Synthesis and reactivity of peroxomolybdenum(VI) complexes of the types 
\[\text{[MoO(O}_2\text{)(QO)}_2\text{]} \quad (\text{QO} = 8\text{-quinolinolate anion}) \] and 
\[\text{[MoO(O}_2\text{)]}_2(\text{L} + \text{L}) \] 
(L = neutral N - N donors), and crystal and molecular structure of 
\[\text{(PPN)}_2[\text{Mo}_2\text{O}_7]\] 

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The binuclear oxo-bridged (peroxo)dimolybdate(VI) anion, \[\text{[Mo}_2\text{O}_7\text{]}^{2-}\] obtained by dissolving MoO\(_3\) in H\(_2\)O \_\(_2\) reacts with QOH(8-quinolinol) producing \[\text{[MoO(O}_2\text{)(QO)}_2\text{]} \] (1); 1,10-phenanthroline(phen), 2,2'-bipyridine(bipy), 2,2'-pyridylbenzimidazole(FBH) and 8-aminoquinoline(AQ), however, form \[\text{[MoO(O}_2\text{)]}_2(\text{L} + \text{L}) \] \[\text{(L} = \text{phen (2), bipy (3), PBIH (4) and AQ (5)).}\] The compounds have been characterized on the basis of \(\nu(\text{Mo=O}), \nu(\text{O=O}), \) and \(\nu(\text{Mo=O})\) vibrations in their infrared and laser Raman spectra. Vibrational data also indicate that while 2-5 have a symmetrical structure, 1 has an asymmetrical structure in the pentagonal bipyramidal framework. 

The electronic spectrum of 1 also corroborates this. All the complexes exhibit a high tendency of stoichiometric oxygen transfer towards R(A(R = Ph; A = P, As, Sb)) and cyclohexene, forming the corresponding R(=AO) and cyclohexene oxide, respectively. The complex 1 is most effective in this regard. Such an oxygen transfer from \[\text{[MoO(O}_2\text{)(L} + \text{L})\text{]}^{2-}\] yields \[\text{MoO}_2^{2-}\], the details of the crystal structure of the PPN salt (6) of which are described herein. Cyclic voltammograms of 2 and 3 show 2-electron (coulometry) oxidation wave (\(-1.8\text{ V vs SCE})

A recent discovery\(^1\) that HOOH on reaction with oxometal anions is capable of generating uncommon or even unknown oxopolymetallates, besides oxometal derivatives as major products, has led to renewal of interest in oxometal chemistry. An earlier report\(^2\), though of preliminary nature, also emphasised on the polymerisation tendency of MoO\(_3^{2+}\) unit in the presence of H\(_2\)O. Again, the heteroligand peroxy complexes represent an interesting set of species which undergo specific catalytic functions in oxidation and oxygen transfer reactions\(^3\-\(^6\). A particular interesting aspect is a current report\(^7\) of an oxidative addition of dioxygen on \[\text{[MoO}_4\text{(CN)}_4]\]\(^2-\), affording the peroxy complex, \[\text{[MoO}_4\text{O}_2\text{(CN)}_4]\]\(^2-\). 

A number of r-peroxo complexes of oxomolybdenum(VI) containing neutral bidentate ligands of the type \[\text{[MoO(O}_2\text{)(L} + \text{L})\text{H}_2\text{O)}\] have recently been reported\(^8\-\(^9\) where L = LH are \(\alpha\)-amino acids, viz., glycine, alanine, proline, valine, leucine and serine, as well as nicotinic acid and \(\alpha\)-nicotinamide. However, such a complex with 8-quinolinol (QOH) reported almost twenty five years back\(^10\) was formulated as \[\text{[MoO(O}_2\text{)(QO)}_2\text{]}\] where apparently an oxygen atom insertion on each of the quinolinolate oxygen had been proposed without adding any valid experimental support or theoretical reasoning. Also, the formulation\(^10\) of the complexes obtained with neutral bidentate ligands (L = L) such as 2,2'-bipyridine (bipy) and 1,10-phenanthroline (phen) as \[\text{[MoO(O}_2\text{)]}_2(\text{L} + \text{L})\] seems to be questionable since the preparation had been made in aqueous H\(_2\)O medium. However, the product of the reaction with bipy was shown to be \[\text{[MoO(O}_2\text{)(bipy)}_2\text{]}\]\(^11\). Hence, the aim of the present work, besides being directed towards the synthesis, structural and reactivity studies of new (peroxo)dimolybdenum(VI) complexes, is to rectify the erroneous chemical compositions suggested\(^10\) earlier for the QO\(^-\) and the phen complexes. Other
L−L ligands (saving bipy and phen) used in the present work are, 2,2’-pyridylbenzimidazole (PBIH) and 8-aminoquinoline (AQ). We have recently shown that the binuclear (oxo)molybdate, \( \text{A}_2[\text{MoO}_2\text{O}_2(\mu_2-\text{O})(\text{O}_2\text{H})\text{H}_2\text{O}] \) \( [\text{A}=\text{PPN}(\text{Ph}_3\text{P}=\text{N}=\text{PPh}_3) \) or \( \text{Ph}_4\text{P} \), furnishes \( \text{A}_2[\text{MoO}_2\text{O}_2] \) by an oxygen transfer reaction to the \( \text{Ph}_3\text{P} \) substrate and have communicated a preliminary structural report of the PPN salt. Details of the crystal structure work of the compound are being described herein. The chemical reactivity studies of the isolated L−L and QO complexes described in this paper include stoichiometric oxygen transfer reaction, whereby \( R_3\text{A} (R=\text{phenyl, A=P, As, Sb}) \) have been converted to their oxides, \( R_3\text{AO} \), and an olefinic group existing in cyclohexene, to its epoxide. Electrochemical reactivity highlights the ease of \( \text{O}^2−\rightarrow\text{O}_2 \) conversion from the coordinated peroxo group.

