

The Structures of Tris(pyridine)(η^6 -toluene)molybdenum Tetraphenylborate, Tetrakis(μ -methanethiolato)-bis(η^6 -toluene)dimolybdenum(Mo—Mo) Tetraphenylborate and Tris(μ -methanethiolato)- μ -methoxooxosulphato(1—)-bis(η^6 -toluene)dimolybdenum(Mo—Mo) Tetraphenylborate

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Abstract

The crystal structures of $[(\eta\text{-C}_6\text{H}_5\text{CH}_3)\text{Mo}(\text{NC}_5\text{H}_5)_3]\text{-}[\text{B}(\text{C}_6\text{H}_5)_4]$, $\text{C}_{22}\text{H}_{23}\text{MoN}_3^+\cdot\text{C}_{24}\text{H}_{20}\text{B}^-$ (I) [monoclinic, $a = 9.542$ (5), $b = 18.972$ (2), $c = 20.882$ (2) Å, $\beta = 94.44$ (2)°, $Z = 4$, $D_c = 1.31$ Mg m⁻³, space group $P2_1/c$, 3278 reflexions, $R = 0.034$, $R_w = 0.042$], $[(\eta\text{-C}_6\text{H}_5\text{CH}_3)\text{Mo}(\mu\text{-SCH}_3)_4\text{Mo}(\eta\text{-C}_6\text{H}_5\text{CH}_3)]\text{-}[\text{B}(\text{C}_6\text{H}_5)_4]_2$, $\text{C}_{18}\text{H}_{28}\text{Mo}_2\text{S}_4^+\cdot 2\text{C}_{24}\text{H}_{20}\text{B}^-$ (II) [triclinic, $a = 11.362$ (1), $b = 11.860$ (1), $c = 13.246$ (2) Å, $\alpha = 68.38$ (1), $\beta = 64.70$ (1), $\gamma = 62.92$ (1)°, $Z = 1$, $D_m = 1.44$, $D_c = 1.42$ Mg m⁻³, space group $P1$, 4324 reflexions, $R = 0.026$, $R_w = 0.032$], and $[(\eta\text{-C}_6\text{H}_5\text{CH}_3)\text{Mo}(\mu\text{-SCH}_3)_3\{\mu\text{-SO}(\text{OCH}_3)\}\text{Mo}(\eta\text{-C}_6\text{H}_5\text{CH}_3)]\text{-}[\text{B}(\text{C}_6\text{H}_5)_4]_2$, $\text{C}_{18}\text{H}_{28}\text{Mo}_2\text{O}_2\text{S}_4^+\cdot 2\text{C}_{24}\text{H}_{20}\text{B}^-$ (III) [triclinic, $a = 11.374$ (3), $b = 11.902$ (4), $c = 13.291$ (3) Å, $\alpha = 68.03$ (2), $\beta = 64.57$ (2), $\gamma = 62.90$ (3)°, $Z = 1$, $D_m = 1.42$, $D_c = 1.45$ Mg m⁻³, space group $P1$, 2058 reflexions, $R = 0.041$, $R_w = 0.053$] have been determined. In (II) and (III) the cations exist as dimers with two ($\eta\text{-C}_6\text{H}_5\text{CH}_3$)Mo species linked to each other by four bridging ligands: four methanethiolato bridges in (II) and three methanethiolato and one methoxooxosulphato bridge in (III), where problems of disorder were encountered. The Mo...Mo distances of 2.614 (1) and 2.644 (1) Å in (II) and (III) respectively, suggest a direct Mo—Mo bond.

Introduction

The reaction between $[(\eta\text{-toluene})_2\text{Mo}]\text{PF}_6$ and pyridine at 323 K gives the new paramagnetic 17-electron cation $[(\eta\text{-toluene})\text{Mo}(\text{pyridine})_3]^+$. Treatment of this cation with methanethiol yields the redox-active diamagnetic cation $[(\eta\text{-toluene})\text{Mo}(\mu\text{-SCH}_3)_4\text{Mo}(\eta\text{-toluene})]^{2+}$, which oxidizes with KMnO_4 to $[(\eta\text{-toluene})\text{Mo}(\mu\text{-SCH}_3)_3\{\mu\text{-SO}(\text{OCH}_3)\}\text{Mo}(\eta\text{-toluene})]^{2+}$. Single crystals suitable for X-ray crystallography of all three complexes were obtained as the

tetraphenylborate salts. A preliminary account of part of this work has appeared (Silverthorn, Couldwell & Prout, 1978).

Experimental

Dark maroon needles of (I) and red irregular-shaped crystals of (II) and (III) were provided by Dr W. E. Silverthorn. Compound (I) is air-sensitive and crystals were mounted under dry nitrogen in glass capillaries. It was not possible to measure their density. The crystals of (II) and (III) selected for data collection were mounted in glass capillaries.

After survey photography by Weissenberg and precession techniques, the crystals were set up on a Nonius CAD-4F diffractometer. Cell dimensions and the orientation matrix were obtained by least squares from the setting angles of 25 reflexions, using graphite-monochromated Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å.

The intensities of each independent reflexion with $\sin \theta/\lambda < 0.59$ (I), 0.62 (II) and 0.55 (III) Å⁻¹ were measured with an $\omega/2\theta$ scan, a variable scan rate and an ω scan angle of $(1.00 + 0.35 \tan \theta)^\circ$. Corrections for Lorentz and polarization effects, but not absorption, were made [$\mu(\text{Mo } K\alpha) = 0.37$ (I), 0.62 (II) and 0.62 (III) mm⁻¹].

Structure solution and refinement

The structures were solved by Patterson and Fourier techniques and refined by blocked-matrix least squares [(I): block 1: scale and dummy overall isotropic temperature factor (Rollett, 1965); block 2: positional parameters of the cation; block 3: U_{ii} components of the temperature factors of the cation; block 4: U_{ij} components of the temperature factors of the cation; block 5: positional parameters of the anion; block 6: U_{ii} components of the temperature factors of the anion; block 7: U_{ij} components of the temperature factors of

Table 1. Compound (I): fractional atomic coordinates and equivalent isotropic temperature factors

