Potentiometric Study of the Molybdenum(VI)–Benzilic Acid System. Structural Characterisation and Electrochemical Properties of $[NH_4]_2[MoO_2\{O_2CC(O)Ph_2\}_2]\cdot 2H_2O$†

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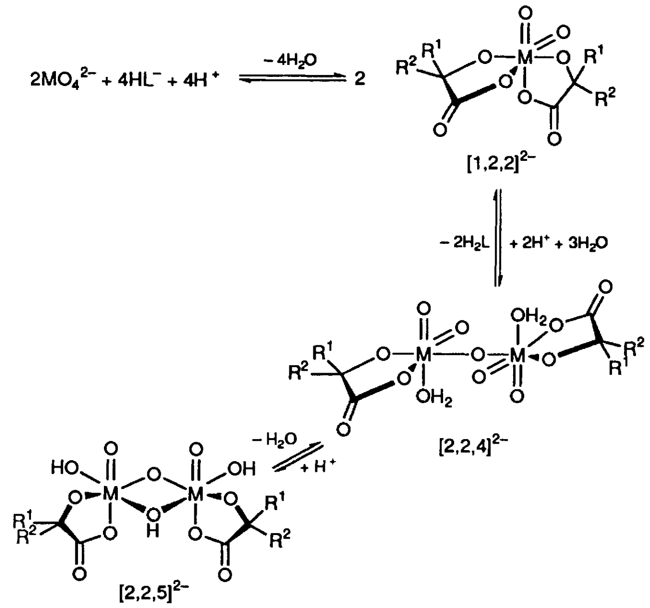
The formation of complexes between molybdate and benzilate (2-hydroxy-2,2-diphenylacetate), $Hbza^-$, ions has been investigated in the range pH 2–7 by potentiometric measurements. Computer treatment of the potentiometric data revealed the formation of two complexes the $[MoO_4]^{2-}$, $Hbza^-$, H^+ stoichiometries of which are [1,2,2] and [2,2,4]; log β_{122} = 17.35, log β_{224} = 29.07. Compared to other less bulky hydroxycarboxylate ligands previously studied, this result indicates that the phenyl groups of benzilate only prevent the formation of [2,2,5] dimeric complex which presumably has a double oxo bridge. The mononuclear [1,2,2] complex has been isolated and its structure determined by X-ray analysis of its ammonium salt, $[NH_4]_2[MoO_2\{O_2CC(O)Ph_2\}_2]\cdot 2H_2O$; monoclinic, space group $P2_1/n$, a = 8.106(2), b = 25.702(8), c = 13.628(4) Å, β = 90.62(2)° and Z = 4. The redox properties of this complex salt were also investigated and compared with those previously found for an analogous complex containing two thiobenzilate ligands.

The capacity of a molybdenum(VI) centre to develop six-co-ordination towards oxygen through the use of different combinations of terminal and core-bridging atoms is presently well known. Among others, mononuclear *fac*-trioxo (MoO_3) and *cis*-dioxo (MoO_2^{2+}) cores as well as dinuclear single-bridged ($Mo_2O_5^{2+}$) cores have been well characterised.[1]

We have been engaged in the development of a general scheme for the formation and interconversion of complexes of Mo^{VI} and W^{VI} with hydroxycarboxylic acids [tartaric, malic, malonic, lactic, oxalic and citric (3-carboxy-3-hydroxypentane-1,5-dioic) acid among others] and polyols [mannitol, sorbitol (D-glucitol) and adonitol (ribitol)].[2] From these previous works, two main features were generally established: (*i*) only the formation of mono- and di-nuclear complexes occurs in aqueous media; (*ii*) the solution pH is the principal variable controlling the formation and interconversion equilibria of these complexes. Thus, for α-hydroxycarboxylic acids, in neutral or weakly acidic solutions, monomeric *fac*-trioxo (tridentate ligands) or *cis*-dioxo (bidentate ligands) complexes with a molybdenum–ligand stoichiometry of 1:1 or 1:2, respectively are the only stable species. At a lower pH these monomeric complexes dimerise in a pH-dependent stepwise manner, forming two different dinuclear complexes with the same 2:2 stoichiometry (see Scheme 1). The interconversion equilibrium involving these two dimeric complexes requires 1 equivalent of protons, and from comparison of their ^1H and ^{13}C NMR spectra we infer that the co-ordination of organic ligand molecules is similar in both complexes, the difference being in the number of μ-oxo bonds connecting the two Mo^{VI}.