Materials and Methods

Molybdic acid (AR) was obtained from J. T. Baker Chemical Co., Phillipsburg, N.J. (U.S.A.). Hydrogen peroxide (30%, purified), 1,10-phenanthroline, 2,2’-bipyridine and 8-hydroxyquinoline were of G.R. (E. Merck, India) grade. Triphenylphosphine and triphenylarsine were obtained from Schuchardt (FRG) and triphenylstibine from Fluka (FRG). Cyclohexene was supplied by Aldrich Chemical Company, Inc. (U.S.A.). Acetonitrile (E. Merck (India)) was further purified by \( \text{P}_2\text{O}_{10} \) (G.R., E. Merck) treatment followed by distillation until a fresh sample of \( \text{P}_2\text{O}_{10} \) was not stained yellow by the solvent. Triply distilled water (all-glass) was used throughout, and all other solvents used were of analytical grades (E. Merck, India) and were further purified by literature methods.

Physical measurements

Spectroscopic data were obtained by using the following instruments: IR spectra (KBr disk, 4000-200 cm\(^{-1}\)), Perkin-Elmer 597 IR spectrophotometer; electronic spectra (2600-200 nm), Hitachi Model U-3400 UV-VIS-near IR spectrophotometer; Raman spectra (solid powders), Spex Model 1403 double-monochromator spectrometer using an argon ion laser (5145 A line). Scattered light at 90° was detected with the help of a cooled Spex datamate R 928/115 photomultiplier tube and a photon-counting processing system. Solution conductances were measured with a Systronics (India) Model 335 digital conductivity bridge. X-ray powder diffraction data were measured with Philips Model PW 1730/PW 1710 XRD systems. The 2θ range was from 5° to 60° with CuK\(_α\) radiation (1.5418 Å). Analytical gas-liquid chromatography was carried out on a Shimadzu GC model instrument, equipped with a flame ionization detector, using OV-17 as the chromatographic column. The chromatographic analysis was carried out at 60°C employing \( \text{N}_2 \) as the carrier gas. The starting alkene (cyclohexene) was checked by gas chromatography to ensure that no oxidation products were present. Voltammetric measurements were done using a microcomputer controlled PAR Model 378-4 electrochemistry system, model 273 potentiostat/galvanostat, model RE 0089 XY recorder and model 377 digital coulometer. The output was also obtained on an IBM PC XT Model HX-12E and printed with an EPSON FX 86e dot matrix printer. The figures presented here are all obtained from XY recorder. All experiments were carried out under a dinitrogen atmosphere in a three-electrode configuration using a stout platinum wire working electrode, a platinum foil auxiliary electrode, and saturated calomel electrode (SCE). All the results were collected at 298 K. The reported potentials are uncorrected for junction contribution. The elements C, H and N were analyzed microanalytically using a Perkin-Elmer 240°C elemental analyzer, and Mo was analyzed by conventional macro method.

