}^-$), Fig. 1(*a*), shows two sharp peaks indexed as (003) and (006) at 8.9 and 4.45 Å, respectively, by assuming the rhombohedral symmetry previously assigned by Miyata[8a] to a similar material. No other phase was observed in this diffraction pattern indicating that only nitrate ions are intercalated in the zinc–aluminium hydroxide layers.

Partial replacement of nitrate ions by the dianionic complex **1**, following the procedure described in the Experimental section, causes a decrease in the intensity of these two peaks assigned to the l.d.h. (A = $NO_3{}^-$) phase which is accompanied by the appearance of three new peaks at 17.6, 8.8 and 5.8 Å [Fig. 1(*b*)]. From the new (00*l*) harmonics, characteristic of a pillared l.d.h. phase, a basal spacing of 17.6 Å was calculated. Since the van der Waals thickness of the brucite sheets is *ca.* 4.7 Å,[13,8a] the calculated basal spacing was indicative of a gallery height of *ca.* 12.9 Å. Such a result together with other previous parameters (12.6 Å)[5] found in a single crystal of its ammonium salt indicate that the dianionic complex **1** intercalates with its C_2 axis parallel to the metal hydroxide layers as shown in Fig. 2. Such an orientation allows both molybdenum co-ordinated oxo groups to interact with potential substrates in gallery centres, away from the zinc–aluminium oxygen layers.

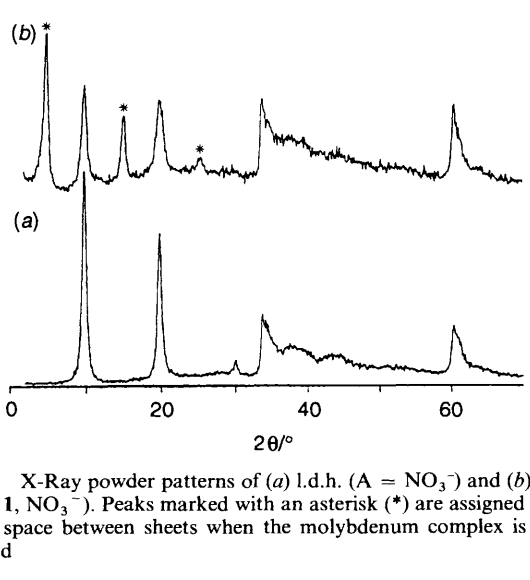


Fig. 1 X-Ray powder patterns of (*a*) l.d.h. (A = $NO_3{}^-$) and (*b*) l.d.h. (A = **1**, $NO_3{}^-$). Peaks marked with an asterisk (*) are assigned to the basal space between sheets when the molybdenum complex is intercalated

While for a methanolic solution of **1** only one band[6] at 374 nm can be observed, the UV/VIS spectrum of l.d.h. (A = **1**, $NO_3{}^-$) displays two bands at 356 and 275 nm whose absorbance ratio was A_{356}/A_{275} = 2.5. Since the molybdenum(VI) centre does not have any electron in the 4d orbitals, all these absorptions must be considered as ligand-to-metal charge-transfer bands.