Although in all these investigations the proton concentration appears to be crucial for the occurrence of a given complex species, it can be conjectured, however, that other factors such as possible tensions in chelate rings and steric constraints from the ligands may favour or disfavour some of the above-mentioned structures.[3] As a paradigmatic example, large multidentate ligands have been devised to prevent dimerisation of molybdenum oxo monomers when modelling molybdenum hydroxylases.[4]



Scheme 1 R^1 = H, R^2 = Me, CH_2CO_2H or $CH(OH)CO_2H$; R^1 = R^2 = CH_2CO_2H

We herein report a potentiometric study of the molybdate–benzilic acid system where the steric encumbrance of the ligand destabilises the formation of the double μ-oxo-bridged complex present under more acidic conditions.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Experimental

Synthesis.—$[NH_4]_2[MoO_2\{O_2CC(O)Ph_2\}_2]\cdot 2H_2O$. Benzilic acid (1 g, 4.4 mmol) dissolved in hot water (85 cm^3) was slowly added to a stirred solution of $[NH_4]_6[Mo_7O_{24}]\cdot 4H_2O$ (0.386 g, 0.31 mmol) in water (25 cm^3), maintaining the pH value close to 6.5 with small additions of NH_4OH. The mixture was refluxed for 1 h. The white solid formed upon solvent elimination was filtered off and recrystallised from methanol (yield 70%) (Found: C, 51.1; H, 4.8; N, 4.1. Calc. for $C_{28}H_{32}MoN_2O_{10}$: C, 51.5; H, 4.9; N, 4.3%). IR (KBr): ν(Mo=O), 880 and 910 cm^{-1}. ^{13}C NMR (MeOH, 50.32 MHz): δ 184.2, 147.0, 143.8, 130.6–129.6 and 94.8.

Crystal Structure Determination of $[NH_4]_2[MoO_2\{O_2CC(O)Ph_2\}_2]\cdot 2H_2O$.—$C_{28}H_{32}MoN_2O_{10}$, $M = 652.5$, monoclinic, space group $P2_1/n$, $a = 8.106(2)$, $b = 25.702(8)$, $c = 13.628(4)$ Å, $\beta = 90.62(2)°$, $U = 2839$ Å^3, $Z = 4$, $D_c = 1.53$ g cm^{-3}, Cu-Kα radiation, $\lambda = 1.541\ 78$ Å, μ(Cu-Kα) = 43 cm^{-1}, $F(000) = 1344$, $T = 298$ K, white prism (0.2 × 0.6 × 0.6 mm).

Data were collected on a Nicolet R3m diffractometer with Cu-Kα radiation (graphite monochromator) using ω scans. 3828 Independent reflections ($2\theta \leqslant 116°$) were measured, of which 3646 with $|F_o| > 3\sigma(|F_o|)$ were considered observed. The data were corrected for Lorentz and polarisation factors; a numerical absorption correction (face-indexed crystal) was applied, maximum and minimum transmission factors 0.478 and 0.221. The structure was solved by the heavy-atom method. Non-hydrogen atoms were refined anisotropically. A ΔF map revealed the presence of two water molecules. Both ammonium and water protons were located from a ΔF map. Their geometries were optimised and they were refined isotropically. The positions of the remaining hydrogen atoms were idealised, C–H 0.96 Å, assigned isotropic thermal parameters, $U(H) = 1.2\ U_{eq}(C)$, and allowed to ride on their parent carbon atoms. The water molecules and the ammonium ions were refined as rigid bodies. Refinement was by block-cascade full-matrix least squares to $R = 0.034$, $R' = 0.042$ [$1/w = \sigma^2(F) + 0.000\ 70F^2$]. The maximum and minimum residual electron densities in the final ΔF map were 0.82 and −0.67 e Å^{-3} respectively. The mean and maximum shift/error in the final refinement were 0.010 and 0.310 respectively. Computations were carried out on an Eclipse S140 computer using the SHELXTL structure determination package.[5]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Potentiometric Titrations.—Mixtures of sodium molybdate and benzilic acid were titrated at 25.0 ± 0.1 °C in a water-bath starting with (2–3) × 10^{-3} mol dm^{-3} $Na_2[MoO_4]$ solutions (*ca.* 40 cm^3), adding HCl from a Crison 738-burette. The ionic strength was kept constant with 0.1 mol dm^{-3} $NaNO_3$. A stream of CO_2-free N_2 pre-saturated with $NaNO_3$ (0.1 mol dm^{-3}) was passed over the surface of the solutions in the reaction vessel during the potentiometric titration.

