Crystal structure of bis(tetrabutylammonium) tetradecabromohexamolybdate, $[(C_4H_9)_4N]_2[Mo_6Br_{14}]$, *at 100 K and 293 K*

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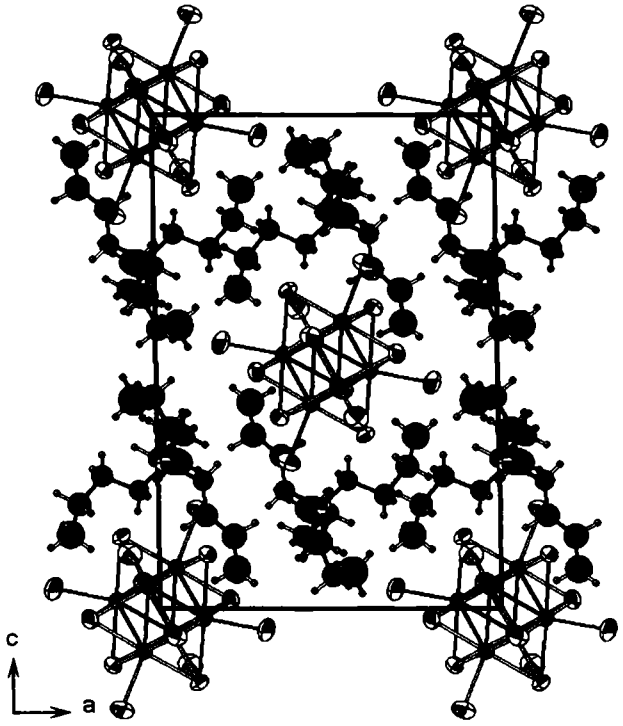
Received December 16, 2004, accepted and available on-line January 26, 2005; CCDC nos. 1267/1445, 1267/1446



Abstract

$C_{32}H_{72}Br_{14}Mo_6N_2$, monoclinic, $P12_1/n1$ (no. 14),
$a = 13.0064(2)$ Å, $b = 11.6547(2)$ Å, $c = 18.9931(4)$ Å,
$\beta = 90.542(1)°$, $V = 2879.0$ Å^3, $Z = 2$,
$R_{gt}(F) = 0.056$, $wR_{ref}(F^2) = 0.152$, $T = 100$ K.

$C_{32}H_{72}Br_{14}Mo_6N_2$, monoclinic, $P12_1/n1$ (no. 14),
$a = 13.2110(2)$ Å, $b = 11.8530(2)$ Å, $c = 18.9280(4)$ Å,
$\beta = 90.843(1)°$, $V = 2963.6$ Å^3, $Z = 2$,
$R_{gt}(F) = 0.038$, $wR_{ref}(F^2) = 0.072$, $T = 293$ K.

Source of materials

$(Bu_4N)_2[Mo_6Br_{14}]$ was prepared according to the procedure described in [1]. Single crystals were obtained by slow evaporation of a saturated solution of $(Bu_4N)_2[Mo_6Br_{14}]$ in acetonitrile.

Discussion

The structure of $(Bu_4N)_2[Mo_6Br_{14}]$ is related to that of the earlier published $(Bu_4N)_2[Mo_6I_{14}]$ [1]. Indeed, contrarily to the latter compound, the carbon atoms belonging to three over the four butyl chains of the tetrabutylammonium cation are dynamically disordered at room temperature. In the corresponding structural model, they have been distributed over two 4*e* crystallographically unequivalent positions and refined isotropically. A data collection performed at 100 K revealed a significant contraction of the unit cell parameters. In the corresponding structural model deduced from the data recorded at 100K, each carbon atom has been localized on a single position and refined anisotropically with reasonable atomic displacement parameters. This finding reveals the dynamic character of the aforementioned room temperature disorder. The Mo—Mo and Mo—Br bond lengths at room temperature are in agreement with those reported for the $Cs_2Mo_6Br_{14}$ starting material and other related compounds [2]. $(Bu_4N)_2[Mo_6Br_{14}]$ soluble in common organic solvents will constitute a relevant precursor for axially substituted clusters containing $M_6Br^i_8$ cluster cores.

