The Crystal and Molecular Structure of π-Allyl-dihydrobis-(3,5-dimethyl-1-pyrazolyl)boratodicarbonylmolybdenum, $H_2B[(CH_3)_2pz]_2Mo(CO)_2C_3H_5$

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π-Allyl-dihydrobis(3,5-dimethyl-1-pyrazolyl)boratodicarbonylmolybdenum, $H_2B[(CH_3)_2pz]_2Mo(CO)_2$-$C_3H_5$, crystallizes in the space group $P\bar{1}$. Unit-cell constants are $a = 8\cdot105 \pm 0\cdot007$, $b = 10\cdot550 \pm 0\cdot009$, $c = 12\cdot324 \pm 0\cdot010$ Å; $\alpha = 108° 12' \pm 3'$, $\beta = 117° 29' \pm 3'$, $\gamma = 95° 22' \pm 4'$ ($D_x = 1\cdot48$ g.cm^{-3}, $D_{ms} = 1\cdot48$ g.cm^{-3}). Data for 2328 reflections were collected at room temperature on a Picker automatic diffracto-meter. The crystal structure was solved by the Patterson method and refined by block-matrix least-squares calculations on 2224 observed reflections to a reliability index $R = 0\cdot054$. The coordination about the molybdenum atom is distorted-octahedral and the coordination about the boron atom is nearly tetrahedral. The average Mo–N distance is 2·21 Å and the average B–N distance is 1·54 Å. Terminal carbon atoms of the allyl group are further from the molybdenum atom than the central carbon atom. The distance of 2·30 Å from the molybdenum atom to a hydrogen atom bonded to boron is rather small for a nonbonded distance and indicates the possibility of bonding between molybdenum and hydrogen.

Introduction

Several molybdenum complexes with the new chelating agent hydrotris-(1-pyrazolyl) borate have recently been prepared (Trofimenko, 1967, 1968, 1969a,b). Thus far, the structures of two molybdenum complexes (Avitabile, Ganis & Nemiroff, 1971; Churchill, Gold & Maw, 1970) with this tridentate ligand have been reported. The present study is the first structural report of the apparent bidentate ligand dihydrobis-(3,5-dimethyl-1-pyrazolyl)boratodicarbonylmolybdenum. Some physicochemical properties of this complex have been investigated and we undertook this structural analysis to confirm the reported results (Trofimenko, 1970).

Experimental

Crystals of π-allyl-dihydrobis(3,5-dimethyl-1-pyrazolyl) boratodicarbonylmolybdenum have been prepared by Trofimenko. From these orange-red crystals, a flat plate with dimensions 0·35 mm × 0·35 mm × 0·10 mm was chosen. Weissenberg photographs showed the crystal to be triclinic, and subsequent refinement confirmed the space group $P\bar{1}$. The crystal was mounted on a Picker automatic diffractometer with the *b* axis as the spindle axis. Unit-cell constants were determined by locating 12 independent reflections using Zr-filtered Mo *Kα* radiation. No attenuators were used. A take-off angle of 3°, a 2θ–θ scan mode, and a scan

range of 1·67° were used for the data collection. The large scan range was chosen because some of the peaks were nearly 1·5° wide. The peak was scanned for 100 seconds and background on either side of the peak was measured for 10 seconds. Data were collected for 2328 reflections, of which 2224 were observed and used for the subsequent refinement. Two standard reflections were measured every 100 reflections. The standard deviation of the intensities of these reflections was about 4%.

Crystal data
Space group $P\bar{1}$ M.W. 396·15
$a = 8\cdot105 \pm 0\cdot007$ Å   Cell volume 886Å^3
$b = 10\cdot550 \pm 0\cdot009$
$c = 12\cdot324 \pm 0\cdot010$ Density $\begin{cases} \text{Observed } 1\cdot48 \pm 0\cdot01 \\ \text{g.cm}^{-3} \text{ (by flotation)} \\ \text{X-ray } 1\cdot48 \text{ g.cm}^{-3} \end{cases}$
$\alpha = 108° 12' \pm 3'$
$\beta = 117° 29' \pm 3'$
$\gamma = 95° 22' \pm 4'$ $\mu(\text{Mo } K\alpha) = 7\cdot4$ cm^{-1}.

The intensities were corrected for Lorentz and polarization factors after subtraction of the background. A reflection was considered observed if the total integrated intensity minus the background was greater than 200 counts for a 100-second scan. No absorption corrections were applied. The maximum and minimum value of μR are 0·219 and 0·074 respectively.