Preparation of complexes

\( \text{MoO}_3 \) (1 g; 6.85 mmol) was dissolved in 30% \( \text{H}_2\text{O}_2 \) (40 ml; 13.9 mmol) by stirring at room temperature when a pale-yellow solution was obtained.

\[ \text{[MoO(O_2)(QO)]_2 (1)} \]

Addition of 8-quinolinol (QOH) (2.0 g; 13.7 mmol) dissolved in dilute acetic acid (10 ml) to the above solution with stirring gave a yellow solid. The solid was filtered off, washed thoroughly with water, 95% ethanol and finally with diethyl ether and dried over \( \text{CaCl}_2 \) in vacuo. The compound had a very low solubility in polar organic solvents and underwent decomposition to \( \text{[Mo}_2\text{O}_2(QO)_4]} \) (vide infra) on attempted crystallization from such solvents. The rate of decomposition (obviously via \( \text{O}_2 \) evolution) to the dimeric oxo form increased with increasing polarity of the solvent medium and with temperature; yield: 2.37 g (~79%).

\[ \text{[MoO(O_2)]_2(phen) (2)} \]

An ethanolic solution (15 ml) of phen (1.37 g; 6.85 mmol) was added with stirring to the solu-
Table 1—Analytical¹, IR², Laser Raman (R)³ and electronic spectral data (nm; ε/dm³ mol⁻¹ cm⁻¹)⁴ for the compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Analysis (%)</th>
<th>Type</th>
<th>ν(Mo=O) (cm⁻¹)</th>
<th>ν(O-O) (cm⁻¹)</th>
<th>ν(MO₂)asym (cm⁻¹)</th>
<th>ν(MO₂)sym (cm⁻¹)</th>
<th>λmax (ε)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[MoO(OC₂)(QO)₂]²</td>
<td></td>
<td>IR</td>
<td>960 (s)</td>
<td>860 (s)</td>
<td>570 (m)</td>
<td>535 (m)</td>
<td>361 (5295)</td>
</tr>
<tr>
<td>[MoO(OC₂)₂phen]²</td>
<td></td>
<td>R</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>261 (13240)</td>
</tr>
<tr>
<td>[MoO(OC₂)₂bipy]²</td>
<td></td>
<td>IR</td>
<td>960 (s)</td>
<td>860 (s)</td>
<td>590 (m)</td>
<td>540 (m)</td>
<td>349 (240)</td>
</tr>
<tr>
<td>[MoO(OC₂)₂BPIL]⁵</td>
<td></td>
<td>R</td>
<td>939 (s)</td>
<td>879 (s)</td>
<td>-</td>
<td>-</td>
<td>297 (2500)</td>
</tr>
<tr>
<td>[MoO(OC₂)₂AQ]²</td>
<td></td>
<td>IR</td>
<td>960 (s)</td>
<td>865 (s)</td>
<td>575 (m)</td>
<td>540 (m)</td>
<td>355 (305)</td>
</tr>
<tr>
<td>[MoO(OC₂)₂AQ]²</td>
<td></td>
<td>R</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>315 (1800)</td>
</tr>
<tr>
<td>[MoO(OC₂)₄]³</td>
<td></td>
<td>IR</td>
<td>955 (s)</td>
<td>860 (s)</td>
<td>560 (m)</td>
<td>540 (m)</td>
<td>372 (320)</td>
</tr>
<tr>
<td>[MoO(OC₂)₄]³</td>
<td></td>
<td>R</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>322 (2310)</td>
</tr>
<tr>
<td>[MoO(OC₂)₄]³</td>
<td></td>
<td>IR</td>
<td>945 (s)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>399 (6355)</td>
</tr>
<tr>
<td>[MoO(OC₂)₄]³</td>
<td></td>
<td>R</td>
<td>920 (s)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>259 (16550)</td>
</tr>
</tbody>
</table>

¹Calculated values are shown in parentheses. ²For the authenticity of assignment see ref. 19. ³For assignment see ref. 13. ⁴Intramolecular bands are excluded. ⁵Compound decomposes on laser irradiation. ⁶ν(Mo=O),sym, 760(m) and 630(w); ⁷R(Mo=O),sym, 923.

Reactions of MoO₃ in aqueous H₂O₂, when a very pale-yellow solid precipitated. The solid was filtered off and washed with water, 95% ethanol and diethyl ether and dried as usual. The compound is very weakly soluble in organic solvents; yield: 2.05 g (~83%). d-spacings: 2.04 (0.59), 3.54 (1.00), 4.79 (0.29), 4.51 (0.69), 3.93 (0.42), 3.49 (0.43), 3.21 (0.22), 3.06 (0.1), 2.75 (0.15), 2.26 (0.19) (Figures in the parentheses indicate the respective I/I₀ values).