Thermogravimetric analysis showed three main endothermic peaks at 507, 535 and 574 K probably related to dehydroxylation and anion loss [Fig. 3(*a*)]. These peaks appear at higher temperatures than that observed by Miyata[8a] for a magnesium(II)–aluminium(III) l.d.h. containing nitrate ions (*ca.* 455 K), indicating a lower interaction of this anion with the zinc(II)–aluminium(III) l.d.h. sheet. The thermogravimetric analysis curve for a sample of l.d.h. (A = **1**, $NO_3{}^-$) showed two additional exothermic peaks at *ca.* 660 and 806 K [Fig. 3(*b*)] that must be assumed to be the decomposition of complex **1** in MoO_3, CO_2 and H_2O. The weight loss corresponding to this decomposition is *ca.* 39.22% which agrees with the chemical composition resulting from the elemental analysis of this l.d.h. (A = **1**, $NO_3{}^-$) sample, expressed by the formula $[Zn_{2.20}Al_{0.80}(OH)_6][\{MoO_2[O_2CC(S)Ph_2]_2\}_{0.13}\text{-}(NO_3)_{0.54}]_{0.13}{\cdot}H_2O$ (see Table 1). No change in the Al/(Al + Zn) ratio was observed between l.d.h. (A = **1**, $NO_3{}^-$) and l.d.h. (A = $NO_3{}^-$), and indicating that leaching of either Zn^{II} or Al^{III} did not occur during the exchange procedure utilized. It is worth noting that our attempts to eliminate the $NO_3{}^-$ ions and form a single-phase l.d.h. (A = **1**, $NO_3{}^-$) were unsuccessful. When a sample of calcinate l.d.h. was stirred in a methanolic solution of **1**, no appreciable intercalation could be observed. However, it is noted that the catalytic properties of l.d.h. (A = **1**, $NO_3{}^-$) do not depend only on the amount of **1** intercalated but also, among other factors, on the accessibility of **1** inside the l.d.h. layer.

Finally, the IR spectrum for l.d.h. (A = NO_3) showed a sharp and strong band at 1382 cm^{-1} that arises from the v_3 stretching

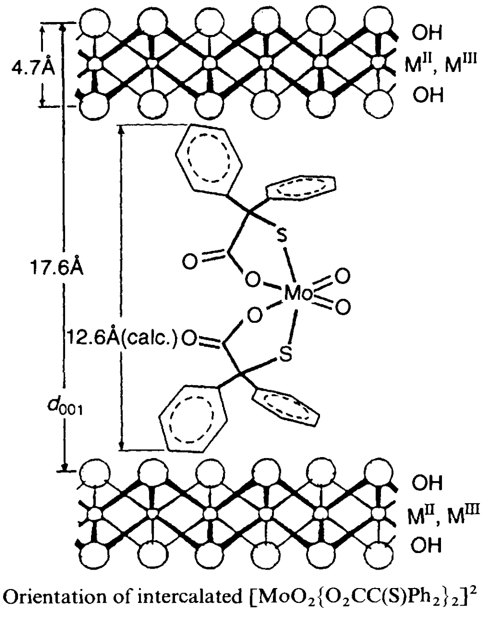


Fig. 2 Orientation of intercalated $[MoO_2\{O_2CC(S)Ph_2\}_2]^{2-}$

Table 1 Analysis of l.d.h. (A = NO_3^-) and l.d.h. (A = **1**, NO_3^-)

	Al (%)	Zn (%)	$[MoO_2\{O_2CC(S)Ph_2\}_2]^{2-}$ (%)	Weight loss (%)
l.d.h. (A = NO_3)	7.43	50.16	—	37.97
l.d.h. (A = **1**, NO_3^-)	4.84	32.08	20.57	39.22

mode of NO_3^-, while the water molecules exhibit a broad bending band ν_2 near 1630 cm^{-1}.[14] The IR spectrum of the yellowish l.d.h. (A = **1**, NO_3^-) product contained bands characteristic of the parent l.d.h. (A = NO_3^-) and the intercalated complex **1**. Thus, the appearance of new bands at 900 (Mo=O) and 1600 cm^{-1} (CO_2^-) constitutes a clear indication of the presence of **1** in the zinc(II)–aluminium(III) l.d.h. host.