Determination of the structure and refinement

The location of the heavy atom was determined by Patterson techniques. The Fourier synthesis, obtained by using structure factors phased in this way, yielded all the non-hydrogen atoms. The model was refined with isotropic thermal parameters by a block-diagonalized matrix least-squares calculation (Immirzi, 1967) to an R value of 0·103. Successive refinements were

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Table 1. *Comparison between observed and calculated structure factors*

H	K	FO	FC
L = 0			
-7	1	156	161
-7	2	265	270
-7	4	214	-221
-7	5	197	-196
-6	1	277	283
-6	2	183	181
-6	3	68	67
-6	4	188	-202
-6	5	233	-208
-6	6	143	144
-6	7	205	214
-5	1	360	366
-5	2	304	314
-5	4	362	-389
-5	5	47	-32
-5	6	275	292
-5	7	200	203
-4	1	550	541
-4	2	45	57
-4	3	245	-245
-4	4	360	-375
-4	5	117	107
-4	6	216	213
-4	7	167	176
-4	8	120	-117
-4	9	187	-180
-3	1	368	407
-3	2	91	68
-3	3	844	-865
-3	4	422	-418
-3	5	438	415
-3	6	255	263
-3	8	218	-211
-3	9	241	-247
-2	1	233	231
-2	2	415	-386
-2	3	646	-726
-2	4	302	-314
-2	5	327	343
-2	6	276	316
-2	7	189	198
-2	8	262	-290
-2	9	311	-339
-2	10	206	228
-1	1	469	442
-1	2	477	-561
-1	3	686	-737
-1	4	366	-336
-1	5	300	347
-1	6	155	184
-1	7	27	-19
-1	8	275	-292
-1	9	127	-128
-1	10	218	233
0	1	403	410
0	2	424	-448
0	3	57	-118
0	4	171	211
0	5	377	416
0	6	194	224
0	7	266	-276
0	8	240	-246
0	9	71	-49
0	10	186	186
1	0	1149	1139
1	1	28	-25
1	2	43	-12
1	3	365	-365
1	4	70	88
1	5	682	707
1	6	206	216
1	7	311	-325
1	8	127	-135
1	9	46	34
1	10	213	210
2	0	155	124
2	1	684	-611
2	2	989	-916
2	3	355	-327
2	4	98	102
2	5	347	350
2	6	131	-120
2	7	300	-321
2	8	178	-184
2	9	176	187
2	10	205	209
3	0	98	119
3	1	462	-446
3	2	598	-566
3	3	165	-149
3	4	479	436
3	5	308	282
3	6	331	-320
3	7	337	-326
3	8	161	-158
3	9	143	131
4	0	66	79
4	1	437	-427
4	2	307	-299
4	3	342	322
4	4	691	633
4	5	158	148
4	6	225	-185
4	7	112	-88
4	8	76	-71
5	1	291	-301
5	2	287	-275
5	3	282	276
5	4	447	434
5	5	125	111
5	6	199	-185
5	7	123	-113
6	1	432	-417
6	2	108	-102
6	3	200	199
6	4	151	149
6	5	38	-24
6	6	164	-162
7	0	230	-240
7	1	304	-315
7	2	64	56
7	3	108	102
7	6	57	37
L = 1			
-8	0	221	235
-8	1	200	201
-7	-5	166	165
-7	-4	38	3
-7	-3	165	-167
-7	-2	185	-189
-7	0	337	345
-7	1	56	47
-7	2	155	-153
-7	3	193	-191
-7	4	83	-90
-7	5	210	202
-6	-7	49	-48
-6	-6	144	148
-6	-5	278	287
-6	-4	99	-92
-6	-3	299	-299
-6	-2	220	-226
-6	-1	314	312
-6	0	357	373
-6	1	36	-34
-6	2	216	-230
-6	3	243	-257
-6	4	148	-156
-6	5	224	241
-6	7	189	-195
-5	-8	174	-161
-5	-6	96	99
-5	-5	311	316
-5	-4	121	-118
-5	-3	454	-452
-5	-2	147	-144
-5	-1	315	334
-5	0	377	399
-5	1	58	27
-5	2	337	-356
-5	3	156	-157
-5	4	63	60
-5	5	305	338
-5	6	103	-108
-5	7	238	-236
-5	8	164	-149
-4	-9	218	-208
-4	-8	188	-163
-4	-6	230	211
-4	-5	408	393
-4	-4	384	-364
-4	-3	563	-537
-4	-2	155	142
-4	-1	283	274
-4	0	451	426
-4	1	319	-302
-4	2	458	-460
-4	3	162	144
-4	4	481	467
-4	5	352	358
-4	6	98	-86
-4	7	211	-212
-4	8	58	-56
-4	9	163	144
-3	-9	252	-237
-3	-8	250	-257
-3	-7	160	155
-3	-6	334	354
-3	-5	180	172
-3	-4	506	-497
-3	-3	310	-303
-3	-2	245	213
-3	-1	195	220
-3	0	196	222
-3	1	421	-454
-3	2	306	-334
-3	3	112	132
-3	4	666	663
-3	5	474	469
-3	6	98	-89
-3	7	314	-338
-3	9	260	254
-3	10	215	213
-2	-9	284	-279
-2	-8	82	-72
-2	-7	311	295
-2	-6	452	445
-2	-5	65	-49
-2	-4	518	-524
-2	-3	156	-164
-2	-2	515	514
-2	-1	154	-209
