Synthesis, Structure and Spectroscopic Characterization of Sodium Tetrabutylammonium Tris(thiobenzilato)-molybdate(IV)†

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The synthesis, structure and spectroscopic properties of the mixed salt $[NBu^n_4]Na[Mo\{O_2CC(S)Ph_2\}_3]\cdot H_2O\cdot MeOH$ are reported. It crystallizes in the space group *Pbca*, with a = 19.369(6), b = 25.175(6), c = 24.273(6) Å, and Z = 8. The molybdenum atom is six-co-ordinated and bonded to both the thiolate sulfur and carboxylate oxygen atoms of each of the three co-ordinated thiobenzilate ligands. The average Mo–S and Mo–O distances are 2.291(4) and 2.076(9) Å, respectively, the former being the shortest observed for any tris(chelate)molybdenum complex. Contrary to the result predicted from previous molecular orbital calculations, the co-ordination polyhedron around the molybdenum atom is essentially trigonal prismatic. The two triangular faces, formed by three sulfur and three oxygen atoms from the thiolate and carboxylate groups, respectively, are nearly parallel and twisted by *ca.* 4.7° with respect to a regular prism. Sodium cations are intercalated between $Mo(S_3O_3)$ units and are also subject to a trigonal-prismatic co-ordination by three carboxylate oxygen atoms, two water and one methanol molecule. Cyclic voltammetry indicates that $[Mo\{O_2CC(S)Ph_2\}_3]^{2-}$ undergoes a reversible one-electron oxidation to $[Mo\{O_2CC(S)Ph_2\}_3]^-$ at −0.26 V (ESR parameters $\langle g \rangle$ = 1.968, $\langle A \rangle = 36 \times 10^{-4}$ cm^{-1}). The latter species can also be generated in solution by chemical oxidation.

The chemistry of molybdenum with sulfur-containing ligands continues to receive a great deal of attention owing to the potential relationship of these species with redox-active molybdoenzymes.[1] We have previously synthesised and characterized the dioxomolybdenum(VI) complex of 2-mercapto-2,2-diphenylacetic acid,[2] a ligand designed to prevent the formation of μ-oxo-molybdenum(V) dimers by steric encumbrance.[3] Under acidic conditions, the reaction of $[NBu^n_4]_2[Mo^{VI}O_2\{O_2CC(S)Ph_2\}_2]$ with thiobenzilic acid yields the monomeric $[NBu^n_4][Mo^VO\{O_2CC(S)Ph_2\}_2]$ as the only complex product, the structure of which has been previously determined by X-ray crystallography.[4] This complex is the first example of a mononuclear five-co-ordinated molybdenum(V) species possessing a $MoO(S_2O_2)$ donor set.

The same ligand, thiobenzilic acid, has been used in the present work to stabilize the first isolable mononuclear molybdenum(IV) complex possessing a $Mo(O_3S_3)$ co-ordination environment. We report herein that under less acidic conditions $[NBu^n_4]_2[Mo^{VI}O_2\{O_2CC(S)Ph_2\}_2]$ can be further reduced by partially neutralized thiobenzilic acid to give $[Mo\{O_2CC(S)Ph_2\}_3]^{2-}$, a stable monomeric molybdenum(IV) complex. There is a close structural relationship between this complex and other tris(chelate) complexes previously characterized containing bidentate (N,S)[5] or (S,S)[6] donor ligands. Among them, the tris(dithiolene) complexes are the oldest known members of this class whose structural, spectroscopic and redox properties have been thoroughly investigated and reviewed.[7] Of particular significance is that these compounds seem to adopt octahedral or trigonal-prismatic geometries, depending on the formal molybdenum oxidation state.

We should also point out that there is only one previous report[8] on the oxidation of a thiocarboxylic acid by molybdate ions, namely that of thioglycolic acid, a non-sterically hindered ligand, the oxidation of which was observed to take place in two steps. First Mo^{VI} is reduced to a dimeric molybdenum(V) thioglycolate complex which is then further reduced to a stable molybdenum(IV) species of unknown structure, whose most significant feature is the absence of Mo=O and Mo–O–Mo IR bands.