Hydrogen-ion concentrations were determined by measuring the electromotive force with a Radiometer pH-meter employing an Orion 91-01 glass electrode and a Ag–AgCl reference electrode kept in a 0.5 mol dm^{-3} NaCl solution connected to the reaction cell by a Wilhelm-type salt bridge containing $NaNO_3$ (0.1 mol dm^{-3}). The standard potential of the cell, E', was calculated by Gran's method. No corrections for the liquid-junction potential were made because this effect was negligible within the pH range studied. The whole apparatus (burette, pH-mV meter, *etc.*) was automated as previously described.[6]

The concentrations of HCl and CO_2-free NaOH solutions were determined by potentiometric titration with tris(hydroxymethyl)aminomethane (Tris) and hydrogenphthalate buffers.

The SUPERQUAD[7] program was used both to define the model system and compute the equilibrium constants. In the last refinement only the points for which significant variations in the extent of formation took place were used.

Other Physical Measurements.—Infrared spectra were recorded as KBr discs on a Perkin-Elmer 1720 FT instrument, absorption spectra in MeOH using a Perkin-Elmer Lambda-9 spectrophotometer and NMR measurements in $(CD_3)_2CO$ on a Bruker 200 instrument.

Cyclic voltammetric measurements were carried out with a triangular wave generator (Newtronics 200P), a potentiostat (HQ-101) and an X-Y recorder (Riken-Denshi F35). A hanging mercury-drop electrode (Metrohm AGCH 9100), amalgamated gold-disc electrode (AGE) and glassy carbon electrode (GCE) were alternatively used as working electrodes. The reference was an aqueous saturated calomel electrode (SCE) separated from the test solution by a salt bridge containing supporting electrolyte solution. A platinum-wire auxiliary electrode and the SCE completed the standard three-electrode cell. Sodium perchlorate (0.15 mol dm^{-3}) and acetic acid–acetate (0.2 mol dm^{-3}) buffer were used as supporting electrolytes in water. For non-aqueous experiments, dry and distilled MeOH, dimethylformamide and MeCN were used with 0.1 mol dm^{-3} tetrabutylammonium hexafluorophosphate and benzoic acid (0.40 mol dm^{-3})–NEt_3 (0.20 mol dm^{-3}) as supporting electrolytes. All experiments were performed at 298 K under an argon atmosphere.

Results and Discussion

Potentiometric Measurements.—Previous studies of molybdenum(VI) complexation with other carboxylate ligands have shown that systems of this nature can be unravelled by computer treatment of high-quality potentiometric data provided all the molybdate and ligand side-equilibria are taken into account.[8] The various protonation, molybdate condensation and complexation reactions which can take place when mixtures of sodium molybdate and sodium benzilate (H_2bza) were titrated with hydrochloric acid can be represented by the general equation (1). For brevity, species with overall formation constants β_{pqr} are denoted by the stoichiometric coefficients describing their composition, *i.e.* $[p,q,r]^{(2p+q-r)-}$. The titration data were treated with the computer program SUPERQUAD[7] to search for the reaction model that would give the best description of the system. In the treatment of the data the molybdate species $[HMoO_4]^-$, $Mo(OH)_6$, $[HMo_2O_7]^-$, $[Mo_7O_{24}]^{6-}$, $[HMo_7O_{24}]^{5-}$, $[H_2Mo_7O_{24}]^{4-}$, $[Mo_8O_{26}]^{4-}$ and $[HMo_8O_{28}]^{7-}$ were taken into account using previously determined equilibrium constants pertaining to a 0.10 mol dm^{-3} $NaNO_3$ medium at 298 K,[9] which were found to be in agreement with other previous reports.[10] The protonation constant of benzilate ($\log \beta_{011} = 2.9$) was evaluated in separate titrations.