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1. Bis(tetrabutylammonium) tetradecabromohexamolybdate, $[(C_4H_9)_4N]_2[Mo_6Br_{14}]$, *at 100 K*

Table 1. Data collection and handling.

Crystal:	yellow prism, size 0.133 × 0.149 × 0.165 mm
Wavelength:	Mo K_α radiation (0.71069 Å)
μ:	110.08 cm^{-1}
Diffractometer, scan mode:	Nonius 95 mm KappaCCD, ω
$2\theta_{max}$:	55°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	12093, 6336
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 4522
$N(param)_{refined}$:	244
Programs:	SIR97 [3], SHELXL-97 [4], ORTEP-3 [5], WinGX [6]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(11A)	4*e*	0.5381	0.4780	0.3049	0.043
H(11B)	4*e*	0.5369	0.3559	0.2705	0.043
H(12A)	4*e*	0.6795	0.5301	0.2409	0.078
H(12B)	4*e*	0.6741	0.4159	0.1972	0.078
H(13A)	4*e*	0.8023	0.4187	0.2950	0.076
H(13B)	4*e*	0.7080	0.4047	0.3455	0.076
H(14A)	4*e*	0.7734	0.2310	0.3185	0.120
H(14B)	4*e*	0.7566	0.2560	0.2381	0.120
H(14C)	4*e*	0.6617	0.2423	0.2876	0.120
H(21A)	4*e*	0.5003	0.6436	0.2376	0.042
H(21B)	4*e*	0.5652	0.6115	0.1717	0.042
H(22A)	4*e*	0.3553	0.6632	0.1672	0.046
H(22B)	4*e*	0.4195	0.6294	0.1009	0.046
H(23A)	4*e*	0.4043	0.8245	0.1015	0.053
H(23B)	4*e*	0.5200	0.7949	0.1165	0.053
H(24A)	4*e*	0.4683	0.9371	0.1934	0.099

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(24B)	4e	0.4936	0.8262	0.2369	0.099
H(24C)	4e	0.3789	0.8590	0.2207	0.099
H(31A)	4e	0.3202	0.4836	0.1969	0.037
H(31B)	4e	0.3589	0.3784	0.2409	0.037
H(32A)	4e	0.3922	0.5818	0.3081	0.050
H(32B)	4e	0.2757	0.5593	0.2932	0.050
H(33A)	4e	0.4035	0.4282	0.3791	0.085
H(33B)	4e	0.2934	0.3865	0.3570	0.085
H(34A)	4e	0.2876	0.4712	0.4684	0.088
H(34B)	4e	0.2209	0.5441	0.4157	0.088

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(34C)	4e	0.3311	0.5861	0.4377	0.088
H(41A)	4e	0.4326	0.4403	0.1056	0.046
H(41B)	4e	0.5519	0.4423	0.1149	0.046
H(42A)	4e	0.4204	0.2609	0.1410	0.062
H(42B)	4e	0.5283	0.2634	0.1784	0.062
H(43A)	4e	0.4984	0.2641	0.0314	0.061
H(43B)	4e	0.6069	0.2728	0.0673	0.061
H(44A)	4e	0.5801	0.0903	0.0283	0.138
H(44B)	4e	0.4803	0.0806	0.0735	0.138
H(44C)	4e	0.5881	0.0892	0.1108	0.138