-2	0	252	-234
-2	1	770	-742
-2	2	397	-397
-2	3	343	328
-2	4	483	527
-2	5	139	137
-2	6	216	-226
-2	7	273	-297
-2	8	82	-92
-2	9	232	246
-2	10	116	126
-1	-10	95	-82
-1	-9	278	-269
-1	-7	336	313
-1	-6	454	396
-1	-5	227	-238
-1	-4	648	-621
-1	-3	316	-271
-1	-2	754	884
-1	-1	926	884
-1	0	88	-126
-1	1	1363	-1659
-1	2	47	-76
-1	3	326	378
-1	4	338	394
-1	5	164	-160
-1	6	418	-448
-1	7	286	-319
-1	8	103	115
-1	9	173	183
-1	10	59	-47
0	-10	155	-135
0	-9	158	-136
0	-8	181	154
0	-7	444	383
0	-6	100	105
0	-5	402	-379
0	-4	843	-742
0	-3	191	-132
0	-2	626	550
0	-1	946	913
0	0	437	-465
0	1	969	-1060
0	2	197	199
0	3	137	125
0	4	295	346
0	6	398	-416
0	7	146	-133
0	8	268	275
0	9	165	179
1	-10	266	-238
1	-9	224	-225
1	-8	428	396
1	-7	505	489
1	-6	114	-91
1	-5	377	-376
1	-4	524	-495
1	-3	424	453
1	-2	761	767
1	-1	76	70
1	0	770	-862
1	1	45	-93
1	2	190	-147
1	3	121	172
1	4	169	202
1	5	130	-158
1	6	383	-416
1	7	133	139
1	8	390	413
1	9	243	256
1	10	95	-96
2	-10	312	-293
2	-9	173	-155
2	-8	216	208
2	-7	176	172
2	-6	36	-31
2	-5	341	-352
2	-4	465	-416
2	-3	645	659
2	-2	1031	1048
2	-1	105	118
2	0	353	-365
2	1	239	-220
2	2	244	247
2	3	674	635
2	4	67	-51
2	5	427	-424
2	6	255	-245
2	7	147	148
2	8	293	289
2	9	202	207
3	-10	185	-169
3	-9	38	25
3	-8	104	94
3	-7	119	120
3	-6	192	-209
3	-5	424	-429
3	-4	253	-253
3	-3	520	526
3	-2	357	391
3	-1	266	-255
3	0	615	-628
3	1	158	115
3	2	578	525
3	3	480	440
3	4	59	-40
3	5	414	-388
3	6	143	-128
3	7	74	77
3	8	179	163
4	-9	118	118
4	-8	246	232
4	-7	156	155
4	-6	211	-217
4	-5	280	-286
4	-4	176	187
4	-3	390	396
4	-2	88	81
4	-1	364	-384
4	0	673	-667
4	2	335	325
4	3	401	364
4	4	166	-162
4	5	449	-419
4	7	130	114
4	8	116	112
5	-8	195	189
5	-6	200	-201
5	-5	202	-214
5	-4	309	326
5	-3	301	310
5	-2	90	91
5	-1	280	-290
5	0	288	-295
5	1	93	90
5	2	281	272
5	3	152	138
5	4	141	-137
5	5	284	-293
5	6	64	-48
5	7	126	111
6	-7	83	-88
6	-6	262	-268
6	-5	196	-207
6	-4	228	242
6	-3	177	178
6	-2	51	-40
6	-1	259	-271
6	0	188	-192
6	1	235	246
6	2	359	366
6	3	47	-47
6	4	139	-132
6	5	103	-86
7	-4	143	141
7	-3	137	146
7	-2	79	-87
7	-1	293	-307
7	0	108	-112
7	1	245	260
7	2	154	125
L = 2			
-8	-2	163	165
-8	-1	109	106
-8	0	64	-49
-8	1	213	-212
-8	2	125	-117
-7	-5	168	-156
-7	-4	228	-241
-7	-3	77	101
-7	-2	196	203
-7	-1	194	201
-7	0	132	-134
-7	1	330	-324
-7	2	113	-115
-7	3	130	129
-7	4	144	144
-7	5	36	-40
-6	-7	241	243
-6	-6	60	46
-6	-5	182	-181
-6	-4	300	-311
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-6	-1	250	254
-6	0	235	-232
-6	1	220	-212
-6	2	31	18
-6	3	164	176
-6	4	137	141
-6	5	96	-102
-6	6	303	-309
-5	-8	247	246
-5	-7	200	192
-5	-6	35	-18
-5	-5	296	-306
-5	-4	287	-297
-5	-3	206	200
-5	-2	357	371
-5	-1	43	-8
-5	0	233	-250
-5	1	387	-397
-5	2	189	188
-5	3	405	418
-5	4	65	68
-5	5	266	-275
-5	6	180	-165
-5	7	156	166
-5	8	233	222
-4	-9	89	-102
-4	-8	188	187
-4	-7	153	157
-4	-6	112	-102
-4	-5	369	-361
-4	-4	174	-178
-4	-3	572	531
-4	-2	390	388
-4	-1	203	-208
-4	0	385	-391
-4	1	343	-345
-4	2	305	280
-4	3	228	228
-4	4	25	32
-4	5	417	-415
-4	6	266	-255
-4	7	137	127
-4	8	363	361
-4	9	58	46
-3	-10	165	-151
-3	-9	117	-116
-3	-8	251	269
-3	-7	78	81
-3	-6	410	-414
-3	-5	420	-423
-3	-4	345	326
-3	-3	544	539
-3	-2	110	149
-3	-1	210	-208
-3	0	198	-243
-3	1	45	40
-3	2	345	390
-3	3	488	474
-3	5	541	-535
-3	6	196	-185
-3	7	98	96
-3	8	189	189
-3	9	48	-33
-2	-10	48	-47
-2	-9	119	109
-2	-8	353	344
-2	-6	277	-288