For H atoms U_{iso} was fixed at 0.05 Å ² .				
	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq} (Å ²)*
Mo(1)	0.09690 (4)	0.17241 (2)	0.02952 (2)	0.0409 (2)
N(10)	0.2348 (4)	0.2149 (2)	0.1148 (2)	0.053 (2)
N(20)	0.2381 (4)	0.2373 (2)	-0.0290 (2)	0.051 (2)
N(30)	-0.0394 (4)	0.2666 (2)	0.0453 (2)	0.054 (2)
C(1)	-0.1013 (6)	0.1121 (3)	0.0094 (3)	0.077 (3)
C(2)	-0.0315 (6)	0.0845 (3)	0.0659 (2)	0.078 (3)
C(3)	0.1073 (7)	0.0633 (3)	0.0657 (3)	0.087 (4)
C(4)	0.1771 (7)	0.0648 (3)	0.0103 (5)	0.120 (5)
C(5)	0.1108 (8)	0.0920 (3)	-0.0452 (3)	0.107 (4)
C(6)	-0.0285 (7)	0.1151 (3)	-0.0476 (2)	0.090 (3)
C(7)	-0.2504 (7)	0.1365 (4)	0.0103 (5)	0.153 (3)
C(11)	0.3042 (5)	0.1717 (3)	0.1574 (2)	0.067 (3)
C(12)	0.4057 (7)	0.1957 (3)	0.2027 (2)	0.086 (4)
C(13)	0.4383 (6)	0.2657 (4)	0.2066 (3)	0.087 (4)
C(14)	0.3640 (6)	0.3105 (3)	0.1646 (3)	0.077 (4)
C(15)	0.2638 (5)	0.2836 (3)	0.1203 (2)	0.062 (3)
C(21)	0.1936 (5)	0.2629 (3)	-0.0864 (2)	0.058 (3)
C(22)	0.2787 (5)	0.2947 (3)	-0.1280 (2)	0.069 (3)
C(23)	0.4187 (5)	0.3008 (3)	-0.1105 (3)	0.077 (4)
C(24)	0.4678 (5)	0.2740 (3)	-0.0524 (3)	0.082 (4)
C(25)	0.3785 (5)	0.2425 (3)	-0.0126 (2)	0.068 (3)
C(31)	-0.0916 (5)	0.3101 (2)	-0.0000 (2)	0.054 (3)
C(32)	-0.1913 (5)	0.3610 (3)	0.0096 (3)	0.066 (3)
C(33)	-0.2384 (6)	0.3686 (3)	0.0690 (3)	0.084 (4)
C(34)	-0.1865 (7)	0.3241 (4)	0.1160 (3)	0.102 (4)
C(35)	-0.0891 (6)	0.2743 (3)	0.1033 (2)	0.087 (4)
B(1)	0.8700 (4)	0.0380 (2)	0.2921 (2)	0.041 (2)
C(41)	0.8127 (4)	0.0057 (2)	0.3589 (2)	0.040 (2)
C(42)	0.8961 (4)	-0.0259 (2)	0.4091 (2)	0.047 (2)
C(43)	0.8432 (5)	-0.0502 (2)	0.4648 (2)	0.053 (2)
C(44)	0.7017 (5)	-0.0454 (2)	0.4735 (2)	0.058 (3)
C(45)	0.6150 (4)	-0.0151 (3)	0.4249 (2)	0.060 (3)
C(46)	0.6685 (4)	0.0096 (2)	0.3692 (2)	0.050 (2)
C(51)	1.0321 (4)	0.0134 (2)	0.2821 (2)	0.039 (2)
C(52)	1.1423 (4)	0.0347 (2)	0.3261 (2)	0.050 (2)
C(53)	1.2831 (4)	0.0212 (3)	0.3178 (2)	0.058 (3)
C(54)	1.3199 (4)	-0.0145 (2)	0.2640 (2)	0.060 (3)
C(55)	1.2157 (4)	-0.0357 (2)	0.2190 (2)	0.054 (3)
C(56)	1.0734 (4)	-0.0219 (2)	0.2283 (2)	0.047 (2)
C(61)	0.7602 (4)	0.0106 (2)	0.2326 (2)	0.045 (2)
C(62)	0.7381 (5)	-0.0617 (3)	0.2233 (2)	0.059 (3)
C(63)	0.6429 (5)	-0.0878 (3)	0.1750 (3)	0.078 (3)
C(64)	0.5690 (5)	-0.0425 (4)	0.1340 (3)	0.094 (3)
C(65)	0.5884 (5)	0.0283 (3)	0.1413 (2)	0.083 (3)
C(66)	0.6839 (4)	0.0547 (3)	0.1897 (2)	0.059 (3)
C(71)	0.8719 (4)	0.1251 (2)	0.2951 (2)	0.041 (2)
C(72)	0.7798 (5)	0.1657 (2)	0.3279 (2)	0.056 (3)
C(73)	0.7821 (6)	0.2389 (3)	0.3282 (2)	0.070 (3)
C(74)	0.8786 (6)	0.2751 (2)	0.2958 (2)	0.076 (3)
C(75)	0.9724 (6)	0.2376 (3)	0.2632 (2)	0.068 (3)
C(76)	0.9681 (5)	0.1643 (2)	0.2617 (2)	0.055 (3)
H(2)	-0.0321	0.0802	0.1061	
H(3)	0.1602	0.0466	0.1058	
H(4)	0.2749	0.0464	0.0083	
H(5)	0.1625	0.0958	-0.0851	
H(6)	-0.0764	0.1336	-0.0887	
H(7)	-0.2843	0.1545	-0.0331	
H(8)	-0.2555	0.1752	0.0427	
H(9)	-0.3108	0.0963	0.0223	
H(11)	0.2811	0.1203	0.1562	
H(12)	0.4559	0.1616	0.2329	

* $U_{\text{eq}} = \frac{1}{3}(U_{11}^2 + U_{22}^2 + U_{33}^2)^{1/2}$.

Table 1 (cont.)

	<i>x</i>	<i>y</i>	<i>z</i>
H(13)	0.5132	0.2837	0.2386
H(14)	0.3830	0.3624	0.1663
H(15)	0.2101	0.3172	0.0907
H(21)	0.0912	0.2588	-0.1000
H(22)	0.2388	0.3129	-0.1705
H(23)	0.4836	0.3243	-0.1392
H(24)	0.5703	0.2774	-0.0386
H(25)	0.4177	0.2229	0.0295
H(31)	-0.0567	0.3058	-0.0438
H(32)	-0.2284	0.3918	-0.0266
H(33)	-0.3089	0.4056	0.0778
H(34)	-0.2199	0.3278	0.1601
H(35)	-0.0530	0.2422	0.1388
H(42)	0.9992	-0.0311	0.4044
H(43)	0.9084	-0.0716	0.4992
H(44)	0.6631	-0.0632	0.5137
H(45)	0.5119	-0.0109	0.4301
H(46)	0.6023	0.0309	0.3351
H(52)	1.1185	0.0608	0.3655
H(53)	1.3575	0.0374	0.3509
H(54)	1.4208	-0.0246	0.2579
H(55)	1.2408	-0.0611	0.1795
H(56)	0.9996	-0.0381	0.1950
H(62)	0.7922	-0.0958	0.2522
H(63)	0.6285	-0.1397	0.1702
H(64)	0.5011	-0.0610	0.0992
H(65)	0.5342	0.0618	0.1118
H(66)	0.6976	0.1068	0.1936
H(72)	0.7084	0.1411	0.3526
H(73)	0.7125	0.2654	0.3524
H(74)	0.8804	0.3278	0.2961
H(75)	1.0447	0.2631	0.2400
H(76)	1.0358	0.1386	0.2360

the anion. (II): block 1: scale, dummy overall isotropic temperature factor and overall isotropic extinction parameter (Larson, 1967); block 2: positional parameters and temperature factors for the cation; block 3: positional parameters for the anion; block 4: temperature factors for the anion. (III): block 1: scale and dummy overall isotropic temperature factor; block 2: positional parameters and temperature factors for the cation; block 3: positional parameters for the anion; block 4: temperature factors for the anion]. Difference syntheses showed some evidence for the H atoms at their expected positions. They were positioned geometrically (C-H = 1.0 Å; $U_{\text{iso}} = 0.05 \text{ Å}^2$) and included in the structure factor calculations, their location being readjusted after each cycle. The weighting scheme was $w = 1/\sum_{r=1}^n A_r T_r^*(X)$, where n is the number of coefficients, A_r , for a Chebyshev series, T_r^* is the polynomial function, and X is $|F_o|/|F_o(\text{max})|$ (Rollett, 1965).