Catalytic Properties.—Compared to the *cis*-dioxomolybdenum(VI) complexes with sterically bulky ligands[2,3] mentioned above, our sterically hindered complex **1** exhibits several unique features: (*i*) anionic character; (*ii*) a proven capacity to oxidize aliphatic thiols;[6] (*iii*) the oxidation product is a monomeric anionic Mo^VO complex $[Mo^VO_2\{O_2CC(S)Ph_2\}_2]^-$ **2**, instead of a neutral monomeric $Mo^{IV}O$ complex always given by all other reported systems; and (*iv*) complexes **1** and **2** are stable in slightly acidic media as well as in the presence of excess of thiol and/or moderate amounts of water, while all the other reported complexes decompose under such conditions. The third feature implies, however, an important limitation to the catalytic activity of complex **1**. Such a limitation stems, as noted above, from the well known difficulty of reoxidising Mo^VO to $Mo^{VI}O_2$.[15]

Yet, we must point out that, apparently, complex **2** is not formed directly from $Mo^{VI}O_2$, but *via* an intermediate $Mo^{IV}O$ species, according to equations (2) and (3).[16]

$$\underset{\mathbf{1}}{[Mo^{VI}O_2\{O_2CC(S)Ph_2\}_2]^{2-}} + 2RSH \rightleftharpoons [Mo^{IV}O\{O_2CC(S)Ph_2\}_2]^{2-} + RSSR + H_2O \quad (2)$$

$$\underset{\mathbf{1}}{[Mo^{VI}O_2\{O_2CC(S)Ph_2\}_2]^{2-}} + [Mo^{IV}O\{O_2CC(S)Ph_2\}_2]^{2-} + 2H^+ \rightleftharpoons \underset{\mathbf{2}}{2[Mo^VO\{O_2CC(S)Ph_2\}_2]^-} + H_2O \quad (3)$$

On the basis of these considerations, if **1** is immobilized by electrostatic forces, its required approach to the also immobilized molybdenum(IV) complex to form a Mo^VO species such as **2** would be suppressed, which means that reaction (3) could not proceed. Then, the resulting reduced complex would be a $Mo^{IV}O$ species, which might be expected to be more easily reoxidized to the starting complex **1** in such a way that catalysis could be sustained.

Thus, we undertook a study of the heterogeneous catalytic activity of l.d.h. (A = **1**, NO_3^-) for the oxidation of thiophenol (PhSH) by dioxygen in ethanol at 80 °C. In a typical experiment l.d.h. (A = **1**, NO_3^-) (250 mg; 0.084 mmol of intercalated complex **1**) and a variable excess of PhSH (0.01–0.58 mol) were stirred in ethanol (20 cm^3) containing amberlite IR-120(H) (0.25 g). The progress of the reaction was monitored by gas chromatography over 70 h (Fig. 4).

Alternatively, time–concentration curves (Fig. 4) indicate a much lower catalytic conversion of thiophenol to disulfide when dioxygen was replaced by air. Such a result allows us to propose the reaction cycle in Scheme 1, whereby the thiophenol acts as the electron donor in the reduction of **1** and dioxygen is the electron acceptor in the oxidation reaction of the reduced $Mo^{IV}O$ complex. The coupling of electron and proton transfer allows the direct formation of products without the formation of less stable intermediates, which would then have to be protonated by hydrolysis.

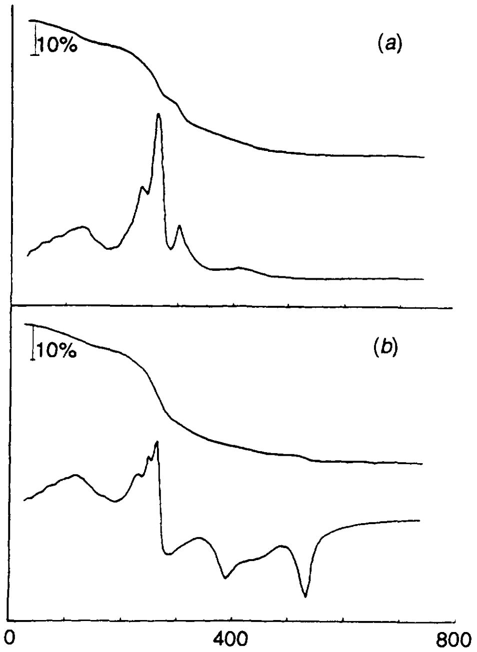


Fig. 3 Differential thermal analysis and thermogravimetric analysis curves for (*a*) l.d.h. (A = NO_3^-) and (*b*) l.d.h. (A = **1**, NO_3^-)