Results and Discussion

Synthesis.—The salt $[NBu^n_4]Na[Mo\{O_2CC(S)Ph_2\}_3]\cdot H_2O\cdot MeOH$ was prepared by following the procedure described in the Experimental section, based on the addition of $[NBu^n_4]_2[Mo^{VI}O_2\{O_2CC(S)Ph_2\}_2]$ to a methanolic solution of thiobenzilic acid (1:3) which had been partially neutralized with sodium methoxide (thiobenzilic acid/NaOMe = 1.5). This procedure gives a final red, ESR-silent, solution from which a crystalline solid precipitated.

With the aim of establishing the reaction stoichiometry and to analyse the oxidation product of thiobenzilic acid, ^{13}C and ^1H NMR spectra were recorded for the final solution of this reaction. The results demonstrated that 1 mol of $[O_2CC(S)Ph_2]_2$ is progressively generated for each mol of molybdenum(VI) complex reacted, as indicated by equation (1).

$$[Mo^{VI}O_2\{O_2CC(S)Ph_2\}_2]^{2-} + 3HSC(Ph)_2CO_2H + 2MeO^- \longrightarrow [Mo^{IV}\{O_2CC(S)Ph_2\}_3]^{2-} + [O_2CC(S)Ph_2]_2{}^{2-} + 2H_2O + 2MeOH \quad (1)$$

An interesting feature of this preparative reaction is the ability of thiobenzilic acid efficiently to remove all oxo groups from the co-ordination sphere of Mo^{VI}. Thus, in addition to acting as the reductant, it appears to be able to stabilize the final

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† *Supplementary data available* (No. SUP 56870, 2 pp.): cyclic voltammograms. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

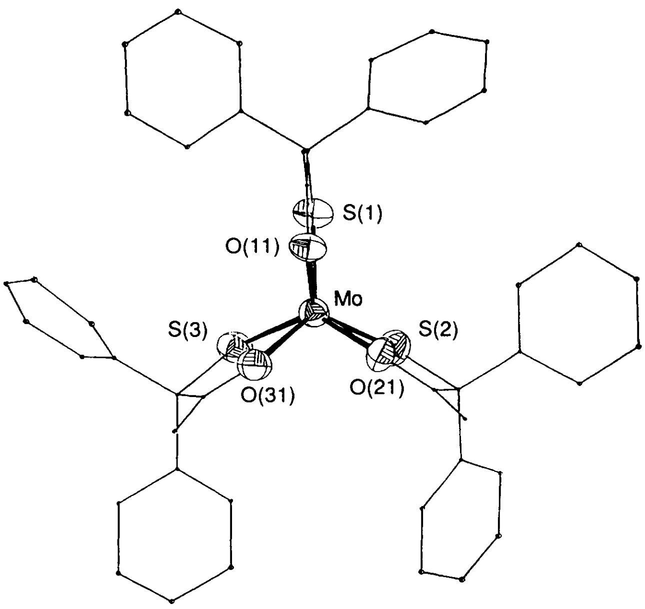

Fig. 1 An ORTEP drawing of the complex anion $[Mo\{O_2CC(S)Ph_2\}_3]^{2-}$ showing 50% probability ellipsoids and the atom labelling scheme. Hydrogen atoms omitted for clarity

Table 1 Selected fractional coordinates ($\times 10^4$) with estimated standard deviations (e.s.d.s) *

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Mo	3 655(1)	3 665(1)	4 266(1)
S(1)	2 475(2)	3 726(1)	4 228(2)
S(2)	3 601(2)	3 119(2)	3 514(2)
S(3)	3 525(2)	2 946(2)	4 836(2)
O(11)	3 527(4)	4 465(4)	4 422(4)
O(21)	4 423(5)	3 989(4)	3 783(4)
O(31)	4 461(5)	3 803(4)	4 830(4)
O(12)	2 959(5)	5 216(4)	4 537(5)
O(22)	5 185(6)	4 007(5)	3 102(5)
O(32)	5 154(6)	3 613(4)	5 521(5)
Na	−157(3)	4 622(2)	572(3)
O(2S)	600(5)	413(4)	4 783(4)
O(3S)	697(7)	4 787(5)	1 249(6)
C(3S)	1 442.1(2)	4 853(9)	1 180.1(1)
C(1)	2 281(8)	4 435(6)	4 363(7)
C(10)	2 969(8)	4 731(6)	4 442(6)
C(2)	4 282(8)	3 351(6)	3 027(6)
C(20)	4 692(8)	3 818(6)	3 199(7)
C(3)	4 208(8)	3 025(6)	5 374(6)
C(30)	4 636(8)	3 514(6)	5 242(7)