-2	-5	457	-456
-2	-4	251	236
-2	-3	657	662
-2	-2	488	416
-2	-1	1274	-1167
-2	0	932	-826
-2	1	434	371
-2	2	759	785
-2	3	500	494
-2	4	153	-188
-2	5	436	-458
-2	6	95	96
-2	7	173	185
-2	8	85	86
-2	9	103	-104
-2	10	221	-229
-1	-11	116	-100
-1	-9	312	297
-1	-8	299	285
-1	-7	113	97
-1	-6	400	-397
-1	-5	275	-288
-1	-4	659	584
-1	-3	492	524
-1	-2	156	-140
-1	-1	435	-466
-1	0	890	-863
-1	1	108	126
-1	2	695	771
-1	3	271	264
-1	4	306	-344
-1	5	422	-449
-1	6	184	197
-1	7	238	256
-1	8	79	96
-1	9	150	-146
-1	10	172	-182
0	-11	222	-206
0	-9	462	425
0	-8	217	210
0	-7	253	-225
0	-6	625	-585
0	-5	52	-87
0	-4	499	522
0	-3	342	358
0	-2	562	-573
0	-1	304	-230
0	0	383	-382
0	1	1061	1037
0	2	30	72
0	3	44	22
0	4	238	-275
0	5	304	-337
0	6	158	185
0	7	345	377
0	8	31	-19
0	9	207	-219
0	10	155	-172
1	-11	158	-146
1	-10	45	-35
1	-9	332	312
1	-8	174	171
1	-7	378	-389
1	-6	586	-575
1	-5	175	-145
1	-4	618	601
1	-3	50	117
1	-2	538	-532
1	-1	247	-315
1	0	93	-71
1	1	665	664
1	2	284	285
1	3	83	-103
1	4	504	-524
1	5	124	-114
1	6	380	406
1	7	349	353
1	8	43	-61
1	9	191	-201
2	-10	98	88
2	-9	280	276
2	-8	83	-87
2	-7	273	-277
2	-6	198	-195
2	-5	108	-78
2	-4	422	452
2	-3	219	198
2	-2	558	-589
2	-1	570	-540
2	0	259	240
2	1	708	679
2	2	57	42
2	3	529	-481
2	4	386	-362
2	5	37	40
2	6	358	360
2	7	184	179
2	8	53	-50
2	9	185	-178
3	-10	210	185
3	-9	223	217
3	-7	214	-224
3	-6	76	-88
3	-5	434	447
3	-4	600	595
3	-3	253	-226
3	-2	562	-559
3	-1	232	-243
3	0	165	183
3	1	493	478
3	2	120	-100
3	3	400	-371
3	4	389	-357
3	5	67	63
3	6	388	374
3	7	73	55
3	8	157	-152
4	-9	94	97
4	-8	157	-167
4	-7	224	-231
4	-6	152	158
4	-5	415	415
4	-4	403	421
4	-3	159	-162
4	-2	253	-252
4	-1	212	-199
4	0	302	308
4	1	268	263
4	2	93	-107
4	3	228	-218
4	4	300	-269
4	5	96	81
4	6	315	303
4	7	52	-28
5	-8	231	-244
5	-7	236	-231
5	-5	296	314
5	-4	225	244
5	-3	358	-375
5	-2	244	-246
5	-1	80	70
5	0	364	343
5	1	184	182
5	2	100	-93
5	3	245	-235
5	5	186	176
5	6	144	131
6	-6	44	23
6	-5	181	187
6	-4	54	64
6	-3	291	-304
6	-2	228	-241
6	-1	64	64
6	0	276	274
6	1	170	171
6	2	227	-233
6	3	177	-170
6	4	120	129
7	-2	40	-34
7	-1	141	151
7	0	144	139
L = 3			
-8	-3	219	238
-8	-2	59	-61
-8	-1	195	-205
-8	0	161	-176
-8	1	59	51
-8	2	214	214
-8	3	92	-87
-7	-6	300	-322
-7	-5	120	-126
-7	-4	136	142
-7	-3	126	136
-7	-2	74	-75
-7	-1	230	-223
-7	0	291	-291
-7	1	180	184
-7	2	261	259
-7	4	164	-175
-7	5	140	-148
-6	-8	151	147
-6	-7	267	-220
-6	-6	235	-239
-6	-5	103	-98
-6	-4	206	203
-6	-3	117	98
-6	-2	99	-100
-6	-1	411	-409
-6	0	126	-120
-6	1	386	404
-6	2	246	246
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0	0	87	84
L = 12			
-6	-6	113	-111
-6	-5	75	65
-6	-4	237	248
-6	-2	184	-186
-6	-1	105	-101
-5	-7	218	-222
-5	-6	86	-63
-5	-5	163	169
-5	-4	148	154
-5	-3	101	-103
-5	-2	169	-161
-5	-1	54	-44
-5	0	70	63
-5	1	143	139
-4	-7	238	-234
-4	-6	93	102
-4	-5	223	215
-4	-4	106	106
-4	-3	183	-187
-4	-2	217	-209
-4	0	217	216
-4	1	80	76
-3	-7	140	-141
-3	-6	110	116
-3	-5	219	217
-3	-4	70	60
-3	-3	194	-203
-3	-2	154	-143
-3	0	248	233
-3	1	61	63
-2	-7	51	-20
-2	-6	116	127
-2	-5	153	150
-2	-4	73	-74
-2	-3	160	-164
-2	-2	105	-121
-2	-1	77	81
-2	0	206	221
-1	-6	162	170
-1	-5	224	224
-1	-4	87	-89
-1	-3	190	-207
-1	-2	54	-68
-1	-1	145	179
L = 13			
-5	-4	204	-213
-5	-3	107	-113
-5	-2	89	97
-4	-5	118	-104
-4	-4	190	-196
-4	-3	82	-88
-4	-2	132	125
-3	-5	103	-105
-3	-4	146	-140
-3	-3	73	61
-3	-2	164	165