$$p\,[MoO_4]^{2-} + q\,Hbza^- + r\,H^+ \longrightarrow [Complex]^{(2p+q-r)-} \quad (1)$$

Two hundred experimental points, from three different titration curves having a 1:2, 1:4 or 1:10 molybdate:benzilate ratio, were used to examine the reaction model. It soon became apparent that complexes $[1,2,2]^{2-}$ and $[2,2,4]^{2-}$ are the only stable species present in the range pH 2–7. The further addition of other species with different molybdate:benzilate ratios in various protonation states, *i.e.* $[1,1,r]$, $[2,2,r]$ and $[2,1,r]$, did not yield better statistical parameters and usually they were rejected by the selector of the SUPERQUAD program, which automatically rejects species for which the relative standard deviation of the formation constant is greater than 33%.

The distribution of both complexes as a function of pH at a 1:2 molybdate:benzilate initial ratio is shown in Fig. 1.

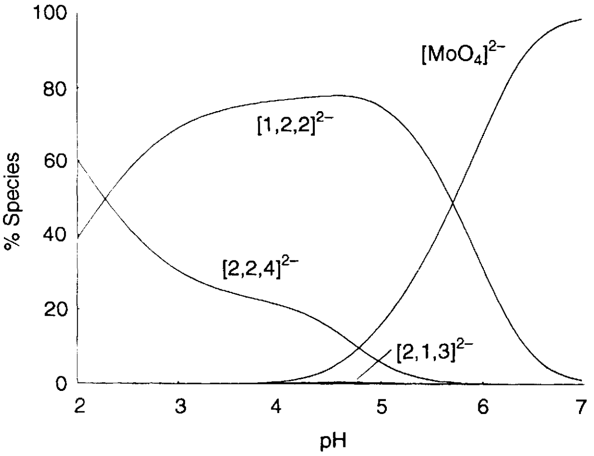

Fig. 1 Distribution of species in the molybdenum(VI)–benzilic acid system as a function of pH. The total concentrations of molybdate and benzilic acid are 0.05 and 0.10 mol dm^{-3}, respectively

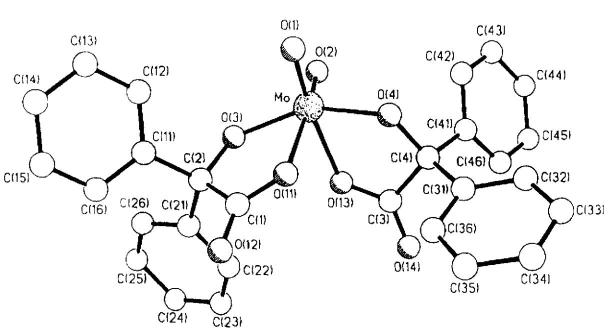

Fig. 2 Molecular structure of the complex anion $[MoO_2\{O_2CC(O)Ph_2\}_2]^{2-}$ showing the atom labelling scheme