* Coordinates of the phenyl rings and NBu_4^+ cation are available as supplementary data.

molybdenum(VI) product. In this regard, the chemical behaviour of thiobenzilic acid is more closely related with that reported for unsaturated 1,2-dithiolate (1,2-dithiolenes) and amine thiol than with non-conjugated dithiolate ligands. In fact, while no tris(chelate) complexes are known for the latter ligands, 1,2-dithiolenes have been found to form tris(chelate) complexes of Mo^{IV}, Mo^{V} and Mo^{VI} displaying an array of interesting electrochemical, structural, and electronic properties.[7] In particular, molybdenum(IV) complexes display two intense absorption bands in the visible region of the spectrum and reversible electron-transfer behaviour.

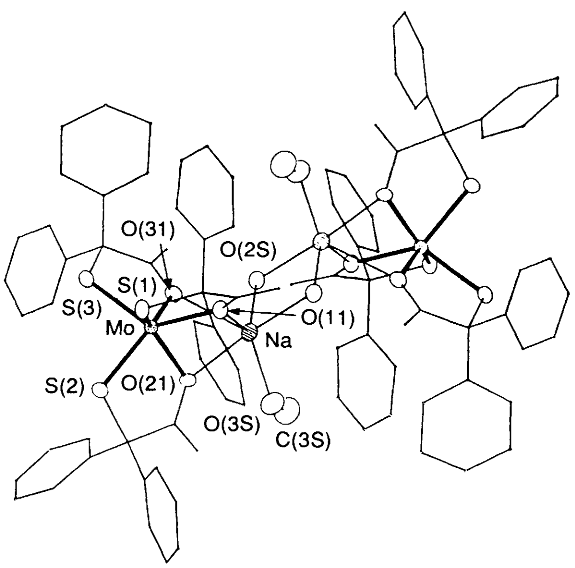

Fig. 2 Crystal structure of $[NBu^n_4]Na[Mo\{O_2CC(S)Ph_2\}_3{\cdot}H_2O{\cdot}MeOH$ showing the co-ordination of the sodium cation

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

Mo–S(1)	2.294(4)	Mo–O(11)	2.064(9)
Mo–S(2)	2.287(4)	Mo–O(21)	2.061(9)
Mo–S(3)	2.293(4)	Mo–O(31)	2.104(10)
O(11)–Na	2.557(14)	O(21)–Na	2.376(14)
O(31)–Na	2.397(14)	Mo···Na	3.355(5)
S(1)–Mo–S(2)	87.89(2)	S(3)–Mo–O(21)	137.3(3)
S(1)–Mo–S(3)	88.2(1)	S(1)–Mo–O(31)	139.0(3)
S(2)–Mo–S(3)	90.1(2)	S(2)–Mo–O(31)	130.7(3)
S(1)–Mo–O(11)	79.8(3)	S(3)–Mo–O(31)	79.6(3)
S(2)–Mo–O(11)	136.6(3)	O(11)–Mo–O(21)	78.7(4)
S(3)–Mo–O(11)	130.3(3)	O(11)–Mo–O(31)	79.0(4)
S(1)–Mo–O(21)	132.0(3)	O(21)–Mo–O(31)	76.7(4)
S(2)–Mo–O(21)	79.5(3)		

Structure of $[NBu^n_4]Na[Mo\{O_2CC(S)Ph_2\}_3]{\cdot}H_2O{\cdot}MeOH$.—A perspective view of the structure and numbering scheme for the anion $[Mo\{O_2CC(S)Ph_2\}_3]^{2-}$ is shown in Fig. 1; atomic coordinates are listed in Table 1, selected interatomic distances and interbond angles in Table 2. The structure of the anion reveals a mononuclear molybdenum(IV) complex in which the molybdenum atom is six-co-ordinate and bonded to both the sulfur and oxygen donor atoms from each of the three ligands. The MoS_3O_3 polyhedron is in accord with the criteria establishing trigonal-prismatic geometry;[9] the average torsion angle between the three-sulfur and three-oxygen planes is *ca.* 4.7°, significantly closer to the trigonal-prismatic limit of 0° than to the ideal octahedral value of 60°. The dihedral angle between these same planes (0.62°) indicates that they are almost perfectly parallel. The average Mo–S and Mo–O distances are 2.291(4) and 2.076(9) Å, respectively and the average lengths of the triangular face edges, S···S and O···O, are 3.203 and 2.618 Å, respectively. Therefore, although the MoO_3S_3 polyhedron is severely tapered, it conforms to approximately C_3 point symmetry. An important feature is that the Mo^{IV}–S distances are far shorter than those reported for molybdenum 1,2-dithiolene complexes (Table 3). Obviously, the origin of this shortening is related to the lower ability of the carboxylate to compete for available empty d orbitals as compared to a thiolate group.[12]