[MoO(OC₂)₂{bipy}²]³

Instead of phen, bipy (1.25 g; 6.85 mmol) was added following the procedure described above for the preparation of 2, which is almost the same as described earlier. The compound was recrystallised from DMF-ether mixture when a pale-yellow microcrystalline solid was obtained; yield: 1.94 (~85%). d-spacings: 6.92 (1.00), 5.79 (1.00), 4.69 (0.79), 4.33 (0.96), 3.80 (0.53), 3.63 (0.49), 3.25 (0.41), 3.12 (0.33), 2.68 (0.26), 2.21 (0.15).

[MoO(OC₂)₂{PBIL}²]⁴

An ethanolic solution (15 ml) of PBIL (1.34 g; 6.85 mmol) was added with stirring to the solution of MoO₃ in aqueous H₂O₂, when a very pale-yellow solid precipitated. The solid was filtered off and washed with water, 95% ethanol and diethyl ether and dried as usual. The compound was recrystallised from DMF-ether mixture when pale-yellow microcrystalline solid was obtained; yield: 1.99 g (~77%).

[MoO(O₂)₂{AQ}²]⁵

The procedure used for the preparation of 4 was followed using an ethanolic solution (15 ml) of 8-aminoquinoline (0.99 g; 6.85 mmol) when a 75% yield of the compound was obtained. The compound underwent decomposition on attempted crystallisation from DMF-ether mixture.

Reaction of [MoO(O₂)(QO)₂]² with Ph₃P

To an acetonitrile solution (50 ml) of [MoO(O₂)(QO)₂]² (0.5 g; 1.15 mmol) a solution (30 ml) of Ph₃P (0.3 g; 1.15 mmol), also in acetonitrile, was added when an instantaneous change in colour of the solution, from yellow to orange, took place. The solution was stirred for 30 min followed by evaporation of the solvent. The solid product obtained by evaporation was extracted with diethyl ether. The diethyl ether extract gave Ph₃PO (yield, 0.30 g, ~95%) on evaporation and the insoluble part was identified as [Mo₂O₄(QO)₄]²⁻ (7) (yield, 0.87 g; ~90%). [Found: C, 77.2; H, 5.5%. Ph₃PO requires: C, 77.7; H, 5.4%]. IR spectrum of the product was superimposable on that of an authentic sample of the compound. For analytical data of the molybdenum compounds see Table 1.

Reaction of [MoO(O₂)(QO)₂]² with Ph₃As

The same procedure as that used in the case of Ph₃P was followed in the case of Ph₃As also. The reaction mixture was stirred for 2-3 h when an orange colour developed. The orange solution
was then allowed to stand for 2 h followed by addition of diethyl ether in small portions. At first \(\text{[Mo}_2\text{O}_5\text{(QO)}_4\text{]}\) (yield, 0.84 g, \(\sim 87\%\)) separated out from the reaction mixture, followed by \(\text{Ph}_3\text{AsO}\) from the dilute solution on addition of more diethyl ether; yield: 0.28 g (\(\sim 80\%\)). [Found: C, 66.8; H, 4.7%. \(\text{Ph}_3\text{AsO}\) requires: C, 67.1; H, 4.7%]. The IR spectrum was superimposable on that of an authentic sample of \(\text{Ph}_3\text{AsO}\).[15] The compound \(\text{[Mo}_2\text{O}_5\text{(QO)}_4\text{]}\) formed in the above reaction gave identical analytical and spectral (IR, UV-Vis, Raman) data to that given by the compound formed during the reaction with \(\text{Ph}_3\text{P}\).

**Reaction of \(\text{[MoO(O}_2\text{(QO)}_2\text{]}\) with \(\text{Ph}_3\text{Sb}\)**

The same procedure as that used for \(\text{Ph}_3\text{As}\) was followed. The only difference was that \(\text{Ph}_3\text{SbO}\) separated earlier than \(\text{[Mo}_2\text{O}_5\text{(QO)}_4\text{]}\) (yield 0.82 g, \(\sim 85\%\)) on addition of diethyl ether to the reaction mixture; yield: 0.29 g (70%). [Found: C, 58.2; H, 4.1%. \(\text{Ph}_3\text{SbO}\) requires: C, 58.6; H, 4.1%]. IR spectrum of the product was superimposable on that of the authentic sample of the compound prepared by the reported method.[15]

**Epoxydation of cyclohexene using \(\text{[MoO(O}_2\text{(QO)}_2\text{]}\)**

Cyclohexene (60 mmol) \(\text{[MoO(O}_2\text{(QO)}_2\text{]}\) (9 mmol) and benzene (30 ml) were placed in a round-bottomed flask fitted with a reflux condenser. The reaction mixture was refluxed for 3 h (for acetone, 2 h) at 80°C and then cooled. The compound \(\text{[Mo}_2\text{O}_5\text{(QO)}_4\text{]}\) (yield 0.81 g, \(\sim 83\%\)) was separated by filtration and the filtrate so obtained was analysed by GLC. The yield of cyclohexene oxide was 25% (based on the peroxo compound used) when benzene was used as the solvent. The yield was somewhat lower in the case of acetone as solvent.