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo(1)	4e	0.54621(6)	0.93764(7)	0.58468(4)	0.0225(4)	0.0297(4)	0.0129(3)	−0.0001(3)	0.0018(3)	−0.0004(3)
Mo(2)	4e	0.63170(6)	1.05539(7)	0.48296(4)	0.0199(4)	0.0336(4)	0.0150(3)	−0.0024(3)	0.0044(3)	−0.0013(3)
Mo(3)	4e	0.53279(6)	0.86373(7)	0.45398(4)	0.0212(4)	0.0297(4)	0.0132(3)	0.0015(3)	0.0030(3)	−0.0025(3)
Br(1)	4e	0.70678(8)	0.85747(9)	0.52155(5)	0.0245(5)	0.0436(6)	0.0213(4)	0.0090(4)	−0.0013(3)	−0.0057(4)
Br(2)	4e	0.44683(8)	0.74933(8)	0.55494(5)	0.0384(6)	0.0302(5)	0.0213(4)	−0.0052(4)	0.0031(4)	0.0010(4)
Br(3)	4e	0.64299(7)	1.12883(8)	0.61184(4)	0.0236(5)	0.0352(5)	0.0170(4)	−0.0026(4)	0.0003(3)	−0.0038(3)
Br(4)	4e	0.38462(7)	1.01733(9)	0.64598(4)	0.0258(5)	0.0423(5)	0.0156(4)	−0.0024(4)	0.0084(3)	−0.0029(4)
Br(5)	4e	0.61122(9)	0.85299(9)	0.70253(5)	0.0484(6)	0.0382(5)	0.0178(4)	0.0040(5)	−0.0031(4)	0.0035(4)
Br(6)	4e	0.58297(9)	0.67590(9)	0.39034(5)	0.0429(6)	0.0366(5)	0.0258(4)	0.0076(5)	−0.0010(4)	−0.0103(4)
Br(7)	4e	0.81723(8)	1.1268(1)	0.46171(6)	0.0263(5)	0.0659(7)	0.0327(5)	−0.0142(5)	0.0104(4)	−0.0069(5)
N(1)	4e	0.4772(7)	0.4786(8)	0.2059(4)	0.024(4)	0.052(5)	0.016(3)	−0.011(4)	0.000(3)	0.004(3)
C(11)	4e	0.5508(8)	0.436(1)	0.2616(5)	0.029(6)	0.060(7)	0.020(4)	−0.004(5)	−0.006(4)	0.006(4)
C(12)	4e	0.662(1)	0.449(2)	0.2432(7)	0.039(7)	0.12(1)	0.040(6)	−0.013(8)	−0.005(5)	0.042(7)
C(13)	4e	0.733(1)	0.390(1)	0.2984(8)	0.038(7)	0.09(1)	0.060(8)	0.000(7)	0.014(6)	0.037(8)
C(14)	4e	0.731(1)	0.270(2)	0.2845(9)	0.06(1)	0.12(2)	0.07(1)	0.03(1)	−0.004(8)	0.01(1)
C(21)	4e	0.4976(9)	0.605(1)	0.1924(5)	0.035(6)	0.049(6)	0.022(4)	−0.009(5)	0.001(4)	0.006(4)
C(22)	4e	0.4230(9)	0.667(1)	0.1463(5)	0.039(6)	0.047(6)	0.029(5)	−0.007(5)	0.002(4)	0.006(5)
C(23)	4e	0.451(1)	0.791(1)	0.1357(5)	0.057(8)	0.052(7)	0.023(5)	−0.002(6)	0.010(5)	0.005(5)
C(24)	4e	0.448(1)	0.860(1)	0.2027(7)	0.10(1)	0.063(9)	0.041(7)	−0.020(8)	0.014(7)	−0.010(6)
C(31)	4e	0.3686(8)	0.4600(9)	0.2334(5)	0.021(5)	0.048(6)	0.023(4)	−0.008(4)	0.002(4)	0.003(4)
C(32)	4e	0.342(1)	0.522(1)	0.3005(5)	0.052(7)	0.045(6)	0.027(5)	−0.001(5)	0.010(5)	0.001(5)
C(33)	4e	0.335(2)	0.454(1)	0.3660(7)	0.10(1)	0.056(9)	0.058(8)	−0.002(8)	0.040(8)	0.006(7)
C(34)	4e	0.289(1)	0.520(1)	0.4276(6)	0.08(1)	0.065(9)	0.032(6)	−0.012(8)	0.027(6)	−0.006(6)
C(41)	4e	0.4886(9)	0.416(1)	0.1362(5)	0.031(6)	0.057(7)	0.026(5)	−0.005(5)	0.009(4)	−0.005(5)
C(42)	4e	0.490(1)	0.289(1)	0.1373(6)	0.061(9)	0.056(8)	0.039(6)	−0.005(7)	0.014(6)	−0.004(6)
C(43)	4e	0.539(1)	0.240(1)	0.0721(6)	0.065(9)	0.060(8)	0.028(5)	0.007(7)	0.010(5)	0.002(5)
C(44)	4e	0.548(2)	0.114(2)	0.0711(8)	0.14(2)	0.08(1)	0.053(9)	0.03(1)	0.04(1)	−0.008(8)