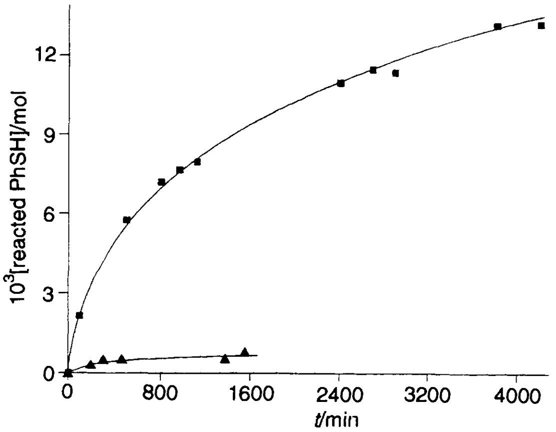


Fig. 4 Thiophenol ($\times 10^3$ mol) oxidized by O_2 (p_{O_2} = 1 atm) (■) and air (p_{air} = 1 atm) (▲) *vs*. time at 353 K in EtOH (20 cm^3). Initial concentration of thiophenol is 3.1 g (28 mmol) in l.d.h. (A = **1**, NO_3^-) (250 mg, 20.57% in **1**) plus protonic amberlite IR-120(H) (250 mg)

Assuming that the initial PhSH oxidation by the accessible intercalated complex **1** is much slower than the oxidation of monomeric $[Mo^{IV}O\{O_2CC(S)Ph_2\}_2]^{2-}$ by O_2, the concentration of **1** can be considered essentially constant, $[\mathbf{1}]_{active}$, during the entire course of the experiment. This implies that the disappearance of PhSH should follow the pseudo-first-order rate law described by equation (4).

$$\ln[PhSH]_0/[PhSH] = k[\mathbf{1}]_{active}\,t = K't \quad (4)$$

Typical plots of ln[PhSH] *vs*. time for reaction systems containing a different initial PhSH concentration $[PhSH]_0$, give straight lines with a nearly constant slope over the entire period of time studied (Fig. 5). Such a result clearly corroborates the thiol oxidation reaction (2) being the rate-limiting process

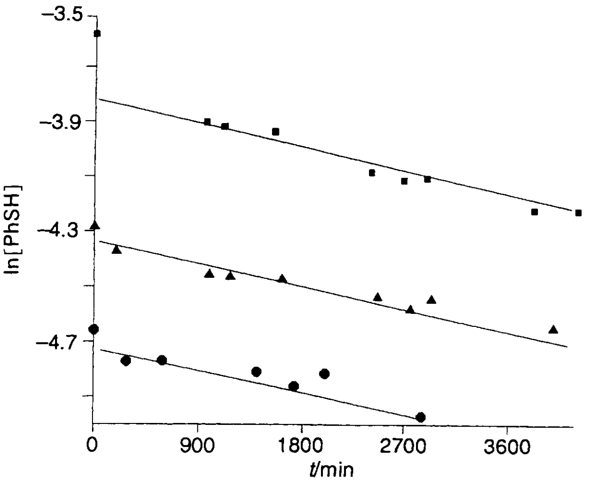
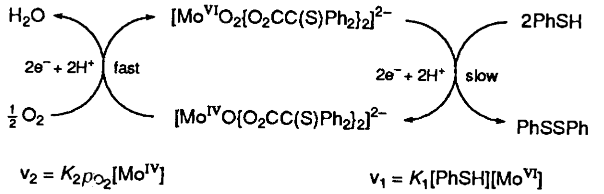


Fig. 5 Pseudo-first-order kinetic plots for the reaction between thiophenol and O_2 at 353 K in EtOH (20 cm^3). Initial concentrations of thiophenol are 3.15 g (28.0 mmol) (■), 1.57 g (14.0 mmol) (▲) and 1.08 g (9.6 mmol) (●) in l.d.h. (A = **1**, NO_3^-) (250 mg, 20.57% in **1**) plus protonic amberlite IR-120(H) (250 mg)



Scheme 1

under these experimental conditions and that the reaction is first order with respect to the concentration of thiol, when this reagent is in a moderate excess (less than 340-fold). No appreciable PhSH oxidation occurred when l.d.h. (A = **1**, NO_3^-) was replaced by l.d.h. (A = NO_3^-).