**X-ray structure analysis of \([\text{Ph}_3\text{P}=\text{N}=\text{PPh}_3\text{]}\)[6]**

Well formed crystals of \((\text{PPN})_2\text{[Mo}_2\text{O}_5\text{]}\) were obtained by slow diffusion of a (1:1) mixture of pentane-diethyl ether into an acetonitrile solution of \((\text{PPN})_2\text{[Mo}_2\text{O}_5\text{]}\). A crystal of suitable dimensions was mounted on a Syntex P3 automated diffractometer. Unit cell dimensions were determined by least-squares refinement of the best angular positions for fifteen independent reflections (2θ > 15°) during normal alignment procedures using molybdenum radiation (\(\lambda = 0.71069\) Å). Intensity data (4185 points) were collected at room temperature using a variable scan rate, a θ-2θ scan mode and a scan width of 1.2° below \(K\alpha\) and 1.2° above \(K\alpha\) to a maximum 2θ value of 45.0°. Backgrounds were measured at each side of the scan for a combined time equal to the total scan time. The intensities of three standard reflections were remeasured after every 97 reflections and as the intensities of these reflections showed less than 6% variation, corrections for decompositon were deemed unnecessary. After removal of space group-forbidden and redundant data, 1961 observed data \([I > 3.0\sigma(I)]\) were used for solution and refinement. The structure was solved for heavy atom positions using direct methods.[16] The remainder of the atoms were located using successive cycles of least-squares refinement.[17] Converged with anisotropic thermal parameters. Hydrogen positions were included in the final cycles of refinement with isotropic thermal parameters, but held invariant. A final difference Fourier synthesis revealed no electron density of interpretable level. Anomalous dispersion corrections were made for molybdenum. Scattering factors were taken from Cromer and Mann.[18] The final cycle of refinement [Function minimized, \(\Sigma[I-F||F|]^{2}\) lead to a final agreement factor, R = 0.055. \([R = \Sigma[I-F||F|]/\Sigma[F|])\). Unit weights were used until the final cycles of refinement when weights equal to 1/σ(F)^2 were introduced. \(R_a = 0.067\).

**Results and Discussion**

**Synthesis, vibrational spectroscopy and structure**

The pale yellow solution formed by dissolution of \(\text{MoO}_3\) in \(\text{H}_2\text{O}_2\) contains largely the binuclear oxo bridged peroxy complex anion, \(\text{[MoO}_3\text{(H}_2\text{O}_2)_2\text{]}\), the pyridinium salt of which had been structurally characterised.[19] Addition of ethanolic solution of 8-quinolinol (QOH) to the above solution affords the neutral peroxy complex, \(\text{[MoO}_3\text{(QO)}_2\text{]}\), 1, while L-L ligands furnish \(\text{[MoO(O}_2\text{)(L-L)}\text{]}\) (L-L = phen (2) or bipy (3)). The IR band around 960 cm \(^{-1}\) (Table 1) is assignable to the \(\nu(Mo=O)\) vibration in all the three complexes, while that around 860 cm \(^{-1}\) is due to the \(\nu(O-O)\) vibration.[19] The weak band around 415 cm \(^{-1}\) can be assigned to the \(\nu(Mo-N)\) vibration. In Raman spectrum, the \(\nu(Mo=O)\) vibration is obtained around 940 cm \(^{-1}\) whilst the \(\nu(O-O)\) band is observed at 875 cm \(^{-1}\) (ref. 20). The medium intensity IR band around 580 and 540 cm \(^{-1}\) in all the compounds may be attributed to the asymmetric and symmetric vibrational modes of \(\nu(Mo=O)\) group.[19] In Raman spectrum, only the
Symmetric vibration appears around 530 cm$^{-1}$. 2 and 3 do not show any N-H vibration. Also, the nature of modification of the QOH and L-L vibrations after complex formation clearly indicates that the ligands behave as bidentate chelates.