2. Bis(tetrabutylammonium) tetradecabromohexamolybdate, $[(C_4H_9)_4N]_2[Mo_6Br_{14}]$, *at 293 K*

Table 4. Data collection and handling.

Crystal:	yellow prism, size 0.133 × 0.149 × 0.165 mm
Wavelength:	Mo K_α radiation (0.71069 Å)
μ:	106.91 cm^{-1}
Diffractometer, scan mode:	Nonius 95 mm KappaCCD, ω
$2\theta_{max}$:	55°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	41381, 6797
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3956
$N(param)_{refined}$:	223
Programs:	SIR97 [3], SHELXL-97 [4], ORTEP-3 [5], WinGX [6]

Table 5. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	x	y	z	U_{iso}
C(111)	4e	0.50(1)	0.555(1)	0.417(2)	0.2583(9)	0.057(2)
H(11A)	4e	0.50	0.5279	0.3429	0.2701	0.069
H(11B)	4e	0.50	0.5578	0.4604	0.3017	0.069
C(121)	4e	0.50	0.663(1)	0.402(1)	0.2312(7)	0.064(3)
H(12A)	4e	0.50	0.6617	0.3531	0.1900	0.077
H(12B)	4e	0.50	0.6898	0.4743	0.2174	0.077
C(131)	4e	0.50	0.731(1)	0.350(2)	0.2888(9)	0.076(3)
H(13A)	4e	0.50	0.6977	0.2830	0.3072	0.091
H(13B)	4e	0.50	0.7935	0.3250	0.2673	0.091
C(141)	4e	0.50	0.757(1)	0.427(2)	0.350(1)	0.108(4)
H(14A)	4e	0.50	0.7984	0.3868	0.3843	0.162
H(14B)	4e	0.50	0.6963	0.4519	0.3723	0.162
H(14C)	4e	0.50	0.7942	0.4911	0.3334	0.162
C(112)	4e	0.50	0.556(1)	0.444(2)	0.2622(9)	0.057
H(11C)	4e	0.50	0.5401	0.4871	0.3043	0.069
H(11D)	4e	0.50	0.5455	0.3652	0.2737	0.069
C(122)	4e	0.50	0.662(1)	0.460(1)	0.2482(8)	0.064

Table 5. Continued.