In an attempt to obtain further evidence to support the assumed nature of this catalytic cycle, a plot of the observed initial rates *vs.* $[PhSH]_0$ was determined for three different temperatures (Fig. 6). Each one of these plots was obtained by varying $[PhSH]_0$ at a constant concentration of l.d.h. (A = **1**, NO_3^-) (0.250 g), temperature and a partial pressure of O_2 of 1 atm; catalytic velocities were determined from the slope at $t = 0$ of plots of [PhSH] *vs.* time. It is evident from Fig. 6 that at adequately high values of [PhSH] substrate saturation kinetics prevail, and thus the reaction rates became virtually independent of [PhSH]. As expected, the [PhSH] concentration needed to reach substrate saturation increases with temperature.

From $v_0 = f[PhSH]_0$ curves in Fig. 6, the value of K' ($= k[\mathbf{1}]_{active}$) at each one of the tested temperatures was obtained by measurement of the slope at $[PhSH]_0$. These pseudo-first-order rate constants were found to be $K'(353\ K) = 7.153 \times 10^{-4}$, $K'(333) = 2.667 \times 10^{-4}$ and $K'(313) = 1.053 \times 10^{-4}\ min^{-1}$. The apparent activation energy obtained by a least-squares fit of these K' values to the Eyring equation was $E_a = 10.5\ kcal\ mol^{-1}$ (*ca.* 43.9 kJ mol^{-1}). Other representative oxo-transfer systems such as $[MoO_2L]$ plus R_3P have activation energies comparable to that for reaction (2) ($E_a = 11.7\ kcal\ mol^{-1}$, *ca.* 49.0 kJ mol^{-1}).[17] Further kinetic experiments are in progress in order to evaluate the above second-order rate constants, K_1 and K_2, indicated in the proposed catalytic cycle and the results will be described in full elsewhere.

Finally, we should mention that under homogeneous conditions and using dimethylformamide as solvent, catalytic aerial oxidations of trialkyl- and triphenyl-phosphines have widely been achieved by using dithiocarbamate complexes of the type $[Mo^{VI}O_2(S_2CNR_2)_2]$.[18] Moreover, dioxygen has been recently utilized for the catalytic oxidation of benzoin to benzyl by $[MoO_2(cysS\text{-}OMe)_2]$ (cysS-OMe = S-deprotonated L-cysteinate methyl ester) and $[Mo^{VI}O_2(S_2CNEt_2)_2]$.[15] These systems, unlike the one reported herein, yield inert μ-oxo dimers which are responsible for the deactivation of the catalyst within the first 20 min, as reported, for example, for $[MoO_2(S_2CNEt_2)_2]$.[15] The present study constitutes, therefore, the first report of a molybdenum-based catalyst for the oxidation of thiols by dioxygen.

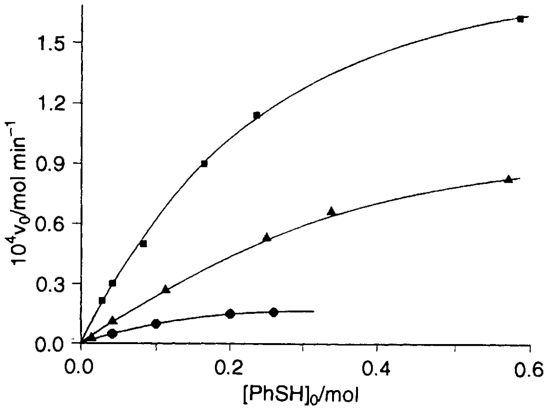


Fig. 6 Variation in the initial rate of the oxidation of thiophenol by O_2 (p_{O_2} = 1 atm) *vs.* the initial concentration of thiophenol; l.d.h. (A = **1**, NO_3^-) (250 mg, 20.57% in **1**) plus protonic amberlite IR-120(H) (250 mg) in EtOH (20 cm^3) at 353 (■), 333 (▲) and 313 K (●)