No condensed species of free molybdate exist, the monomer $[1,2,2]^{2-}$ complex, corresponding to the formula $[MoO_2\{O_2CC(O)Ph_2\}_2]^{2-}$, being the predominant species between pH 7 and 5. A reversible pH-dependent equilibrium interconverts this species into the dinuclear species $[2,2,4]^{2-}$, $[Mo_2O_5(H_2O)_2\{O_2CC(O)Ph_2\}_2]^{2-}$, which reaches an estimable concentration below pH 4. The formation constants of these species were found to be log β_{122} = 17.35 and log β_{224} = 29.07. In the light of previous work on complex formation of molybdenum with other α-hydroxycarboxylate ligands such as lactate (log β_{122} = 15.71 and log β_{224} = 24.97)[11] both species included in the model are quite acceptable. However, the latter ligands differ from benzilate in that they form a second dinuclear $[2,2,5]^-$ species which is logically stable at lower pH values than those where $[2,2,4]^{2-}$ is predominant. This difference may be attributed to the steric hindrance exerted by the phenyl groups of benzilate which are considerably more bulky than are the methyl groups of lactate.

In most structurally characterised single-bridged complexes, $[(MoO_2L)_2O]$ (M = Mo or W),[1] the ligands L are usually in a *trans* (*anti*) position with respect to the Mo–O–Mo bridge (C_i symmetry) and, therefore, no steric constraints seem to exist. However, previous findings based on ^{13}C and ^1H NMR spectra for complex systems containing malic acid,[12] mannitol[13] and citric acid[14] ligands indicate that the structural changes involved in protonation of the single oxo-bridged $[2,2,4]^{2-}$ species can be rationalised in terms of the formation of a double oxo-bridged $[2,2,5]^-$ species having a *cis* arrangement of organic ligands (see Scheme 1). Under this assumption, steric effects from the phenyl groups of benzilate might be invoked to explain the absence of a $[2,2,5]^-$ species in the present molybdenum(VI)-benzilate system.

Structure of $[NH_4]_2[MoO_2\{O_2CC(O)Ph_2\}_2]\cdot 2H_2O$.—By following the procedure described in the Experimental section, the $[1,2,2]^{2-}$ complex has been isolated in the solid state as an ammonium salt, the crystal structure of which has been determined. Although complexes containing the $[MoO_2]^{2+}$ entity are quite common in the chemistry of molybdenum(VI),[1] few structures for hydroxycarboxylate ligands are known. Thus, only the structures of complexes with tartaric,[15] malic[16] and recently with salicylic (H_2sal)[17] acids have been determined by X-ray diffraction analysis. All these complexes have a distorted-octahedral geometry which is directly attributable to polydentate ligand constraints or ligand–ligand repulsions.

For the present complex the structural analysis shows the presence of monomeric anions having two chelated benzilate molecules co-ordinated to the central molybdenum atom, which is also multiply bonded to two terminal oxygen atoms in the conventional *cis* disposition. The overall octahedral geometry of this anion and the atom-labelling scheme used is shown in Fig. 2. The molecule has a C_2 axis which bisects the O(1)–Mo–O(2) angle but the co-ordination geometry is considerably distorted. As usual for oxomolybdenum complexes, the molybdenum atom is not at the centre of the co-ordination octahedron but is shifted toward the terminal unshared oxygen atoms. Moreover, the MoO_2 group has the general property of compressing those bond angles involving other atoms to less than the octahedral values of 90 or 180°. Atomic coordinates are given in Table 1, selected distances and angles in Table 2. Distances and angles within the ligand framework are unexceptional and are available as supplementary material.

The powerful *trans*-influencing ability of the multiply bonded oxygen can explain the disposition of the other co-ordinated groups on the ligand, which will arrange themselves with the weaker π-bonding donor atoms *trans* to these oxo groups. In our case, these positions are considered to be occupied by carboxylate groups which have a sp^2 and a p type lone pair forming part of a delocalised four-electron π system. The remaining two co-ordination positions, *trans* to one another and *cis* to the terminal oxygen atoms, should be filled by the oxygen-donor atoms of the alcoholic groups. This assumption is confirmed by the observed arrangement of benzilate, and also by the arrangement of the above-mentioned hydroxycarboxylate ligands in all previously characterised $Mo^{VI}O_2$ complexes.