The crystal structure of this complex salt consists of monomeric tris(thiobenzilato)molybdate(IV) anions with sodium and tetrabutylammonium as the counter ions and one water and one methanol, per atom of molybdenum, as solvent molecules of crystallization. The packing is mainly achieved by Coulomb interactions with sodium ions occupying the cavities between the complex anions which have a clear dipolar structure that favours sodium co-ordination through the three carboxylate

Table 3 Comparative structural and spectroscopic parameters for molybdenum(IV) tris(chelate) complexes

Compound	Mo–S (Å)	S···S (Å)[a]	φ[b]/°	*b*[c]	λ_{max} (ε)[d]	Ref.
$[Mo(mnt)_3]^{2-}$	2.374	3.188	28	1.32	389 (9900) 667 (5800)	11
$[Mo\{S_2C_2(CO_2Me)_2\}_3]^{2-}$	2.393	3.18	10.6	1.29	356 (11500) 650 (5800)	6*c*
$[Mo(qdt)_3]^{2-}$	2.393	3.142	4.5	1.30	276 (10700) 561 (5500)	6*b*
$[Mo\{O_2CC(S)Ph_2\}_3]^{2-}$	2.291	3.203	4.7	1.28	310 (11600) 485 (5900)	This work

[a] Interligand *cis*. [b] Twist angle (0 for trigonal prism, 60° for octahedron). [c] Normalized bite as defined by Kepert (ref. 10). [d] nm (dm^3 mol^{-1} cm^{-1}).

groups on one of the triangular faces of the prism (Fig. 2). Therefore, the sodium cation is also subject to trigonal-prismatic co-ordination by three carboxylate oxygen atoms on one base and two water and one methanol molecules on the other (torsion angle 5.7°, dihedral angle 1.32°). The orientations of the phenyl rings from the ligands around each $Mo(O_3S_3)$ unit do not appear to be constrained.

As already noted, much of the interest shown in tris(chelate) complexes has concentrated on attempts to elucidate what factors are responsible for the preference of trigonal prismatic over octahedral co-ordination. It is generally considered that prism stability is due to electronic rather than steric or/and packing effects. Using this assumption, early reports[13] proposed a molecular orbital scheme for tris(chelate dithiolene) complexes in which the prism stability may be attributed to three kinds of interactions: (1) between the d_{z^2} orbital and ligand in-plane π_h orbitals; (2) of d_{xy} and $d_{x^2-y^2}$ with delocalized π_v orbitals which are perpendicular to the ligand plane and (3) interligand conjugation. The first d_{z^2} interaction represents at least formally a sulfur–sulfur bonding interaction, and gives rise to a bonding orbital localized primarily on the π_h ligand orbitals and an antibonding orbital which is largely metal d_{z^2} in character. Upon reduction, the occupation of this antibonding π_h orbital in molybdenum(V) monoanionic and molybdenum(IV) dianionic tris(dithiolene) complexes was expected to destabilize the Mo–S bonding features of this interaction, leading to a twist toward octahedral co-ordination. Although any assignment of formal oxidation state to these complexes possessing highly delocalized orbitals is artificial, pertinent examples to sustain this assumption were the earliest structural determinations for the neutral complexes $[Mo(S_2C_2H_2)_3]$,[14] $[Mo\{Se_2C_2(CF_3)_2\}_3]$[15] and $[Mo(S_2C_6H_4)_3]$[16] and for the dianionic complexes $[Mo(mnt)_3]^{2-}$ and $[W(mnt)_3]^{2-}$ [mnt = $S_2CC(CN)_2{}^{2-}$].[11] Thus the first three are formally d^0 complexes and exhibit regular trigonal-prismatic geometry about the Mo atom, while $[Mo(mnt)_3]^{2-}$ and $[W(mnt)_3]^{2-}$, being formally d^2 complexes, exhibit a structure intermediate between the octahedral and trigonal prismatic. Photoelectron spectroscopy supports the molybdenum(VI) formulation for the former species.[17]