Based on the above vibrational spectroscopic data, the conceivable structures for the complex 1 are represented as I-VII, while those for 2 and 3 are represented by VIII and IX respectively. It was not possible to get diffractable crystals (see experimental) and, hence, unequivocal conclusion regarding the structure of the molecules is not possible. However, if it is assumed that the complexes are likely to be monomeric involving a seven-coordinate system similar to those of the pentagonal bipyramidal compounds [MoO(O$_2$)$_2$($\alpha$-$AA$)$_2$] where $\alpha$-$AA$=glycine or proline, then the pentagonal plane of the compounds 2 and 3 will be occupied by two peroxy oxygens and a L-L nitrogen, with the axial positions possessed by the Mo=O oxygen and another L-L nitrogen. This proposition is supported by the appearance of a single $\nu$(O-O) vibration in 2 and 3. So, structures of 2 and 3 are best represented by VIII. These observations rule out the formulae suggested by earlier workers$^{10}$ for the QO$^-$ and L-L complexes.

**Electronic spectroscopy**

The present compounds are non-electrolytes in dimethylformamide (DMF). Acetonitrile solution of 1 shows three electronic spectral bands while those of 2 and 3 show only two bands (excluding the QO$^-$, phen or bipy internal transitions). However, the high intensity 261 nm band in 1 may very well be another QO$^-$ internal transition, first one occurring at 241 nm which is in the immediate neighbourhood of that observed in pure QOH. Also, interestingly, this band disappears in [MoO$_2$(QO)$_2$]. Moreover, this is also a region where O$_2^-$-M LMCT transitions are normally not exhibited. So, this splitting of the internal QO$^-$ transition may be due to the inequivalencies of QO$^-$ ligand in the pentagonal bipyramidal structural arrangement, compatible with the structures I-IV, where the molecular symmetry is certainly lower than that in V, VI and VII. Other two electronic spectral bands in 1 and the two bands in 2 and 3 may be due to L-L (QO$^-$, phen or bipy)-Mo(VI) and O$_2^-$-Mo(VI) LMCT transitions, observed in the order of increasing energy (Table 1).

The possible isosctructurality of 2 and 3 is beautifully exhibited in their X-ray powder diffraction patterns. The calculated $d$-spacings and their relative intensities are shown in the experimental sec-
Chemical reactivity

Coordinated peroxo groups are known to be effective centres for oxygen transfer reaction in the presence of a suitable oxygen receptor. The compound 1 is most effective in this regard, and 2 and 3 are less so. The stoichiometric reactivity is represented in the Scheme 1. Interestingly, besides Ph₃P, which is a rather common substrate, even Ph₅Sb undergoes a 70% conversion to Ph₅SbO. These oxygen transfer reactions towards the Ph₅A substrates are very much faster than that achieved by H₂O₂ treatment and do not involve an intermediate of the type (R₃AO),H₂O₂ which requires decomposition at a reduced pressure to generate R₃AO. Moreover, Ph₅Sb is not convertible to its oxide by H₂O₂ alone.

Epoxidation of cyclohexene with 1 gives cyclohexene oxide in a reasonably good yield for a purely stoichiometric reaction in the absence of any catalyst. The gas-liquid chromatographic analysis shows that the epoxide is the sole product and no cyclohexanone or cyclohexanol is obtained. The latter products are normally obtained as a result of free radical pathway.

The details of the experimental procedures for the reactions shown in Scheme 1 have been described in the experimental section. In all the above cases the molybdenum compound ultimately obtained has been formulated as a dimeric species, 6, shown in Scheme 1. The well known monomeric compound, [MoO₂(QO₂)], actually shows threeν(Mo-O) vibrations in the range 900-1000 cm⁻¹, but in the present case only two such vibrations have been obtained. In an analogous compound containing the [OMo(O₂)₂MoO]₄⁺ core previous workers also observed two ν(Mo=O) vibrations. In the present case also the above core coordinated with two QO⁻ ligands per Mo atom can very well be generated during oxygen transfer reaction as shown in the Scheme 2 (see also ref. 9). Moreover, only one ν(Mo=O) has been obtained in the Raman spectrum (at 932 cm⁻¹) which is assignable to the corresponding symmetric vibration of the above core. [MoO₂(QO₂)] shows the LMCT transition at 370 nm while the present compound shows it at 399 nm. Again, the 8-quinolinol internal transition is split in this dimer into two bands at 259 and 241 nm. This, as explained earlier in the peroxo cases, is due to the inequivalence of the QO⁻ ligands which is quite possible in the proposed dimeric structure X.

Also, the peroxodimolybdate anion [Mo₂O₃⁺(μ-O)(O₂)₂(H₂O)] reacts with Ph₃P furnishing Mo₂O₃ with a 100% conversion of the organic substrate to Ph₃PO. The PPN salt of Mo₂O₃ shows interesting structural aspects (for preliminary report of the structure see ref. 18).