(a) Compound (I). All non-hydrogen atoms had anisotropic temperature factors. For the weighting scheme, three coefficients, A_r , were used with values of 133.4, 181.5 and 55.5, respectively, and the final R_w was 0.042 for 3278 reflexions [$I > 3\sigma(I)$].†

† $\sigma(I)$ is the standard deviation based on counting statistics.

Table 2. Compound (II): fractional atomic coordinates and equivalent isotropic temperature factors

For H atoms U_{150} was fixed at 0.05 Å².

	x	y	z	U_{eq} (Å ²)
Mo(1)	0.02846 (2)	0.02146 (2)	0.38947 (2)	0.0288 (2)
S(1)	0.03893 (7)	0.16350 (6)	0.47897 (6)	0.040 (3)
S(2)	0.20801 (6)	-0.11271 (6)	0.48504 (6)	0.038 (3)
C(1)	-0.1020 (4)	0.3210 (3)	0.4870 (4)	0.078 (2)
C(2)	0.3322 (3)	-0.0412 (4)	0.4616 (3)	0.065 (2)
C(3)	0.1113 (3)	0.1577 (3)	0.2087 (2)	0.053 (2)
C(4)	0.2075 (3)	0.0313 (3)	0.2157 (2)	0.053 (2)
C(5)	0.1698 (4)	-0.0760 (4)	0.2369 (3)	0.069 (2)
C(6)	0.0364 (5)	-0.0541 (5)	0.2419 (3)	0.101 (3)
C(7)	-0.0649 (4)	0.0677 (6)	0.2471 (3)	0.099 (2)
C(8)	-0.0298 (4)	0.1760 (4)	0.2360 (3)	0.063 (2)
C(9)	0.1555 (4)	0.2700 (4)	0.1809 (3)	0.067 (2)
B(1)	0.2483 (3)	0.2524 (3)	0.7658 (2)	0.031 (1)
C(11)	0.0818 (2)	0.2703 (2)	0.8212 (2)	0.032 (1)
C(12)	-0.0197 (3)	0.3735 (3)	0.7757 (2)	0.043 (1)
C(13)	-0.1600 (3)	0.3887 (3)	0.8225 (3)	0.051 (2)
C(14)	-0.2049 (3)	0.3007 (3)	0.9168 (2)	0.048 (2)
C(15)	-0.1093 (3)	0.1990 (3)	0.9662 (2)	0.043 (1)
C(16)	0.0313 (3)	0.1847 (3)	0.9189 (2)	0.036 (1)
C(21)	0.2834 (3)	0.3327 (2)	0.8203 (2)	0.033 (1)
C(22)	0.4218 (3)	0.3078 (3)	0.8085 (2)	0.042 (1)
C(23)	0.4563 (3)	0.3813 (3)	0.8452 (3)	0.052 (2)
C(24)	0.3554 (4)	0.4808 (3)	0.8966 (3)	0.058 (2)
C(25)	0.2171 (3)	0.5079 (3)	0.9124 (2)	0.050 (1)
C(26)	0.1833 (3)	0.4344 (3)	0.8741 (2)	0.040 (1)
C(31)	0.2916 (3)	0.3060 (2)	0.6252 (2)	0.033 (1)
C(32)	0.3918 (3)	0.3654 (3)	0.5631 (2)	0.044 (2)
C(33)	0.4335 (3)	0.4045 (3)	0.4451 (2)	0.048 (2)
C(34)	0.3745 (3)	0.3886 (3)	0.3818 (2)	0.045 (2)
C(35)	0.2745 (4)	0.3310 (3)	0.4389 (2)	0.057 (2)
C(36)	0.2347 (3)	0.2918 (3)	0.5570 (2)	0.047 (2)
C(41)	0.3365 (2)	0.0954 (2)	0.7965 (2)	0.032 (1)
C(42)	0.3628 (3)	0.0121 (3)	0.7312 (2)	0.042 (1)
C(43)	0.4277 (3)	-0.1223 (3)	0.7600 (3)	0.053 (2)
C(44)	0.4714 (3)	-0.1774 (3)	0.8558 (3)	0.059 (2)
C(45)	0.4465 (3)	-0.0986 (3)	0.9234 (3)	0.055 (2)
C(46)	0.3800 (3)	0.0351 (3)	0.8937 (2)	0.045 (2)
H(111)	-0.0864	0.3697	0.5248	
H(112)	-0.1929	0.3077	0.5324	
H(113)	-0.1039	0.3717	0.4080	
H(221)	0.4001	-0.1033	0.5040	
H(222)	0.2813	0.0412	0.4901	
H(223)	0.3834	-0.0221	0.3781	
H(4)	0.3057	0.0159	0.2055	
H(5)	0.2384	-0.1664	0.2481	
H(6)	0.0140	-0.1263	0.2418	
H(7)	-0.1630	0.0813	0.2586	
H(8)	-0.1044	0.2621	0.2474	
H(91)	0.2586	0.2381	0.1641	
H(92)	0.1075	0.3126	0.2477	
H(93)	0.1298	0.3340	0.1126	
H(12)	0.0097	0.4389	0.7068	
H(13)	-0.2289	0.4643	0.7872	
H(14)	-0.3054	0.3105	0.9491	
H(15)	-0.1406	0.1352	1.0358	
H(16)	0.0988	0.1102	0.9564	
H(22)	0.4981	0.2345	0.7724	
H(23)	0.5562	0.3610	0.8337	
H(24)	0.3808	0.5334	0.9226	
H(25)	0.1419	0.5797	0.9509	
H(26)	0.0831	0.4657	0.8859	
H(32)	0.4354	0.3801	0.6064	
H(33)	0.5068	0.4447	0.4055	

Table 2 (cont.)

	x	y	z
H(34)	0.4032	0.4178	0.2966
H(35)	0.2309	0.3176	0.3947
H(36)	0.1617	0.2513	0.5958
H(42)	0.3339	0.0504	0.6607
H(43)	0.4424	-0.1784	0.7117
H(44)	0.5206	-0.2732	0.8758
H(45)	0.4760	-0.1376	0.9936
H(46)	0.3628	0.0902	0.9439

(b) Compound (II). All non-hydrogen atoms had anisotropic temperature factors. In the final stages of refinement, an overall isotropic extinction parameter (165.0) was introduced, as well as the weighting scheme with three coefficients, A_r , with values of 2.29, 3.02 and 1.17, respectively. The final R_w was 0.032 for 4324 reflexions [$I > 3\sigma(I)$].