For the present compound with 'innocent' ligands,[18] exhibiting no extensive intraligand π conjugation as 1,2-dithiolene ligands do and containing a π-donor carboxylate group weaker than thiolate, any of the three interactions above mentioned may be important in stabilizing its trigonal-prismatic geometry. The average S···S distance in this structure (3.203 Å), compared with the values reported for the 1,2-dithiolene complexes (see Table 3), cannot reasonably be associated with strong interligand attractive interactions. Nevertheless, this is not an exceptional case since, more recently, another two dianionic molybdenum(IV) complexes, namely $[Mo\{S_2C_2(CO_2Me)_2\}_3]^{2-}$ [ref. 6(*c*)] and $[Mo(qdt)_3]^{2-}$ (qdt = quinoxaline-2,3-dithiolate),[6b] have been structurally characterized and found to have an essentially prismatic geometry. Therefore, it seems that stability arguments based on the d^0 formalism are of limited utility and that the nature of the co-ordinated donor atoms* and/or the solid-state packing interactions may be the determining factor. In relation to the nature of the donor atoms on the ligand, with independence of the relative importance of σ and π bonding, for a given d-electron configuration, the proper matching of metal d-orbital energies with the energy of the appropriate ligand orbitals is likely to be an important factor in maintaining the trigonal-prismatic geometry in tris(chelate) complexes of the transition metals.[19] On this basis, in the compound under investigation the presence of the carboxylate groups which are less covalently bonded to the metal ion may result in a more covalent bonding of the remaining thiolate groups to the molybdenum centre, thus stabilizing a prismatic geometry. This explanation is consistent with the Mo–S distance which is significantly shorter in this carboxylate complex than in any other molybdenum(IV) dithiolene complex previously characterized (see Table 3). We are currently investigating this interpretation by extended-Hückel molecular orbital calculations.

Finally, in discussing the possible influence that Na^+ ions could have on the observed structure, we must note first that the octahedron is preferred on the basis of all arguments concerning interligand repulsion.[10] However, it has been also pointed out that this octahedral geometry must enlarge the ligand–ligand distance within one triangular face, with a possible weakening of the sodium–carboxylate bonding. In this regard, it is also worth noting that attempts to crystallize, from different solvents, other salts containing only ammonium, butylammonium or tetraphenylphosphonium have been unsuccessful.

Spectrophotometric and Electrochemical Properties.—The UV/VIS spectrum of $[Mo\{O_2CC(S)Ph_2\}_3]^{2-}$ in methanol is essentially characterized by two absorption bands whose positions, 485 (ε 5900) and 310 nm (ε 11 600 dm^3 mol^{-1} cm^{-1}), are not changed on going from the solid state to solution. These bands are comparable to those reported for the mentioned 1,2-dithiolene complexes (see Table 3). The differences in excitation energy and in absorption coefficients are probably related to the different donor abilities of the carboxylate and RS^- moieties. As previously pointed out,[6b] this dependence clearly indicates that these bands are due to metal-to-ligand charge-transfer transitions.

Cyclic voltammograms (see SUP 56870) of $[Mo^{IV}\{O_2CC(S)Ph_2\}_3]^{2-}$ in dimethylformamide (dmf) only show a peak when scanned in the anodic direction. However, a reduction peak could be observed in the cathodic direction after the first anodic scanning. This couple corresponds to a quasi-reversible one-electron process. The formal potential $[E^{\circ\prime} = (E_{p_a} +$

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* Another point is that the co-ordination polyhedron of tris(bidentate chelate) complexes also depends on the normalized bite of the ligand.[10] With smaller bite, more distortion of the polyhedron toward a trigonal prism can be expected and is indeed observed. The thiobenzilate normalized bite is 1.28 Å which is quite similar to those found for mnt, qdt and $[S_2C_2(CO_2Me)_2]^{2-}$ 1,2-dithiolate ligands (see Table 3).

$E_{p_c})/2]$ remains independent of scan rate, being −0.260 V *vs.* saturated calomel electrode (SCE) at a glassy carbon electrode and the ratio i_{p_a}/i_{p_c} is 1:1. This last result strongly supports the electrochemical generation of a stable molybdenum(V) species similar to the parent $[Mo^{IV}\{O_2CC(S)Ph_2\}_3]^{2-}$. Oxidation occurs at a potential at which oxidation should be readily accomplished by chemical oxidants. In fact addition of I_2 to a tetrahydrofuran (thf) solution of $[Mo^{IV}\{O_2CC(S)Ph_2\}_3]^{2-}$ produced a molybdenum(V) ESR signal ($\langle g \rangle = 1.968$, $\langle A \rangle = 36 \times 10^{-4}$ cm^{-1}) consistent with the formation of a monomeric complex $[Mo^{V}\{O_2CC(S)Ph_2\}_3]^{-}$.