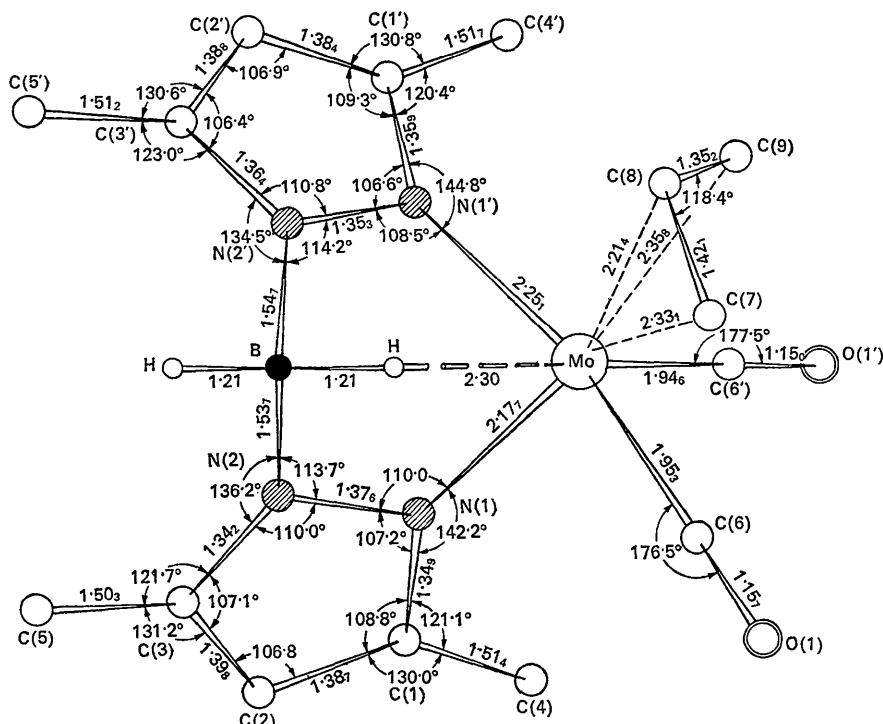
Fig. 1. Molecular geometry of π-allyl-dihydrobis-(3,5-dimethyl-1-pyrazolyl)boratodicarbonylmolybdenum. The most important conformational parameters are shown.