The introduction of the sterically demanding phenyl groups has no significant effect on the bond angles or distances at the molybdenum centre. Thus, the chelate rings have bite angles of 75.2 and 75.5° and neither are planar [O(4)–C(4)–C(3)–O(13) and O(3)–C(2)–C(1)–O(11) dihedral angles 19.3 and 11.0°, respectively]. The Mo=O bond distances (1.713 and 1.717 Å) as well as the O(1)–Mo–O(2) angle (102.5°) are in the range found for other *cis*-dioxomolybdenum(VI) complexes. The single-bond $Mo–O_{lig}$ distances vary from 1.966 to 2.177 Å, and these variations may be ascribed to the different donor natures of the alcoholate and carboxylate oxygen atoms, and *trans* effects of terminal oxo groups. Thus, the two $Mo–O_{carboxylate}$ bonds *trans* to terminal oxide ligands (2.177 and 2.166 Å) are significantly longer than the two $Mo–O_{alcoholate}$ bonds (1.966 and 1.977 Å). These $Mo–O_{carboxylate}$ distances are comparable with those found in the $[MoO_3(H_2O)(C_2O_4)]^{2-}$ (ref. 18) and $[MoO_2(sal)_2]^{2-}$ (ref. 17) (2.14 and 2.15 Å, respectively), although they are shorter than 2.24 Å, a value found in the $[MoO_2(Hmal)_2]^{2-}$ complex[16] where the co-ordination of hydrogenmalate ligands occurs through a protonated carboxylate group.

Finally, there is a complicated network of hydrogen bonds involving ammonium and water protons and all oxygen atoms co-ordinated to Mo^{VI} (Table 3). The cation in this solid salt is not NH_4^+ but cyclic hydrated diammonium $[(NH_4\cdot H_2O)_2]^{2+}$, which is a square-planar cation linking adjacent complex anions having their O(3)–Mo–O(4) axis perpendicular to the two-

Table 1 Atomic coordinates (× 10^4) for $[NH_4]_2[MoO_2\{O_2CC(O)Ph_2\}_2]$ with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Mo	811(1)	2530(1)	2524(1)	C(4)	339(3)	1534(1)	3610(2)
O(1)	2406(3)	2521(1)	1711(2)	C(3)	−581(3)	1951(1)	4221(2)
O(2)	−890(3)	2514(1)	1763(2)	O(13)	−718(3)	2389(1)	3790(2)
O(3)	476(2)	3269(1)	2835(2)	O(14)	−1127(3)	1851(1)	5032(2)
C(2)	1417(3)	3539(1)	3564(2)	C(41)	−1024(3)	1199(1)	3124(2)
C(1)	2499(3)	3140(1)	4123(2)	C(42)	−1200(4)	1178(1)	2127(2)
O(11)	2534(3)	2691(1)	3723(2)	C(43)	−2484(4)	895(1)	1699(3)
O(12)	3289(3)	3264(1)	4852(2)	C(44)	−3590(4)	634(1)	2274(3)
C(11)	2625(3)	3915(1)	3079(2)	C(45)	−3442(4)	657(1)	3273(3)
C(12)	2994(4)	3872(1)	2103(2)	C(46)	−2160(4)	938(1)	3705(2)
C(13)	4224(4)	4191(2)	1687(3)	C(31)	1543(3)	1225(1)	4266(2)
C(14)	5021(4)	4555(1)	2260(3)	C(32)	1660(4)	691(1)	4228(2)
C(15)	4642(4)	4598(1)	3221(3)	C(33)	2741(4)	432(1)	4851(3)
C(16)	3470(4)	4286(1)	3645(3)	C(34)	3708(4)	699(2)	5505(3)
C(21)	167(3)	3802(1)	4259(2)	C(35)	3643(4)	1237(2)	5528(3)
C(22)	−503(4)	3517(1)	5023(2)	C(36)	2562(4)	1494(1)	4904(2)
C(23)	−1697(4)	3729(2)	5616(3)	O(20)	−5075(3)	1863(1)	3026(2)
C(24)	−2225(4)	4230(2)	5454(3)	O(30)	−3134(3)	3356(1)	3127(2)
C(25)	−1573(4)	4515(2)	4685(3)	N(40)	−4030(4)	2561(1)	4671(2)
C(26)	−378(4)	4297(1)	4096(3)	N(50)	−4252(3)	2684(2)	1655(2)
O(4)	1257(2)	1797(1)	2881(1)				