Electrochemical studies

Voltammetry of 2 and 3 was carried out in acetonitrile solutions at a platinum working electrode. Tetraethylammonium perchlorate (TEAP) was used as an inert electrolyte in each case. All the potentials are referenced to the saturated calomel electrode (SCE). The formal potentials are also expressed (in parentheses at relevant places) relative to E°₂₉₈ of the [Fe(η-C₆H₅)₂]⁺-[Fe(η-C₆H₅)₂]²⁺ couple (vs SCE) separately measured under identical experimental conditions, solvents and inert electrolytes as used for the measurement of unknown solution.

The compounds 2 and 3 show an oxidative response (irreversible, Fig. 1) at 1.8 V (vs SCE). Coulometry of both the compounds using a platinum gauze working electrode and a platinum foil counter electrode with SCE as a reference electrode confirmed the oxidative response to be a two-electron process shown in equation (1).
more facile when the former is coordinated to molybdenum(VI) than that when it exists in a proton-bound state. It may be recalled, we have noted that coordinated $O_2^-$ is a better oxidant towards organic substrates than free $H_2O_2$, implying thereby an essential difference in the mode of chemical and electrochemical reactivities of the above peroxo complexes.

An irreversible reductive response in the case of 2 and 3 at $-1.2$ V vs SCE (Fig. 1), obviously$^{26}$ centered on the metal ion, has been found to be a one-electron process by coulometry. This may correspond to an electrode reaction shown in equation (3).

$$[MoVI O(OC(2cl(L-L))] + e \rightarrow \frac{-1.2 V}{(-1.58 V)} [MoIV(OC(2cl(L-L))]^-$$

Since the product $[MoIV(OC(2cl(L-L))]^-$ is supposed to be very much unstable towards dimerisation, the overall reaction becomes irreversible in nature. It is noteworthy, that the above potential is in the range where dioxomolybdenum(VI) complexes containing predominantly oxygen donor ligands undergo irreversible one-electron reduction at the metal centre$^{26}$.

As discussed earlier, 1 on dissolution in organic solvents (here DMF) changes to a dimer, $[MoO_2(OO)(bipy)]$. Hence, the voltammetry of 1 is essentially that of the dimer. Here an irreversible 2-electron (coulometry) oxidative response (Fig. 1) is found at $+1.26$ V vs SCE in DMF solution. The ligand QOH does not show any electrochemical response in the range $-1.8$ to $+2.5$ V vs SCE. The specific region of the $E_{pa}$ peak and two-electron involvement in the oxidation may be attributed$^{25}$ to the process described by equation (4).

$$O_2^+ \rightarrow \frac{-1.26 V}{(1.23 V)} O_2 + 2e$$

It may be assumed that the bridging oxide ligands of 7 are electrooxidised to dioxygen converting one mole of the said complex to two moles of a presumable monomer, $[MoOQOO)]^2+$. The electronic spectrum of the electrolysed species does not show any significant change, specially in the region where coordinated QO$^-$ absorbs. An irreversible reductive response (Fig. 1) at $-1.44$ V vs SCE should be metal-centered and may represent the reduction of $M_2O_4^+$ moiety as shown in equation (5). Since the cationic moiety $MoO_4^{2-}$ is very much prone to undergo a chemical change to $Mo_2O_5^{4-}$, electrode process remains irreversible.

In free $H_2O_2$, this oxidation process occurs at 1.1 V (vs SCE) in acetonitrile solution with TEAP as the supporting electrolyte as shown in equation (2). It is also known$^{25}$ that $H_2O_2$ to $O_2$ conversion in aqueous acidic media occurs at 0.7 V. Here also the two-electron change has been confirmed by coulometry.

$$O_2^+ \rightarrow \frac{-1.44 V}{(0.72 V)} O_2 + 2e$$

So, it may be argued that the irreversible oxidation process of the peroxo group to dioxygen is

Fig. 1 - Cyclic voltammograms of (a) $[MoO(OCC(L-L))]$ in acetonitrile in the potential range of 1.0 V to 2.2 V/scan rates (i) 50, (ii) 100 and (iii) 200 mV s$^{-1}$; (b) $[MoO(OC(2cl(L-L))]$ in acetonitrile in the potential range of $-0.9$ V to $-1.5$ V at scan rate (i) 50, (ii) 100 and (iii) 200 mV s$^{-1}$; (c) $[MoO_2(OO)(QO)]$ in DMF in the potential range of 0.0 V to 2.0 V at scan rates 100 mV s$^{-1}$; (d) $[MoO_4(QO)]$ in DMF in the potential range of 0.0 V to $-2.0$ V at scan rate 100 mV s$^{-1}$. 

$$[MoO(OCC(L-L))] \rightarrow [MoO(OCC(L-L)]^2+ + O_2 + 2e$$

$\text{(1)}$
the two equivalent $\text{O}_3^-$ groupings in the anion are essentially perpendicular to their respective Mo–O bonds in a nearly eclipsed conformation and the Mo–O–Mo angle is 153.6°.