performed with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms, except those of boron and the methyl groups, were included with an isotropic thermal factor $(B = 3·5 \text{ Å}^2)$. The R value was lowered to 0·060. At this stage a difference

Fourier synthesis showed the positions of all the hydrogen atoms. It clearly indicated H'(C4), H'(C5), H'(C4') and H'(C5') to be *trans* respectively to N(1), N(2), N(1') and C(2') and the hydrogen atoms around the boron atom to be close to tetrahedral geometry.
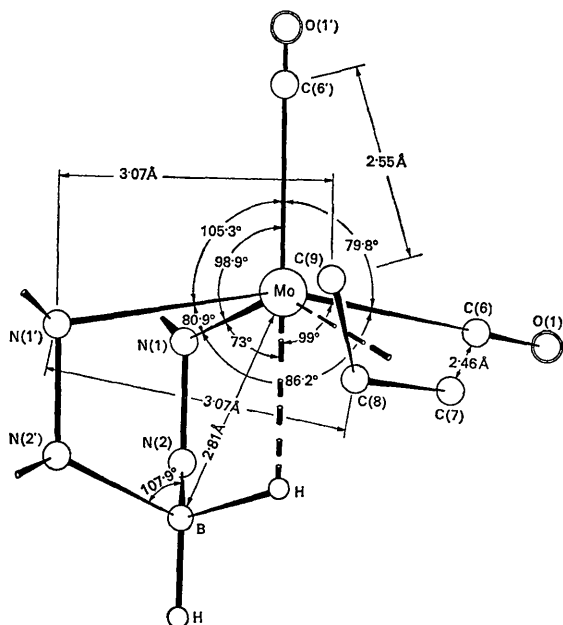

Fig. 2. Representation of the distorted octahedral geometry of the molybdenum atom.

Table 2. *Positional parameters in fractional coordinates for the nonhydrogen atoms*

Standard deviations are in parentheses

	x/a	y/b	z/c
Mo	0·05263 (6)	0·19313 (4)	0·34486 (4)
O(1)	−0·2042 (7)	−0·0011 (6)	0·3532 (5)
O(1')	0·2808 (8)	−0·0588 (5)	0·3549 (6)
N(1)	−0·1335 (6)	0·1361 (5)	0·1395 (4)
N(2)	−0·2168 (7)	0·2465 (5)	0·1049 (5)
N(1')	0·1829 (7)	0·3252 (5)	0·2893 (5)
N(2')	0·0565 (7)	0·4115 (5)	0·2412 (5)
C(1)	−0·2133 (9)	0·0283 (6)	0·0353 (6)
C(2)	−0·3477 (10)	0·0703 (7)	−0·0652 (7)
C(3)	−0·3464 (9)	0·2094 (7)	−0·0185 (6)
C(4)	−0·1545 (11)	−0·1111 (7)	0·0402 (7)
C(5)	−0·4625 (12)	0·3095 (8)	−0·0817 (8)
C(1')	0·3423 (9)	0·3576 (7)	0·2906 (7)
C(2')	0·3156 (10)	0·4664 (7)	0·2455 (7)
C(3')	0·1331 (9)	0·5002 (6)	0·2145 (6)
C(4')	0·5140 (10)	0·2792 (9)	0·3388 (8)
C(5')	0·0273 (12)	0·6114 (7)	0·1632 (7)
C(6)	−0·1086 (9)	0·0742 (7)	0·3536 (6)
C(6')	0·1983 (9)	0·0358 (7)	0·3502 (6)
C(7)	0·0367 (10)	0·2751 (8)	0·5385 (7)
C(8)	0·1935 (10)	0·3311 (7)	0·5431 (6)
C(9)	0·3320 (10)	0·2510 (7)	0·5387 (6)
B	−0·1430 (10)	0·3784 (7)	0·2149 (7)