Atom	Site	Occ.	x	y	z	U_{iso}
H(12C)	4e	0.50	0.6779	0.5394	0.2513	0.077
H(12D)	4e	0.50	0.6753	0.4353	0.2003	0.077
C(132)	4e	0.50	0.733(1)	0.394(1)	0.300(1)	0.076
H(13C)	4e	0.50	0.8019	0.4216	0.2959	0.091
H(13D)	4e	0.50	0.7115	0.4051	0.3481	0.091
C(142)	4e	0.50	0.729(1)	0.269(2)	0.281(1)	0.108
H(14D)	4e	0.50	0.7718	0.2280	0.3135	0.162
H(14E)	4e	0.50	0.7522	0.2588	0.2340	0.162
H(14F)	4e	0.50	0.6607	0.2428	0.2848	0.162
H(21A)	4e		0.5029	0.6371	0.2394	0.077
H(21B)	4e		0.5666	0.6056	0.1733	0.077
H(22A)	4e		0.3589	0.6545	0.1681	0.097
H(22B)	4e		0.4226	0.6225	0.1017	0.097
H(23A)	4e		0.5223	0.7869	0.1195	0.107
H(23B)	4e		0.4088	0.8164	0.1031	0.107
H(24A)	4e		0.4707	0.9243	0.1920	0.206
H(24B)	4e		0.4952	0.8159	0.2365	0.206
H(24C)	4e		0.3825	0.8479	0.2191	0.206
C(311)	4e	0.55(1)	0.378(1)	0.445(1)	0.2364(9)	0.059(2)
H(31A)	4e	0.55	0.3797	0.3670	0.2526	0.070
H(31B)	4e	0.55	0.3276	0.4493	0.1986	0.070
C(321)	4e	0.55	0.344(2)	0.521(2)	0.2980(9)	0.075(3)
H(32A)	4e	0.55	0.2761	0.5488	0.2887	0.090
H(32B)	4e	0.55	0.3892	0.5849	0.3026	0.090
C(331)	4e	0.55	0.346(1)	0.451(1)	0.3672(8)	0.089(4)
H(33A)	4e	0.55	0.3092	0.3816	0.3583	0.107
H(33B)	4e	0.55	0.4156	0.4309	0.3775	0.107
C(341)	4e	0.55	0.303(1)	0.505(2)	0.433(1)	0.107(4)
H(34A)	4e	0.55	0.3070	0.4518	0.4713	0.161
H(34B)	4e	0.55	0.2333	0.5245	0.4243	0.161
H(34C)	4e	0.55	0.3409	0.5710	0.4447	0.161
C(312)	4e	0.45	0.372(1)	0.471(2)	0.238(1)	0.059
H(31C)	4e	0.45	0.3263	0.5117	0.2063	0.070
H(31D)	4e	0.45	0.3491	0.3929	0.2388	0.070
C(322)	4e	0.45	0.362(2)	0.519(2)	0.311(1)	0.075

Table 5. Continued.

Atom	Site	Occ.	x	y	z	U_{iso}
H(32C)	4e	0.45	0.4240	0.5034	0.3371	0.090
H(32D)	4e	0.45	0.3558	0.6005	0.3069	0.090
C(332)	4e	0.45	0.277(2)	0.477(2)	0.352(1)	0.089
H(33C)	4e	0.45	0.2144	0.4873	0.3247	0.107
H(33D)	4e	0.45	0.2857	0.3973	0.3608	0.107
C(342)	4e	0.45	0.272(2)	0.539(2)	0.418(1)	0.107
H(34D)	4e	0.45	0.2190	0.5075	0.4459	0.161
H(34E)	4e	0.45	0.2577	0.6166	0.4081	0.161
H(34F)	4e	0.45	0.3354	0.5323	0.4425	0.161
C(411)	4e	0.65(2)	0.492(1)	0.407(1)	0.1378(6)	0.068(3)
H(41A)	4e	0.65	0.4369	0.4292	0.1063	0.082
H(41B)	4e	0.65	0.5541	0.4334	0.1163	0.082
C(421)	4e	0.65	0.496(1)	0.286(1)	0.1385(7)	0.082(3)
H(42A)	4e	0.65	0.4277	0.2558	0.1424	0.099
H(42B)	4e	0.65	0.5355	0.2601	0.1787	0.099
C(431)	4e	0.65	0.543(1)	0.247(1)	0.0704(7)	0.078(3)
H(43A)	4e	0.65	0.6154	0.2587	0.0714	0.094
H(43B)	4e	0.65	0.5137	0.2863	0.0301	0.094
C(441)	4e	0.65	0.517(2)	0.119(2)	0.0671(9)	0.137(6)
H(44A)	4e	0.65	0.5441	0.0876	0.0246	0.205
H(44B)	4e	0.65	0.4453	0.1093	0.0674	0.205
H(44C)	4e	0.65	0.5471	0.0818	0.1073	0.205
C(412)	4e	0.35	0.475(2)	0.427(2)	0.134(1)	0.068
H(41C)	4e	0.35	0.5384	0.4439	0.1102	0.082
H(41D)	4e	0.35	0.4211	0.4641	0.1072	0.082
C(422)	4e	0.35	0.457(2)	0.299(2)	0.133(1)	0.082
H(42C)	4e	0.35	0.4859	0.2676	0.1759	0.099
H(42D)	4e	0.35	0.3849	0.2857	0.1335	0.099
C(432)	4e	0.35	0.500(2)	0.231(2)	0.070(1)	0.078
H(43C)	4e	0.35	0.4428	0.1942	0.0477	0.094
H(43D)	4e	0.35	0.5249	0.2861	0.0370	0.094
C(442)	4e	0.35	0.582(3)	0.142(3)	0.077(2)	0.137
H(44D)	4e	0.35	0.6092	0.1255	0.0314	0.205
H(44E)	4e	0.35	0.5544	0.0741	0.0968	0.205
H(44F)	4e	0.35	0.6358	0.1689	0.1077	0.205