Table 2 Selected interatomic distances (Å) and angles (°) with e.s.d.s in parentheses

Mo–O(1)	1.713(3)	Mo–O(2)	1.717(3)
Mo–O(3)	1.966(2)	Mo–O(4)	1.977(2)
Mo–O(11)	2.177(2)	Mo–O(13)	2.166(3)
O(1)–Mo–O(2)	102.5(1)	O(1)–Mo–O(13)	163.0(1)
O(1)–Mo–O(3)	105.0(1)	O(2)–Mo–O(11)	164.2(1)
O(2)–Mo–O(3)	92.4(1)	O(2)–Mo–O(13)	90.8(1)
O(2)–Mo–O(4)	105.6(1)	O(3)–Mo–O(11)	75.2(1)
O(3)–Mo–O(4)	153.2(1)	O(3)–Mo–O(13)	84.7(1)
O(1)–Mo–O(4)	90.5(1)	O(13)–Mo–O(4)	75.5(1)
O(11)–Mo–O(4)	83.2(1)	C(2)–O(3)–Mo	123.1(2)
O(11)–Mo–O(13)	78.6(1)	C(1)–O(11)–Mo	118.4(2)
O(1)–Mo–O(11)	90.3(1)		

Table 3 Hydrogen-bonding geometries[a]

	X···Y	H···Y	X–H···Y/°
O(20)···O(4)	2.98	2.09	173
O(30)···O(3)	2.97	2.08	168
N(40)···O(12)	2.84	2.03	149
N(40)···O(20)	2.99	2.13	159
N(40)···O(1)	3.01	2.26	141
N(40)···O(30)	3.03	2.21	150
N(50)···O(14)	2.93	2.06	162
N(50)···O(2)	2.76	1.93	154
N(50)···O(30)	2.79	1.97	152
N(50)···O(1)[b]	2.74	2.22	116
N(50)···O(20)[b]	2.90	2.10	148

[a] X–H distances constrained to 0.90 Å. [b] Bifurcated hydrogen bond.

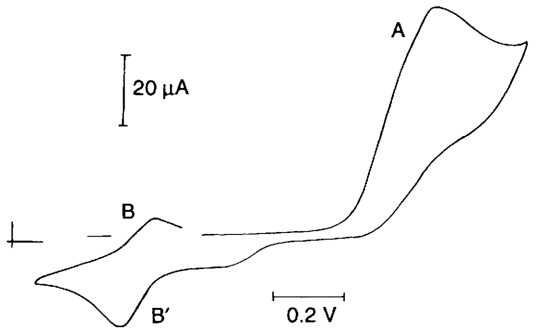

Fig. 3 Cyclic voltammogram of $[NH_4]_2[MoO_2\{O_2CC(O)Ph_2\}_2]\cdot 2H_2O$ (1.20 × 10^{-3} mol dm^{-3}) in methanol: GCE electrode; 0.10 mol dm^{-3} $[NBu^n{}_4][PF_6]$; scan rate = 0.17 V s^{-1}

dimensional hydrogen-bond sheets. This cation is a nearly perfect square with O···O and N···N distances of 4.12 and 4.15 Å, respectively, and a dihedral angle of only 2.7°. Although hydrogen bonding can have an important influence on solid-state structure, it appears to have little effect on the co-ordination geometry of the present complex because, despite differences in their hydrogen bonding and cation approaches, both benzilate molecules are symmetrically co-ordinated to molybdenum.