Table 3. *Thermal parameters for the non-hydrogen atoms*

Parameters are in the form: $\exp[-\frac{1}{4}(B_{11}a^{*2}h^2 + B_{22}b^{*2}k^2 + B_{33}c^{*2}l^2 + 2B_{12}a^*b^*hk + 2B_{13}a^*c^*hl + 2B_{23}b^*c^*kl)]$

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mo	2·369 (0·022)	2·701 (0·023)	2·790 (0·023)	−0·028 (0·018)	0·857 (0·019)	1·096 (0·019)
O(1)	4·708 (0·259)	5·919 (0·295)	6·526 (0·309)	−1·400 (0·219)	1·745 (0·236)	3·823 (0·251)
O(1')	4·965 (0·269)	3·770 (0·236)	6·506 (0·307)	1·659 (0·206)	1·721 (0·237)	1·927 (0·214)
N(1)	2·292 (0·196)	2·683 (0·211)	2·380 (0·202)	−0·341 (0·161)	0·506 (0·167)	0·940 (0·167)
N(2)	2·771 (0·210)	2·693 (0·215)	3·328 (0·224)	−0·197 (0·170)	1·195 (0·183)	1·301 (0·177)
N(1')	2·143 (0·201)	2·557 (0·211)	4·109 (0·247)	−0·463 (0·163)	1·162 (0·185)	1·282 (0·183)
C(1)	3·490 (0·287)	3·321 (0·284)	3·312 (0·280)	−0·550 (0·225)	1·643 (0·241)	0·643 (0·225)
C(2)	3·694 (0·309)	4·085 (0·327)	3·460 (0·305)	−0·635 (0·252)	0·547 (0·252)	1·209 (0·249)
C(3)	2·973 (0·269)	4·264 (0·317)	3·315 (0·284)	−0·359 (0·234)	1·051 (0·232)	1·768 (0·243)
C(4)	4·807 (0·360)	3·297 (0·304)	4·317 (0·345)	−0·073 (0·265)	1·895 (0·294)	0·757 (0·262)
C(5)	4·993 (0·380)	5·138 (0·401)	4·481 (0·369)	0·835 (0·315)	0·734 (0·308)	2·772 (0·315)
C(1')	3·008 (0·277)	3·139 (0·288)	5·115 (0·355)	−0·857 (0·226)	1·997 (0·265)	0·757 (0·251)
C(2')	3·831 (0·309)	3·666 (0·308)	4·452 (0·331)	−0·957 (0·246)	1·920 (0·272)	1·175 (0·254)
C(3')	4·069 (0·297)	2·395 (0·251)	3·170 (0·275)	−0·890 (0·218)	1·661 (0·242)	0·555 (0·208)
C(4')	2·960 (0·305)	6·485 (0·450)	6·112 (0·432)	0·617 (0·297)	1·980 (0·306)	2·249 (0·353)
C(5')	5·939 (0·409)	3·378 (0·317)	4·681 (0·366)	0·744 (0·288)	2·224 (0·327)	1·702 (0·273)
C(6)	3·488 (0·288)	3·746 (0·303)	3·304 (0·287)	0·032 (0·234)	0·856 (0·240)	1·925 (0·240)
C(6')	3·327 (0·282)	3·552 (0·288)	2·990 (0·275)	−0·451 (0·229)	0·938 (0·233)	0·950 (0·225)
C(7)	4·331 (0·341)	5·312 (0·380)	3·074 (0·294)	0·641 (0·289)	1·746 (0·268)	1·037 (0·268)
C(8)	3·781 (0·307)	3·571 (0·303)	2·950 (0·284)	−0·560 (0·245)	0·640 (0·244)	0·423 (0·233)
C(9)	3·454 (0·302)	3·949 (0·324)	3·043 (0·290)	−0·742 (0·250)	0·266 (0·243)	0·596 (0·241)
B	2·689 (0·282)	3·143 (0·302)	3·435 (0·311)	0·098 (0·232)	1·256 (0·249)	1·209 (0·247)

From this evidence, geometric positions of the hydrogen atoms could be calculated and the next refinement included these hydrogen atoms with an isotropic thermal factor ($B = 3\cdot5$ Å^2). The R value was lowered to 0·054. After this calculation, the variations of all the parameters were of the same order as the standard deviations. The standard deviations of the electron density were lower than 0·15 e.Å^{-3}. The best distribution of $\sum w(\varDelta F)^2$ was found using a unit weight for all reflections. Atomic scattering factors were taken from Moore (1963). Anomalous scattering for the molybdenum atom was not considered.