Conclusion

To our knowledge, this study constitutes the first report of a molybdenum-based catalyst for the oxidation of thiols by molecular oxygen. The bulk of our results concerning the catalytic activity of l.d.h. (A = **1**, NO_3^-) with O_2 as oxidant, are consistent with complex **1** being the active oxidant and a transient $Mo^{IV}O$ species the active reductant. Formation of a mononuclear $Mo^{V}O$ species such as that previously observed under homogeneous conditions [equation (3)] can be ruled out since such a species has been shown to decompose immediately in the presence of dioxygen.[7b] Our results demonstrate the potential of intercalation into l.d.h.s as a new strategy to prevent the formation of monomeric and dimeric molybdenum(V) species. Such a strategy is probably of general applicability to anionic complexes as an alternative to the use of sterically-hindered bulky ligands.[3]

An important advantage of the intercalation strategy is the fact that water can be used as a solvent. We are not aware of any other previously studied $Mo^{VI}O_2$ catalytic system that does not require the use of aprotic solvents, with the water generated during the oxidation of the thiol [reaction (2)] or benzoin precipitating and/or decomposing the molybdenum catalyst.

Experimental

Preparation.—All chemicals were used as purchased without further purification. The zinc–aluminium l.d.h. (A = NO_3^-) was prepared by coprecipitation, using deionized and decarbonated water throughout, according to the following procedure. A solution prepared by dissolving $Zn(NO_3)_2 \cdot 4H_2O$ (97.03 g, 0.36 mol) and $Al(NO_3)_3 \cdot 9H_2O$ (45.93 g, 0.12 mol) in water (180 cm^3) was mixed dropwise with another solution prepared by dissolving NaOH (31.02 g, 0.76 mol) and $NaNO_3$ (54.95 g, 0.64 mol) in water (235 cm^3) to obtain a gel of the composition $2.25\ Zn(NO_3)_2 : 0.75\ Al(NO_3)_3 : 4.75\ NaOH : 4NaNO_3$.

The resulting thick slurry had a pH of 8. It was transferred to a stainless-steel autoclave, in which crystallization took place under autogeneous pressure at 80 °C for 18 h. The solid was then filtered and washed until NO_3^- ions were not detected in the washing water, and afterwards it was dried at 340 K overnight to obtain 41.5 g of l.d.h. (A = NO_3^-). Partial substitution of intercalated nitrate ions by complex **1** was achieved by the addition of the l.d.h. precursor (24 g) to an orange solution of $Na_2[MoO_2\{O_2CC(S)Ph_2\}_2]$ (20.8 g, 29.2 mmol) in glycol–methanol–water (1 : 1 : 1, 2 l), followed by stirring at room temperature for 48 h. The resulting yellowish solid was then washed with methanol and dried in the oven at 340 K for 18 h, giving 26 g of l.d.h. (A = **1**, NO_3^-).

Characterization.—The l.d.h. (A = NO_3^-) precursor and the intercalated catalyst were characterized by powder X-ray diffraction, thermogravimetry, differential thermal analysis, diffuse reflectance and infrared spectroscopy. The powder diffraction spectra were recorded using Cu-Kα radiation on a Phillips PW 1830 diffractometer at a scanning speed of 2.4° min^{-1} and the FTIR and UV/VIS diffuse reflectance spectra on a Nicolet 710 and Shimadzu UV-2101 PC spectrometer, respectively. Thermal analyses were undertaken with a thermobalance STA 409 NETZSCH, using α-Al_2O_3 as reference material.