(c) Compound (III). All non-hydrogen atoms except the O and C atoms of the bridging groups had anisotropic temperature factors. The H atoms of the bridging groups were not located. During the refinement it was evident that disorder is present in the region of the bridging groups in the cation. As no better result was obtained in space group $P1$, the final calculations were made in space group $P\bar{1}$. The most plausible model, on both chemical and crystallographic grounds, appears to be that the crystals contain [(toluene)- $\text{Mo}(\mu\text{-SCH}_3)_3\{\mu\text{-SO}(\text{OCH}_3)\}\text{Mo}(\text{toluene})]^{2+}$ with each of the four bridging groups being 75% SCH_3 and 25% $\text{SO}(\text{OCH}_3)$. For this model, the occupancies of C(1) and C(2) were set equivalent, as were the occupancies of C(111), C(222), O(1), O(2), O(3) and O(4). The distances and angles about the S atoms involving O and C were refined with constraints (Waser, 1963; Rollett, 1969). For the weighting scheme, three coefficients, A_r , were used with values 17.28, 22.75 and 9.46, respectively, and the final R_w was 0.053 for 2058 reflexions [$I > 3\sigma(I)$].

Calculations were performed with *CRYSTALS* (Carruthers, 1978) on the Oxford University ICL 1906A and 2980 computers, and the University of London CDC 7600 computer. Complex neutral-atom scattering factors were taken from *International Tables for X-ray Crystallography* (1974).

Results and discussion

Final atomic coordinates are given in Tables 1, 2 and 3,* and bond lengths and angles, with e.s.d.'s calculated

* Lists of structure factors and anisotropic thermal parameters and details of molecular-planes calculations for all three compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36463 (95 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Compound (III): fractional atomic coordinates and equivalent isotropic temperature factors

For C(1) through O(4), U_{iso} was fixed at 0.08 Å² and for H atoms U_{iso} was fixed at 0.05 Å².

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq} (Å ²)
Mo(1)	0.02901 (8)	0.02165 (8)	0.38835 (6)	0.3868 (4)
S(1)	0.0366 (3)	0.1645 (3)	0.4826 (3)	0.0918 (2)
S(2)	0.2058 (3)	-0.1124 (2)	0.4875 (2)	0.0625 (2)
C(1)	-0.100 (1)	0.326 (1)	0.498 (1)	
C(2)	0.335 (2)	-0.048 (1)	0.463 (1)	
C(111)	-0.162 (5)	0.342 (5)	0.568 (4)	
C(222)	0.389 (5)	-0.081 (5)	0.516 (5)	
O(1)	0.150 (3)	0.073 (3)	0.475 (2)	
O(2)	0.149 (3)	-0.188 (3)	0.496 (2)	
O(3)	-0.135 (3)	0.324 (3)	0.472 (2)	
O(4)	0.311 (3)	-0.003 (3)	0.459 (3)	
C(3)	0.113 (1)	0.154 (1)	0.2082 (8)	0.074 (5)
C(4)	0.207 (1)	0.029 (1)	0.2160 (8)	0.063 (6)
C(5)	0.170 (1)	-0.077 (1)	0.2381 (9)	0.088 (5)
C(6)	0.039 (2)	-0.056 (2)	0.245 (1)	0.017 (3)
C(7)	-0.064 (2)	0.065 (2)	0.247 (1)	0.015 (3)
C(8)	-0.026 (1)	0.174 (1)	0.2337 (9)	0.084 (5)
C(9)	0.157 (1)	0.266 (1)	0.179 (1)	0.090 (9)
B(1)	0.249 (1)	0.2542 (9)	0.7650 (8)	0.039 (5)
C(11)	0.0827 (8)	0.2722 (7)	0.8199 (6)	0.040 (5)
C(12)	-0.0189 (9)	0.3763 (8)	0.7761 (7)	0.049 (5)
C(13)	-0.1575 (9)	0.3937 (9)	0.8231 (8)	0.057 (6)
C(14)	-0.2045 (9)	0.3040 (9)	0.9167 (7)	0.058 (5)
C(15)	-0.1092 (9)	0.2005 (9)	0.9629 (7)	0.050 (6)
C(16)	0.0306 (8)	0.1863 (8)	0.9162 (7)	0.043 (5)
C(21)	0.2848 (8)	0.3333 (7)	0.8193 (6)	0.036 (4)
C(22)	0.4227 (9)	0.3075 (8)	0.8066 (7)	0.048 (5)
C(23)	0.4574 (9)	0.3807 (8)	0.8439 (8)	0.058 (6)
C(24)	0.355 (1)	0.4789 (8)	0.8964 (7)	0.059 (6)
C(25)	0.220 (1)	0.5058 (8)	0.9108 (7)	0.055 (5)
C(26)	0.1851 (9)	0.4337 (8)	0.8729 (7)	0.047 (5)
C(31)	0.2923 (8)	0.3066 (7)	0.6246 (7)	0.042 (5)
C(32)	0.3936 (9)	0.3644 (8)	0.5605 (7)	0.049 (6)
C(33)	0.4371 (9)	0.4014 (9)	0.4435 (7)	0.054 (6)
C(34)	0.377 (1)	0.3866 (8)	0.3819 (7)	0.049 (5)
C(35)	0.276 (1)	0.3324 (9)	0.4389 (7)	0.063 (6)
C(36)	0.236 (1)	0.2925 (9)	0.5563 (7)	0.057 (6)
C(41)	0.3366 (7)	0.0964 (7)	0.7972 (7)	0.039 (5)
C(42)	0.3640 (9)	0.0130 (8)	0.7315 (8)	0.052 (6)
C(43)	0.428 (1)	-0.1197 (9)	0.7613 (9)	0.065 (6)
C(44)	0.4694 (9)	-0.1743 (8)	0.859 (1)	0.069 (6)
C(45)	0.444 (1)	-0.0962 (9)	0.9251 (9)	0.063 (6)
C(46)	0.3794 (9)	0.0355 (8)	0.8952 (7)	0.048 (5)
H(4)	0.3056	0.0132	0.2054	
H(5)	0.2391	-0.1669	0.2486	
H(6)	0.0161	-0.1296	0.2493	
H(7)	-0.1615	0.0786	0.2578	
H(8)	-0.0992	0.2605	0.2427	
H(91)	0.2600	0.2339	0.1631	
H(92)	0.1083	0.3094	0.2444	
H(93)	0.1328	0.3284	0.1096	
H(12)	0.0110	0.4414	0.7069	
H(13)	-0.2259	0.4721	0.7895	
H(14)	-0.3054	0.3150	0.9492	
H(15)	-0.1400	0.1346	1.0307	
H(16)	0.0975	0.1107	0.9534	
H(22)	0.4984	0.2351	0.7700	
H(23)	0.5572	0.3611	0.8321	
H(24)	0.3803	0.5303	0.9238	
H(25)	0.1453	0.5775	0.9488	
H(26)	0.0849	0.4552	0.8847	
H(32)	0.4372	0.3797	0.6031	

Table 3 (cont.)

	<i>x</i>	<i>y</i>	<i>z</i>
H(33)	0.5126	0.4391	0.4033
H(34)	0.4056	0.4149	0.2967
H(35)	0.2302	0.3216	0.3952
H(36)	0.1640	0.2513	0.5948
H(42)	0.3363	0.0512	0.6605
H(43)	0.4434	-0.1760	0.7133
H(44)	0.5178	-0.2699	0.8797
H(45)	0.4721	-0.1353	0.9958
H(46)	0.3624	0.0902	0.9452

from the variance-covariance matrix, in Tables 4, 5 and 6. Projections of the molecules are shown in Figs. 1, 2 and 3. Details of selected molecular planes have been deposited.*

For compound (I) the asymmetric unit contains one cation and one anion, both in general positions. The shortest inter-ionic distance (not involving H atoms) is C(35)···C(75) 3.417 Å, with C(75) related by $x - 1, y, z$ to the parameters in Table 1.