Comparison of this structure with that previously reported[19] for the related thiobenzilate complex $[NH_4]_2[MoO_2\{O_2CC(S)Ph_2\}_2]\cdot 2H_2O$ allows the effects of oxygen *vs.* sulfur co-ordination in otherwise identical ligands to be evaluated. The distorted-octahedral co-ordination unit of this last complex possesses features related to the preceding benzilate complex, namely an imposed C_2 axis which bisects the O=Mo=O angle and a *trans* orientation of sulfur atoms with both carboxylate groups *trans* to terminal oxo atoms. No significant differences in the mean values of the Mo–$O_{carboxylate}$ and Mo=O bond distances exist. The most important differences are a larger *trans* S–Mo–S angle of 158.7° *vs.* the $O_{alkoxide}$–Mo–$O_{alkoxide}$ angle of 153.2°, a much larger Mo–S distance of 2.422(1) Å compared to the mean Mo–$O_{alkoxide}$ of 1.971(2) Å.

Although the replacement of an alcoholate by thiolate group on the ligand appears to have little effect on the co-ordination geometry, it leads to important differences in the two-dimensional structure formed by the hydrated cyclic cation $[(NH_4\cdot H_2O)_2]^{2+}$, which is perpendicular to the complex anion axis S–Mo–S. This cation adopts now a rhombic structure with a long N···N axis (5.03 Å) and a short O···O axis (2.916 Å). The extensive hydrogen-bonding network has one N which bonds exclusively with Mo=O oxygens, while the other only interacts with carboxyl oxygens. In the benzilate complex, as mentioned above, the shape of the cation becomes a square in order to take part in additional hydrogen bonding with axial alcoholate oxygens which are not available in the sulfur complex.

Electrochemistry.—The cyclovoltammetric response observed for the *cis*-dioxomolybdenum(VI)–benzilate complex (see Fig. 3) at a glassy carbon working electrode and using methanol as solvent shows a prominent reduction peak at −1.45 V *vs.*

SCE, which is irreversibly associated with an oxidation peak at -0.44 V. The reversible nature of this oxidation process was evidenced in a second and successive scans by the development of its cathodic counterpart at -0.68 V.

According to the peak current of the primary reduction step ($I_{pc} = 950$ A cm $s^{1/2}$ $V^{-1/2}$ mol^{-1} at 0.10 V s^{-1}), two electrons are irreversibly transferred from the electrode to the $[Mo^{VI}O_2\{O_2CC(O)Ph_2\}_2]^{2-}$ complex, [20] while the half intensity of the reversible process indicates that the reoxidation of the electrochemically produced molybdenum(IV) complex is a one-electron process ($I_{pc} = 350$ A cm $s^{\frac{1}{2}}$ $V^{-\frac{1}{2}}$ mol^{-1} at 0.10 V s^{-1}). This behaviour is similar to that reported for the *cis*-dioxomolybdenum(VI)–thiobenzilate complex.[21] Accordingly, one can describe the more negative cathodic step by equation (2), whereas the reversible oxidation process is described by equation (3).

$$[Mo^{VI}O_2\{O_2CC(O)Ph_2\}_2]^{2-} + 2H^+ + 2e^- \longrightarrow [Mo^{IV}O\{O_2CC(O)Ph_2\}_2]^{2-} + H_2O \quad (2)$$

$$[Mo^{IV}O\{O_2CC(O)Ph_2\}_2]^{2-} \rightleftharpoons [Mo^{V}O\{O_2CC(O)Ph_2\}_2]^{-} + e^{-} \quad (3)$$

The irreversibility of the first cathodic step is a common feature in the electrochemistry of dioxomolybdenum(VI) complexes, attributable to the rearrangement of the coordination sphere accompanying oxo loss. Interestingly, the measured potential for the reduction of $[NH_4]_2[MoO_2[\{O_2CC(O)Ph_2\}_2]$ is approximately 200 mV higher than that previously recorded for $[NH_4]_2[MoO_2\{O_2CC(S)Ph_2\}_2]$. This is consistent with the observed electrochemistry of other dioxomolybdenum(VI) compounds in which replacement of oxygen by sulfur results in an anodic shift of their reduction potentials.[22,23] To explain this, the $[MoO_2(CO_2)_2]$ fragment can be viewed as a 'hard' acid and, when 'soft' sulfur donors are replaced by 'hard' oxygen atoms, a stronger metal–oxygen interaction will result in a more negative reduction potential.[23]

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