The five atoms (O, Mo, O, and O) lie in one of the two mutually perpendicular mirror planes of a $C_2v$ structure. In the subsequent structural analysis of the dimolybdate anion containing $\left[\left(\eta^1-C_4H_8Me\right)\text{Mo}(CO)_2(\mu-dppm)\text{Pt}(dppmW}\right]^-$ as the counter ion, no such imposed $C_2$ symmetry is present and instead the above mentioned atoms lie in a pseudo mirror plane. The Mo–O–Mo angle is 160°.

The present structural results on the PPN salt of dimolybdate ion (6) differ markedly from the previous results obtained using other salts, viz., 8 and 9, especially with regard to symmetry. Fig. 1 shows clearly that $\text{MoO}_2^-$ ion displays the highest possible molecular symmetry of $D_{3d}$ in which the two equivalent $\text{O}_3^-$ groupings in the anion are essentially perpendicular to their respective Mo–O bonds in a nearly eclipsed conformation and the Mo–O–Mo angle is 153.6°.

Molecular structure of $(\text{PPN})_2[\text{Mo}_2\text{O}_7]^-$ (6)

Final fractional coordinates and thermal parameters are given in Table 2, and selected bond lengths (Å) and bond angles in Table 3. The projection view of the $\text{Mo}_2\text{O}_7^-$ ions is shown in Fig. 2. The structural analysis revealed that the crystal is composed of discrete PPN$^+$ cations and $\text{Mo}_2\text{O}_7^-$ anions in which the two $\text{Mo}_2\text{O}_7$ tetrahedra share vertex. All the Mo–O bond lengths and O–Mo–O bond angles are practically equal (Table 3) and the mean planes of the two $\text{O}_3^-$ groupings are oriented normal to a linear Mo–O–Mo axis in a staggered conformation.

The previous structural determination of the $(n-C_4H_{10})_4\text{N}$-salt$^{27}$ of $\text{Mo}_2\text{O}_7$ (8), revealed that

$$\text{Mo}^{VI}_2\text{O}^{IV}_7^+ + 2e^- \rightarrow \text{Mo}^{IV}_2\text{O}^{VI}_3^+ \quad \text{at} \quad \frac{-1.44 \text{ V}}{1.82 \text{ V}}$$

The two equivalent $\text{O}_3^-$ groupings in the anion are essentially perpendicular to their respective Mo–O bonds in a nearly eclipsed conformation and the Mo–O–Mo angle is 153.6° (5°). The five atoms (O, Mo, O, and O) lie in one of the two mutually perpendicular mirror planes of a $C_2v$ structure. In the subsequent structural analysis of the dimolybdate anion containing $\left[\left(\eta^1-C_4H_8Me\right)\text{Mo}(CO)_2(\mu-dppm)\text{Pt}(dppmW}\right]^-$ as the counter ion, no such imposed $C_2$ symmetry is present and instead the above mentioned atoms lie in a pseudo mirror plane. The Mo–O–Mo angle is 160°.

The present structural results on the PPN salt of dimolybdate ion (6) differ markedly from the previous results obtained using other salts, viz., 8 and 9, especially with regard to symmetry. Fig. 1 shows clearly that $\text{Mo}_2\text{O}_7^-$ ion displays the highest possible molecular symmetry of $D_{3d}$ in which...
the oxygen atom common to both the molybdenum centre (i.e. O1) is situated in a crystallographic inversion point and is equidistant from all the six terminal oxygen atoms. Here, the average values of three independent Mo-O bond lengths and six independent O1-Mo-O bond angles are 1.69 (4) Å and 109.5 (1)°, respectively. Due to the staggered conformation of the two MoO₃ groupings, the average O₂ ... O₂', O₃ ... O₃' and O₄ ... O₄' separation of 5.777 (2) Å is considerably larger than that of 4.134 (13) Å observed in the previously reported eclipsed analogue. Also, this average distance is larger than the other O ... O distances [average = 5.073 (3)], viz., O₂ ... O₃, O₂ ... O₅ etc. In view of the perfect linearity of Mo-O₆-Mo axis in (PPN)₂[MozO₇], it will be interesting to examine whether or not the Cr-O₆-Cr axis in the corresponding dichromate salt is also linear.

Supplementary material

The fractional atomic coordinates for hydrogen atoms, the anisotropic thermal parameters and the structure factor tables are available from the authors on request (32 pages).

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