For compound (II) the unit cell contains one cation with the structure shown in Fig. 2, together with two tetraphenylborate anions. The cation exists as a discrete dimeric species of crystallographic point-group symmetry C_i . The successful refinement in $P1$, which requires the cation to have the centre of symmetry, was taken as confirmation of this space group and no calculations were made in $P1$. The shortest inter-ionic distance (not involving H atoms) is C(6)···C(15), 3.388 Å, with C(15) related by $\bar{x}, \bar{y}, 1 - z$ to the parameters in Table 2.

For compound (III) the unit cell contains one cation, one of the four possible orientations of the disordered cation being shown in Fig. 3, together with two tetraphenylborate anions. As no better result was obtained in $P1$, the space group chosen was $P\bar{1}$, which requires the cation to have a centre of symmetry. The shortest inter-ionic distances (not involving H atoms) are C(111)···C(34), 3.136 Å, and C(111)···C(33), 3.235 Å, with C(33) and C(34) related by $\bar{x}, 1 - y, 1 - z$ to the parameters in Table 3.

In all three compounds, the tetraphenylborate anions have almost regular tetrahedral geometry about the B atom. The B—C lengths, in the ranges (I) 1.645 (5)–1.654 (6), (II) 1.638 (4)–1.656 (4) and (III) 1.64 (1)–1.66 (1) Å, and the C—B—C angles, in the ranges (I) 106.3 (3)–112.2 (3), (II) 106.6 (2)–110.9 (2) and (III) 106.5 (6)–110.8 (6)°, compare well with values found for this anion in other structures (Nolte & Singleton, 1976; Di Vaira, 1975; Di Vaira & Orlandini, 1972). Each phenyl ring is planar within experimental error and the C—C bond lengths are normal, (I) 1.362 (8)–1.411 (6), (II) 1.366 (5)–1.409 (4) and (III) 1.36 (1)–1.41 (1) Å. However, the angles in the rings indicate

* See deposition footnote.

some hindrance between the substituents at B, similar to that found previously (Di Vaira, 1975; Di Vaira & Orlandini, 1972), the angles at the C atom bonded to B

Table 4. *Compound (I): interatomic distances (Å) and bond angles (°)*

Mo(1)—N(10)	2.278 (4)	C(11)—C(12)	1.377 (7)
Mo(1)—N(20)	2.253 (3)	C(12)—C(13)	1.364 (8)
Mo(1)—N(30)	2.249 (4)	C(13)—C(14)	1.378 (8)
Mo(1)—C(1)	2.223 (5)	C(14)—C(15)	1.377 (7)
Mo(1)—C(2)	2.237 (5)	C(15)—N(10)	1.336 (6)
Mo(1)—C(3)	2.203 (5)	N(20)—C(21)	1.331 (5)
Mo(1)—C(4)	2.228 (6)	C(21)—C(22)	1.374 (6)
Mo(1)—C(5)	2.193 (5)	C(22)—C(23)	1.362 (7)
Mo(1)—C(6)	2.216 (5)	C(23)—C(24)	1.365 (7)
C(1)—C(2)	1.411 (7)	C(24)—C(25)	1.372 (7)
C(2)—C(3)	1.385 (8)	C(25)—N(20)	1.361 (6)
C(3)—C(4)	1.379 (9)	N(30)—C(31)	1.324 (5)
C(4)—C(5)	1.377 (9)	C(31)—C(32)	1.381 (6)
C(5)—C(6)	1.396 (9)	C(32)—C(33)	1.359 (7)
C(6)—C(1)	1.425 (8)	C(33)—C(34)	1.358 (8)
C(1)—C(7)	1.497 (9)	C(34)—C(35)	1.366 (8)
N(10)—C(11)	1.345 (6)	C(35)—N(30)	1.341 (6)
N(10)—Mo(1)—N(20)	84.1 (1)	C(14)—C(15)—N(10)	123.2 (5)
N(10)—Mo(1)—N(30)	84.8 (1)	Mo(1)—N(20)—C(21)	121.7 (3)
N(20)—Mo(1)—N(30)	91.3 (1)	Mo(1)—N(20)—C(25)	121.4 (3)
C(7)—C(1)—C(2)	119.4 (6)	C(25)—N(20)—C(21)	116.1 (4)
C(7)—C(1)—C(6)	121.6 (6)	N(20)—C(21)—C(22)	124.5 (4)
C(6)—C(1)—C(2)	119.0 (5)	C(21)—C(22)—C(23)	118.8 (5)
C(1)—C(2)—C(3)	119.6 (5)	C(22)—C(23)—C(24)	118.0 (5)
C(2)—C(3)—C(4)	121.4 (6)	C(23)—C(24)—C(25)	120.9 (5)
C(3)—C(4)—C(5)	119.5 (6)	C(24)—C(25)—N(20)	121.7 (5)
C(4)—C(5)—C(6)	121.5 (5)	Mo(1)—N(30)—C(31)	125.4 (3)
C(5)—C(6)—C(1)	118.8 (5)	Mo(1)—N(30)—C(35)	117.9 (3)
Mo(1)—N(10)—C(11)	121.8 (3)	C(35)—N(30)—C(31)	116.0 (4)
Mo(1)—N(10)—C(15)	121.0 (3)	N(30)—C(31)—C(32)	123.9 (5)
C(15)—N(10)—C(11)	116.8 (4)	C(31)—C(32)—C(33)	119.1 (5)
N(10)—C(11)—C(12)	122.5 (5)	C(32)—C(33)—C(34)	117.8 (5)
C(11)—C(12)—C(13)	120.5 (5)	C(33)—C(34)—C(35)	120.3 (5)
C(12)—C(13)—C(14)	117.4 (5)	C(34)—C(35)—N(30)	123.0 (5)
C(13)—C(14)—C(15)	119.7 (5)		
B(1)—C(41)	1.654 (6)	C(55)—C(56)	1.411 (6)
B(1)—C(51)	1.645 (5)	C(56)—C(51)	1.390 (5)
B(1)—C(61)	1.646 (6)	C(61)—C(62)	1.398 (6)
B(1)—C(71)	1.654 (6)	C(62)—C(63)	1.395 (6)
C(41)—C(42)	1.401 (5)	C(63)—C(64)	1.369 (8)
C(42)—C(43)	1.383 (6)	C(64)—C(65)	1.362 (8)
C(43)—C(44)	1.379 (6)	C(65)—C(66)	1.400 (6)
C(44)—C(45)	1.384 (6)	C(66)—C(61)	1.391 (6)
C(45)—C(46)	1.388 (6)	C(71)—C(72)	1.389 (6)
C(46)—C(41)	1.411 (5)	C(72)—C(73)	1.389 (6)
C(51)—C(52)	1.402 (5)	C(73)—C(74)	1.369 (7)
C(52)—C(53)	1.391 (6)	C(74)—C(75)	1.366 (7)
C(53)—C(54)	1.379 (6)	C(75)—C(76)	1.392 (6)
C(54)—C(55)	1.375 (6)	C(76)—C(71)	1.408 (6)
C(41)—B(1)—C(51)	112.2 (3)	C(53)—C(54)—C(55)	119.0 (4)
C(41)—B(1)—C(61)	106.7 (3)	C(54)—C(55)—C(56)	120.2 (4)
C(41)—B(1)—C(71)	110.0 (3)	C(55)—C(56)—C(51)	122.5 (4)
C(51)—B(1)—C(61)	111.4 (3)	B(1)—C(61)—C(62)	119.7 (4)
C(51)—B(1)—C(71)	106.3 (3)	B(1)—C(61)—C(66)	124.6 (4)
C(61)—B(1)—C(71)	110.4 (3)	C(66)—C(61)—C(62)	115.7 (4)
B(1)—C(41)—C(42)	125.7 (3)	C(61)—C(62)—C(63)	122.1 (5)
B(1)—C(41)—C(46)	119.9 (3)	C(62)—C(63)—C(64)	120.3 (5)
C(46)—C(41)—C(42)	114.4 (4)	C(63)—C(64)—C(65)	119.4 (5)
C(41)—C(42)—C(43)	123.3 (4)	C(64)—C(65)—C(66)	120.5 (5)
C(42)—C(43)—C(44)	120.9 (4)	C(65)—C(66)—C(61)	122.0 (5)
C(43)—C(44)—C(45)	117.9 (4)	B(1)—C(71)—C(72)	124.6 (4)
C(44)—C(45)—C(46)	121.1 (4)	B(1)—C(71)—C(76)	121.0 (4)
C(45)—C(46)—C(41)	122.5 (4)	C(76)—C(71)—C(72)	114.4 (4)
B(1)—C(51)—C(52)	120.0 (3)	C(71)—C(72)—C(73)	123.1 (4)
B(1)—C(51)—C(56)	124.6 (3)	C(72)—C(73)—C(74)	120.7 (5)
C(56)—C(51)—C(52)	115.1 (3)	C(73)—C(74)—C(75)	118.5 (4)
C(51)—C(52)—C(53)	123.2 (4)	C(74)—C(75)—C(76)	120.8 (5)
C(52)—C(53)—C(54)	120.1 (4)	C(75)—C(76)—C(71)	122.4 (4)