Catalytic Oxidation of Thiophenol by Dioxygen or Air.—The properties of l.d.h. (A = **1**, NO_3^-) as catalyst for the oxidation of thiophenyl by dioxygen or air were studied in quantitative detail by following the progress of the reaction with a Varian 3400 gas chromatograph equipped with a 15 m phenylmethylsilicone 5% semi-capillary column. Each experiment was conducted by adding l.d.h. (A = **1**, NO_3^-) (0.25 g, 0.084 mmol of intercalated complex) and different amounts of PhSH (0.01–0.58 mol) to ethanol (20 cm^3) which contained Amberlite IR-120 (H) (0.25 g) acting as a proton source. Reactions were carried out at 80 °C under a constant oxygen (or air) pressure of one atmosphere.

Acknowledgements

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References

1 R. H. Holm, *Chem. Rev.*, 1987, **87**, 1401; *Coord. Chem. Rev.*, 1990, **100**, 183.
2 J. M. Berg and R. H. Holm, *J. Am. Chem. Soc.*, 1985, **107**, 917, 925.
3 S. A. Roberts, C. G. Young, W. E. Cleland, R. B. Ortega and J. H. Enemark, *Inorg. Chem.*, 1988, **27**, 3044.
4 J. P. Caradonna, E. W. Harlan and R. H. Holm, *J. Am. Chem. Soc.*, 1986, **108**, 7856.
5 P. Palanca, T. Picher, V. Sanz, P. Gómez-Romero, E. Llopis, A. Doménech and A. Cervilla, *J. Chem. Soc., Chem. Commun.*, 1990, 531.
6 V. Sanz, T. Picher, P. Palanca, E. Llopis, J. A. Ramírez, D. Beltrán and A. Cervilla, *Inorg. Chem.*, 1991, **30**, 3115.
7 (*a*) R. Almann, *Chimia*, 1970, **24**, 99; (*b*) H. F. W. Taylor, *Mineral. Mag.*, 1973, **39**, 377.
8 (*a*) S. Miyata, *Clays Clay Miner.*, 1975, **23**, 369; (*b*) 1980, **28**, 50.
9 T. Tatsumi, K. Yamamoto, H. Tajima and H. Tominaga, *Chem. Lett.*, 1992, 815.
10 F. Cavani, F. Trifiro and A. Vaccari, *Catal. Today*, 1991, **11**, 173.
11 T. Kwon, G. A. Tsigdinos and T. J. Pinnavaia, *J. Am. Chem. Soc.*, 1988, **110**, 3653; E. D. Dimotakis and T. J. Pinnavaia, *Inorg. Chem.*, 1990, **29**, 2393.
12 M. E. Pérez-Bernal, R. Ruano-Casero and T. J. Pinnavaia, *Catal. Lett.*, 1991, **11**, 55.
13 D. D. Elleman and D. Williams, *J. Chem. Phys.*, 1956, **26**, 742.
14 K. Nakamoto, in *Infrared Spectra of Inorganic and Coordination Compounds*, Wiley, New York, 2nd edn., 1970, pp. 88–98.
15 N. Ueyama, N. Yoshinaga and A. Nakamura, *J. Chem. Soc., Dalton Trans.*, 1990, 387.
16 E. Llopis, A. Doménech, J. A. Ramírez, A. Cervilla, P. Palanca, T. Picher and V. Sanz, *Inorg. Chim. Acta*, 1991, **189**, 29.
17 J. P. Caradonna, P. R. Reddy and R. H. Holm, *J. Am. Chem. Soc.*, 1988, **110**, 2139.
18 W. E. Newton, J. L. Corbin, D. C. Bravard, J. E. Searles and J. W. McDonald, *Inorg. Chem.*, 1974, **13**, 1100; R. Barral, C. Bocard, I. Serée de Roch and L. Sajus, *Tetrahedron Lett.*, 1972, 1963; N. Ueyama, M. Yano, H. Miyashita, A. Nakamura, M. Kamachi and S. Nozakamura, *J. Chem. Soc., Dalton Trans.*, 1984, 1447.

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