The foregoing results demonstrate that the sterically hindered thiobenzilic acid can form a monomeric tris(chelate) complex of Mo^{IV} which displays structural, spectrophotometric and electrochemical properties resembling those previously reported for tris(1,2-dithiolene)molybdenum(IV) complexes.

Experimental

Instrumentation.—Absorption spectra in MeOH were measured by using a Perkin-Elmer Lambda-9 spectrophotometer. Cyclic voltammetry was carried out under an argon atmosphere using platinum and glassy-carbon disks as working electrodes, a platinum-wire auxiliary electrode and an SCE as reference electrode. Distilled MeOH and dmf were used with 0.1 mol dm^{-3} tetrabutylammonium hexafluorophosphate as supporting electrolyte.

Materials and Methods.—All reactions were carried out in dry, deoxygenated solvents under an argon atmosphere. The ligand 2-mercapto-2,2-diphenylacetic acid and the molybdenum(VI) complex $[NBu^n{}_4]_2[MoO_2\{O_2CC(S)Ph_2\}_2]$ were obtained by the previously published procedure.[2]

$[NBu^n{}_4]Na[Mo\{O_2CC(S)Ph_2\}_3]$. The ligand thiobenzilic acid (0.26 g, 1.05 mmol) and NaOMe (0.04 g, 0.7 mmol) were dissolved in methanol (7 cm^3). The solution was deaerated by bubbling argon and, then $[NBu_4]_2[MoO_2\{O_2CC(S)Ph_2\}_2]$ (0.4 g, 0.35 mmol) was added and the vessel sealed with a septum stopper. Storage at room temperature for 10–12 h produced a red crystalline solid which was collected to give 0.25 g (60%) of product (Found: C, 60.3; H, 6.1; N, 1.1; Na, 1.9; S, 8.8. $C_{59}H_{72}MoNNaO_8S_3$ requires C, 59.7; H, 6.6; N, 1.3; Na, 2.1; S, 9.0%).

Crystal-structure Determination.—$C_{59}H_{72}MoNNaO_8S_3$, $M_r = 1138.3$, orthorhombic, space group *Pbca*, $a = 19.369(6)$, $b = 25.175(6)$, $c = 24.273(6)$ Å, $U = 11\,836(6)$ Å^3, $Z = 8$, $D_c = 1.277$ g cm^{-3}, red prism (0.4 × 0.35 × 0.15 mm) sealed in a special C. Super Co glass capillary previously purged with argon, Mo-Kα radiation, $\lambda = 0.7093$ Å, $\mu = 4.3$ cm^{-1}, $F(000) = 4392$, $T = 298$ K.

Data were collected on an Enraf-Nonius CAD-4 diffractometer. Lattice parameters were obtained by the centring of 25 strong reflections at high 2θ angles. Intensity data for 9546 reflections (graphite-monochromated Mo-Kα radiation) were collected at room temperature in the θ–2θ scan mode. Three standard reflections collected every 100 showed no significant change (total decay −0.5%). The intensity data were corrected for Lorentz polarization but not for absorption. The observed systematic absences were uniquely consistent with space group *Pbca*. The structure was solved using Patterson maps and developed with SHELX 76 using successive full-matrix least-square refinements and Fourier difference syntheses. Due to the limited amount of significant data and the large number of atoms per asymmetric unit, only the Mo, S, O and Na atoms were refined anisotropically at the end. Benzilic hydrogen positions and CH_2 groups were calculated, fixed and assigned a common refined thermal parameter. A Fourier difference synthesis was essentially featureless (maximum 0.57 e Å^{-3}). The final reliability factors were $R = 0.064$, $R' = 0.068$ $\{w = 1.1/[\sigma^2(F) + 0.0029F^2]\}$ for 2732 unique reflections with $I > 3\sigma(I)$ and 365 refined parameters. Programs used and sources of scattering factor data are given in ref. 20(*a*) and the structure drawn using the ORTEP program.[20b]

Acknowledgements

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