Table 5. *Compound (II): interatomic distances (Å) and bond angles (°)*

Mo(1)—Mo(1 ¹)	2.614 (1)	Mo(1)—C(8)	2.287 (3)
Mo(1)—S(1)	2.456 (1)	S(1)—C(1)	1.828 (3)
Mo(1)—S(1 ¹)	2.451 (1)	S(2)—C(2)	1.825 (3)
Mo(1)—S(2)	2.462 (1)	C(3)—C(4)	1.394 (5)
Mo(1)—S(2 ¹)	2.452 (1)	C(4)—C(5)	1.418 (5)
Mo(1)—C(3)	2.416 (3)	C(5)—C(6)	1.392 (6)
Mo(1)—C(4)	2.338 (3)	C(6)—C(7)	1.381 (7)
Mo(1)—C(5)	2.292 (3)	C(7)—C(8)	1.451 (6)
Mo(1)—C(6)	2.386 (3)	C(8)—C(3)	1.413 (5)
Mo(1)—C(7)	2.324 (3)	C(3)—C(9)	1.499 (5)
S(1)—Mo(1)—S(1 ¹)	115.61 (2)	C(2)—S(2)—Mo(1)	116.0 (1)
S(1)—Mo(1)—S(2)	73.38 (2)	C(2)—S(2)—Mo(1 ¹)	116.2 (1)
S(1)—Mo(1)—S(2 ¹)	73.60 (2)	C(8)—C(3)—C(4)	118.1 (3)
S(1 ¹)—Mo(1)—S(2)	73.52 (2)	C(3)—C(5)—C(4)	121.8 (3)
S(1 ¹)—Mo(1)—S(2 ¹)	73.65 (2)	C(4)—C(5)—C(6)	119.3 (4)
S(2)—Mo(1)—S(2 ¹)	115.73 (2)	C(5)—C(6)—C(7)	119.8 (4)
Mo(1)—S(1)—Mo(1 ¹)	64.39 (2)	C(6)—C(7)—C(8)	120.4 (3)
Mo(1)—S(2)—Mo(1 ¹)	64.27 (2)	C(7)—C(8)—C(3)	118.9 (4)
C(1)—S(1)—Mo(1)	116.9 (1)	C(8)—C(3)—C(9)	121.1 (3)
C(1)—S(1)—Mo(1 ¹)	114.4 (1)	C(4)—C(3)—C(9)	120.6 (3)
B(1)—C(11)	1.651 (4)	C(25)—C(26)	1.401 (4)
B(1)—C(21)	1.638 (4)	C(26)—C(21)	1.396 (4)
B(1)—C(31)	1.656 (4)	C(31)—C(32)	1.404 (4)
B(1)—C(41)	1.651 (4)	C(32)—C(33)	1.384 (4)
C(11)—C(12)	1.399 (4)	C(33)—C(34)	1.379 (4)
C(12)—C(13)	1.391 (4)	C(34)—C(35)	1.386 (4)
C(13)—C(14)	1.374 (4)	C(35)—C(36)	1.386 (4)
C(14)—C(15)	1.377 (4)	C(36)—C(31)	1.404 (4)
C(15)—C(16)	1.397 (4)	C(41)—C(42)	1.398 (4)
C(16)—C(11)	1.401 (3)	C(42)—C(43)	1.397 (4)
C(21)—C(22)	1.409 (4)	C(43)—C(44)	1.384 (5)
C(22)—C(23)	1.391 (4)	C(44)—C(45)	1.384 (5)
C(23)—C(24)	1.366 (5)	C(45)—C(46)	1.394 (4)
C(24)—C(25)	1.387 (5)	C(46)—C(41)	1.399 (4)
C(11)—B(1)—C(21)	110.6 (2)	C(23)—C(24)—C(25)	119.2 (3)
C(11)—B(1)—C(31)	110.9 (2)	C(24)—C(25)—C(26)	119.7 (3)
C(11)—B(1)—C(41)	106.6 (2)	C(25)—C(26)—C(21)	122.9 (3)
C(21)—B(1)—C(31)	108.5 (2)	B(1)—C(31)—C(32)	123.2 (2)
C(21)—B(1)—C(41)	110.7 (2)	B(1)—C(31)—C(36)	122.8 (2)
C(31)—B(1)—C(41)	109.5 (2)	C(36)—C(31)—C(32)	114.0 (2)
B(1)—C(11)—C(12)	122.6 (2)	C(31)—C(32)—C(33)	123.5 (3)
B(1)—C(11)—C(16)	122.4 (2)	C(32)—C(33)—C(34)	120.4 (3)
C(16)—C(11)—C(12)	115.0 (2)	C(33)—C(34)—C(35)	118.5 (3)
C(11)—C(12)—C(13)	122.6 (3)	C(34)—C(35)—C(36)	120.2 (3)
C(12)—C(13)—C(14)	120.6 (3)	C(35)—C(36)—C(31)	123.5 (3)
C(13)—C(14)—C(15)	119.0 (3)	B(1)—C(41)—C(42)	121.6 (2)
C(14)—C(15)—C(16)	120.0 (3)	B(1)—C(41)—C(46)	122.8 (2)
C(15)—C(16)—C(11)	122.7 (2)	C(46)—C(41)—C(42)	115.4 (2)
B(1)—C(21)—C(22)	121.0 (2)	C(41)—C(42)—C(43)	123.0 (3)
B(1)—C(21)—C(26)	123.9 (2)	C(42)—C(43)—C(44)	119.6 (3)
C(26)—C(21)—C(22)	115.0 (2)	C(43)—C(44)—C(45)	119.3 (3)
C(21)—C(22)—C(23)	122.4 (3)	C(44)—C(45)—C(46)	120.0 (3)
C(22)—C(23)—C(24)	120.8 (3)	C(45)—C(46)—C(41)	122.7 (3)