Table 6. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo(1)	4e	0.54829(3)	0.93910(4)	0.58446(2)	0.0378(3)	0.0487(3)	0.0325(2)	−0.0010(2)	0.0007(2)	−0.0018(2)
Mo(2)	4e	0.62819(3)	1.05710(5)	0.48220(2)	0.0321(2)	0.0552(3)	0.0367(3)	−0.0050(2)	0.0046(2)	−0.0038(2)
Mo(3)	4e	0.53367(4)	0.86730(4)	0.45326(2)	0.0384(3)	0.0476(3)	0.0356(3)	0.0021(2)	0.0018(2)	−0.0075(2)
Br(1)	4e	0.70658(4)	0.86469(6)	0.51989(3)	0.0403(3)	0.0708(5)	0.0544(4)	0.0137(3)	−0.0035(3)	−0.0104(3)
Br(2)	4e	0.45366(5)	0.75215(6)	0.55468(3)	0.0654(4)	0.0501(4)	0.0511(4)	−0.0101(3)	−0.0019(3)	0.0036(3)
Br(3)	4e	0.64113(4)	1.12844(6)	0.61171(3)	0.0453(3)	0.0583(4)	0.0418(3)	−0.0062(3)	−0.0048(2)	−0.0079(3)
Br(4)	4e	0.38919(4)	1.01289(6)	0.64718(3)	0.0481(3)	0.0797(5)	0.0372(3)	−0.0046(3)	0.0135(2)	−0.0080(3)
Br(5)	4e	0.61721(6)	0.85702(6)	0.70205(3)	0.0836(5)	0.0664(5)	0.0464(4)	−0.0030(4)	−0.0133(3)	0.0090(3)
Br(6)	4e	0.58549(6)	0.68500(7)	0.38884(4)	0.0880(5)	0.0681(5)	0.0711(5)	0.0201(4)	−0.0063(4)	−0.0294(4)
Br(7)	4e	0.80869(5)	1.13105(8)	0.45883(4)	0.0453(4)	0.1164(7)	0.0767(5)	−0.0276(4)	0.0140(3)	−0.0053(5)
N(1)	4e	0.4795(3)	0.4745(5)	0.2073(2)	0.050(3)	0.076(4)	0.043(3)	−0.012(3)	0.000(2)	0.006(3)
C(21)	4e	0.5002(5)	0.5988(6)	0.1941(3)	0.053(4)	0.088(6)	0.052(4)	−0.013(4)	0.007(3)	0.005(4)
C(22)	4e	0.4256(6)	0.6591(7)	0.1475(4)	0.084(5)	0.087(6)	0.070(5)	−0.008(5)	−0.011(4)	0.012(4)
C(23)	4e	0.4543(7)	0.7829(7)	0.1379(4)	0.105(6)	0.097(7)	0.066(5)	0.012(5)	0.012(4)	0.003(5)
C(24)	4e	0.4503(9)	0.8481(8)	0.2016(5)	0.20(1)	0.110(9)	0.105(8)	0.011(8)	−0.009(8)	−0.020(7)

Acknowledgments. We are indebted to the French Research Ministry for ACI Nanosciences 2001 contract (grant no. 18-01), as well as to CNRS for PICS – 1433 and "Fondation L'anglois". Dr. O. Hernandez is greatly acknowledged for useful advices and discussions.

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