Symmetry code: (i) $\bar{x}, y, 1 - z$.

being smaller than 120° [(I) 114.4 (4)—115.7 (4), (II) 114.0 (2)—115.4 (2) and (III) 112.7 (7)—116.0 (7)°] and those at the adjacent C atoms being greater than 120° [(I) 122.0 (5)—123.3 (3), (II) 122.4 (3)—123.5 (3) and (III) 121.7 (8)—124.6 (8)°].

For compound (I), the monodentate pyridine ligands are disposed about the Mo atom with a very regular geometry [N(10)—Mo(1)—N(20) 84.1 (1), N(10)—Mo(1)—N(30) 84.8 (1), N(20)—Mo(1)—N(30) 91.3 (1)°]. They also have pseudo threefold symmetry relative to the toluene ligand, where the angles are Tol—Mo(1)—N(10) 132.0, Tol—Mo(1)—N(20) 124.6,

Table 6. Compound (III): interatomic distances (Å) and bond angles ($^\circ$)

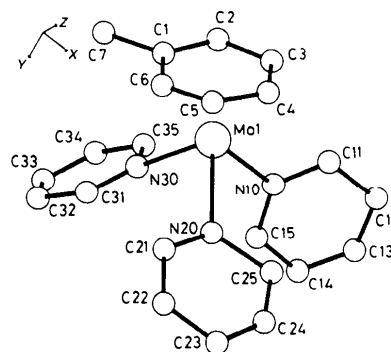
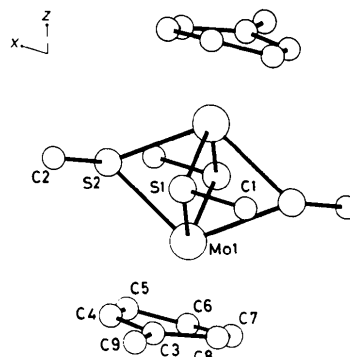
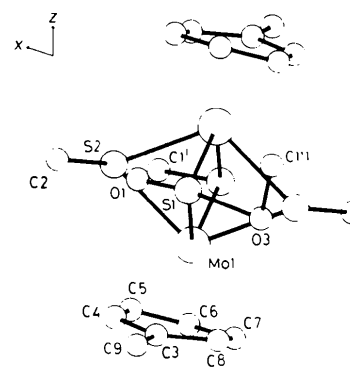
Mo(1)—Mo(1')	2.644 (1)	S(1)—O(3)	2.02 (2)
Mo(1)—S(1)	2.507 (3)	S(2)—O(4)	1.98 (2)
Mo(1)—S(1')	2.444 (3)	O(3)—C(111)	1.25 (3)
Mo(1)—S(2)	2.471 (3)	O(4)—C(222)	1.24 (3)
Mo(1)—S(2')	2.438 (3)	S(1)—O(1)	1.25 (3)
Mo(1)—C(3)	2.39 (1)	S(2)—O(2)	1.28 (3)
Mo(1)—C(4)	2.32 (1)	C(3)—C(4)	1.38 (2)
Mo(1)—C(5)	2.29 (1)	C(4)—C(5)	1.39 (2)
Mo(1)—C(6)	2.35 (1)	C(5)—C(6)	1.37 (2)
Mo(1)—C(7)	2.32 (1)	C(6)—C(7)	1.38 (2)
Mo(1)—C(8)	2.28 (1)	C(7)—C(8)	1.46 (2)
S(1)—C(1)	1.86 (1)	C(8)—C(3)	1.39 (2)
S(2)—C(2)	1.82 (1)	C(3)—C(9)	1.49 (2)
S(1)—Mo(1)—S(1')	115.45 (7)	O(2)—S(2)—Mo(1')	79 (1)
S(1)—Mo(1)—S(2)	72.9 (1)	O(3)—S(1)—Mo(1)	104 (1)
S(1)—Mo(1)—S(2')	72.6 (1)	O(3)—S(1)—Mo(1')	111 (1)
S(1')—Mo(1)—S(2)	73.1 (1)	O(4)—S(2)—Mo(1)	106 (1)
S(1')—Mo(1)—S(2')	74.6 (1)	O(4)—S(2)—Mo(1')	108 (1)
S(2)—Mo(1)—S(2')	114.82 (7)	S(1)—O(3)—C(111)	95 (2)
Mo(1)—S(1)—Mo(1')	64.55 (7)	S(2)—O(4)—C(222)	98 (2)
Mo(1)—S(2)—Mo(1')	65.18 (7)	C(8)—C(3)—C(4)	119 (1)
C(1)—S(1)—Mo(1)	122.1 (5)	C(3)—C(4)—C(5)	122 (1)
C(1)—S(1)—Mo(1')	115.8 (5)	C(4)—C(5)—C(6)	119 (1)
C(2)—S(2)—Mo(1)	117.3 (5)	C(5)—C(6)—C(7)	121 (1)
C(2)—S(2)—Mo(1')	118.2 (5)	C(6)—C(7)—C(8)	118 (1)
O(1)—S(1)—Mo(1)	75 (1)	C(7)—C(8)—C(3)	119 (1)
O(1)—S(1)—Mo(1')	76 (1)	C(8)—C(3)—C(9)	120 (1)
O(2)—S(2)—Mo(1)	74 (1)	C(4)—C(3)—C(9)	121 (1)
B(1)—C(11)	1.65 (1)	C(25)—C(26)	1.40 (1)
B(1)—C(21)	1.64 (1)	C(26)—C(21)	1.39 (1)
B(1)—C(31)	1.65 (1)	C(31)—C(32)	1.40 (1)
B(1)—C(41)	1.66 (1)	C(32)—C(33)	1.37 (1)
C(11)—C(12)	1.39 (1)	C(33)—C(34)	1.37 (1)
C(12)—C(13)	1.37 (1)	C(34)—C(35)	1.37 (1)
C(13)—C(14)	1.39 (1)	C(35)—C(36)	1.38 (1)
C(14)—C(15)	1.36 (1)	C(36)—C(31)	1.40 (1)
C(15)—C(16)	1.39 (1)	C(41)—C(42)	1.41 (1)
C(16)—C(11)	1.40 (1)	C(42)—C(43)	1.38 (1)
C(21)—C(22)	1.40 (1)	C(43)—C(44)	1.39 (1)
C(22)—C(23)	1.40 (1)	C(44)—C(45)	1.37 (1)
C(23)—C(24)	1.37 (1)	C(45)—C(46)	1.38 (1)
C(24)—C(25)	1.36 (1)	C(46)—C(41)	1.41 (1)
C(11)—B(1)—C(21)	110.8 (6)	C(23)—C(24)—C(25)	119.4 (8)
C(11)—B(1)—C(31)	110.7 (6)	C(24)—C(25)—C(26)	120.4 (8)
C(11)—B(1)—C(41)	106.5 (6)	C(25)—C(26)—C(21)	122.1 (8)
C(21)—B(1)—C(31)	109.2 (6)	B(1)—C(31)—C(32)	123.7 (7)
C(21)—B(1)—C(41)	110.2 (6)	B(1)—C(31)—C(36)	123.5 (7)
C(31)—B(1)—C(41)	109.4 (6)	C(36)—C(31)—C(32)	112.7 (7)
B(1)—C(11)—C(12)	122.9 (7)	C(31)—C(32)—C(33)	124.6 (8)
B(1)—C(11)—C(16)	123.1 (7)	C(32)—C(33)—C(34)	119.6 (8)
C(16)—C(11)—C(12)	114.0 (7)	C(33)—C(34)—C(35)	118.9 (8)
C(11)—C(12)—C(13)	123.2 (8)	C(34)—C(35)—C(36)	120.6 (8)
C(12)—C(13)—C(14)	120.9 (8)	C(35)—C(36)—C(31)	123.6 (8)
C(13)—C(14)—C(15)	118.1 (8)	B(1)—C(41)—C(42)	121.5 (7)
C(14)—C(15)—C(16)	120.2 (8)	B(1)—C(41)—C(46)	123.1 (7)
C(15)—C(16)—C(11)	123.5 (8)	C(46)—C(41)—C(42)	115.3 (7)
B(1)—C(21)—C(22)	120.5 (7)	C(41)—C(42)—C(43)	122.6 (9)
B(1)—C(21)—C(26)	123.4 (7)	C(42)—C(43)—C(44)	119.6 (9)
C(26)—C(21)—C(22)	116.0 (7)	C(43)—C(44)—C(45)	119.6 (8)
C(21)—C(22)—C(23)	121.7 (8)	C(44)—C(45)—C(46)	120.4 (9)
C(22)—C(23)—C(24)	120.4 (8)	C(45)—C(46)—C(41)	122.6 (9)

Symmetry code: (i) $\bar{x}, \bar{y}, 1 - z$.

Tol—Mo(1)—N(30) 126.1° (Tol is the centroid of the six-membered ring). The three Mo—N bond distances of 2.249 (4), 2.253 (3) and 2.278 (4) Å compare well with the values found in other Mo=pyridine complexes: 2.163 (15)–2.223 (15) Å in trichlorotris(pyridine)molybdenum (Brenö, 1974) and 2.311 (9) Å

in (2,2'-bipyridine)tricarbonylpyridinemolybdenum (Griffiths, 1971). Each of the three pyridine rings is planar within experimental error* and the C—N [1.324 (5)–1.361 (6) Å] and C—C [1.358 (8)–1.381 (6) Å] distances, and the C—N—C [116.0 (4)–116.8 (4) $^\circ$], N—C—C [121.7 (5)–124.5 (4) $^\circ$] and C—C—C [117.4 (5)–120.9 (5) $^\circ$] angles are similar to

* Details of molecular planes have been deposited. See deposition footnote.

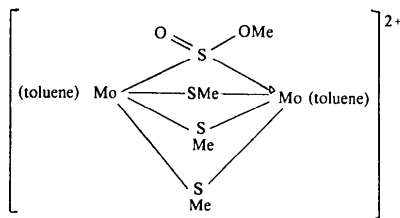
Fig. 1. The [(toluene)Mo(pyridine)₃]⁺ cation.Fig. 2. The [(toluene)Mo(μ -SCH₃)₂Mo(toluene)]²⁺ cation.Fig. 3. The [(toluene)Mo(μ -SCH₃)₃(μ -SO(OCH₃))Mo(toluene)]²⁺ cation, showing one of the orientations of the disordered ion.

values found previously (Brenčić, 1974; Griffiths, 1971).

For the toluene ligands, the Mo—C(ring) distances are in the ranges (I) 2.193 (5)–2.237 (5), (II) 2.287 (3)–2.416 (3), (III) 2.28 (1)–2.39 (1) Å, the perpendiculars to the rings are 1.722 (I), 1.871 (II) and 1.858 Å (III), and these meet the rings close [0.02 (I), 0.02 (II), and 0.03 Å (III)] to their centroids, similar to values found in other Mo–arene complexes (Mason, Thomas & Heath, 1975; Prout & Rees, 1974). In the rings C—C distances [(I) 1.377 (9)–1.425 (8), (II) 1.381 (7)–1.451 (6) and (III) 1.37 (2)–1.46 (2) Å] are normal. While the ring is planar within experimental error in compound (I), it is significantly non-planar in (II) and (III) being folded by 9.6° (II) and 7.7° (III) about the C(3)···C(6) vector.

In compound (II), the two (toluene)Mo species are linked to each other by four symmetrically positioned bridging methanethiolato ligands [Mo—S distances 2.451 (1)–2.462 (1) Å] and the molecular structure is very similar to those of the $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{SCH}_3)_2]_2^+$ complexes ($n = 0$ or $+1$) (Connelly & Dahl, 1970). It is suggested that there is a direct metal–metal bond between the Mo atoms, and this is in accord with the short Mo—Mo distance of 2.614 (1) Å, the acute Mo—S—Mo bridging angles of 64.39 (2) and 64.27 (2)° (Dahl, De Gil & Feltham, 1969), and the observed diamagnetism of the cation. The crystallographic symmetry requires that the four bridging S atoms form a plane, the Mo atoms being 1.307 Å above and below this plane and the nonbonding S···S distances are 2.939 (1) and 2.940 (1) Å.

Compound (III) is the KMnO_4 oxidation product of compound (II). Comparison of the NMR data to that on other methoxooxosulphato complexes indicates that one of the sulphur methyl groups has migrated to an O atom. This suggests the following structure for the cation:



which is quite plausible based on the valence of the S atom, and is consistent with both the IR and NMR

data. Compound (III) is the first example of the oxidation of a coordinated mercaptide, and of a bridging methoxooxosulphato ligand.

Unfortunately, because of the disorder in the cation, the X-ray structural analysis is not unambiguous. But the most sensible crystallographic model seems to confirm that deduced from spectral data.

The molecular structure is very similar to that in compound (II) [Mo—S 2.438 (3)–2.507 (3) Å, Mo—S—Mo 64.55 (7), 65.18 (7)° and S···S 2.957 (4) and 2.928 (4) Å], the slightly longer Mo···Mo distance [2.644 (1) Å] and Mo–plane of S atoms distance (1.321 Å) occurring because of the additional two O atoms in the bridging groups. The bond distances and angles involving O and C about the S atoms, while not well resolved, are acceptable.

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