Table 1 shows a comparison of observed and calculated structure factors. Table 2 lists positional and thermal parameters for all non-hydrogen atoms. Table 3 contains the anisotropic thermal parameters for the non-hydrogen atoms. Positional parameters for the hydrogen atoms are given in Table 4.

Table 4. *Positional parameters for the hydrogen atoms*

The isotropic thermal parameter B has been assumed equal to 3·5 Å^2.

	x/a	y/b	z/c
H(C2)	−0·436	0·008	−0·161
H(C4)	−0·046	−0·106	0·135
H(C4)	−0·103	−0·155	−0·029
H(C4)	−0·273	−0·172	0·018
H(C5)	−0·423	0·408	−0·013
H(C5)	−0·608	0·286	−0·115
H(C5)	−0·440	0·307	−0·162
H(C2')	0·417	0·516	0·236
H(C4')	0·484	0·202	0·368
H(C4')	0·627	0·346	0·420
H(C4')	0·553	0·235	0·263
H(C5')	−0·112	0·608	0·152
H(C5')	0·021	0·600	0·071
H(C5')	0·097	0·707	0·230

Table 4 (*cont.*)

	x/a	y/b	z/c
H(C7)	−0·076	0·337	0·542
H(C7)	0·030	0·171	0·532
H(C8)	0·202	0·435	0·550
H(C9)	0·453	0·291	0·542
H(C9)	0·322	0·147	0·532
H1(B)	−0·140	0·366	0·310
H2(B)	−0·242	0·467	0·184

Description of the structure

The most relevant conformational parameters of π-allyl-dihydrobis-(3,5,-dimethyl-1-pyrazolyl)boratodicarbonylmolybdenum are reported in Figs. 1 and 2 and in Table 5. Fig. 1 shows the geometry of the coordination of molybdenum and boron atoms. Except for the allyl group, the molecule is characterized by a pseudo C_s symmetry as found by Trofimenko through nuclear magnetic resonance studies (Trofimenko, 1970). The coordination of molybdenum is distorted-octahedral. Two nitrogen atoms of the pyrazolyl rings, one carbonyl group and the allyl group, occupy the corners of a square; the other carbonyl group is bonded in one apical position, while on the opposite side a hydrogen atom is bonded to the boron. The B atom shows a slightly distorted tetrahedral coordination. The distance Mo...B(2·8 Å) is very short compared with the corresponding distance found in the similar compound hydrotris-(1-pyrazolyl)boratobenzenediazodicarbonylmolybdenum. This fact could be explained in terms of a possible electronic interaction between H1(B) and Mo, since this bond distance is unusually short (2·3 Å°). In previous studies (Trofimenko, 1968, 1970), it has been suggested that the molybdenum atom has a 16-electron configuration; however, if the two electrons of the H1(B)–Mo bond are counted among those

shared by molybdenum, which has a formal charge 1+, the molybdenum atom would have an 18-electron configuration.

Table 5. *Bond distances and angles*

Standard deviations are in parentheses.

Distances

Mo——N(1)	2·177 (6) Å
Mo——N(1')	2·251 (6)
Mo——C(6)	1·953 (8)
Mo——C(6')	1·946 (8)
Mo——C(7)	2·331 (8)
Mo——C(8)	2·214 (8)
Mo——C(9)	2·358 (9)
B——N(2)	1·537 (10)
B——N(2')	1·547 (11)
N(1)–N(2)	1·376 (7)
N(1)–C(1)	1·349 (10)
C(1)–C(2)	1·387 (12)
C(2)–C(3)	1·398 (11)
C(3)–N(2)	1·342 (10)
C(1)–C(4)	1·514 (10)
C(3)–C(5)	1·503 (12)

Table 5 (*cont.*)

Distances

N(1')–N(2')	1·353 (8)
N(1')–C(1')	1·359 (10)
C(1')–C(2')	1·384 (10)
C(2')–C(3')	1·388 (12)
C(3')–N(2')	1·364 (9)
C(1')–C(4')	1·517 (12)
C(3')–C(5')	1·512 (11)
O(1) –C(6)	1·157 (10)
O(1')–C(6')	1·150 (9)
C(7)—C(8)	1·421 (12)
C(8)—C(9)	1·352 (11)
Mo—H1(B)	2·30

Angles

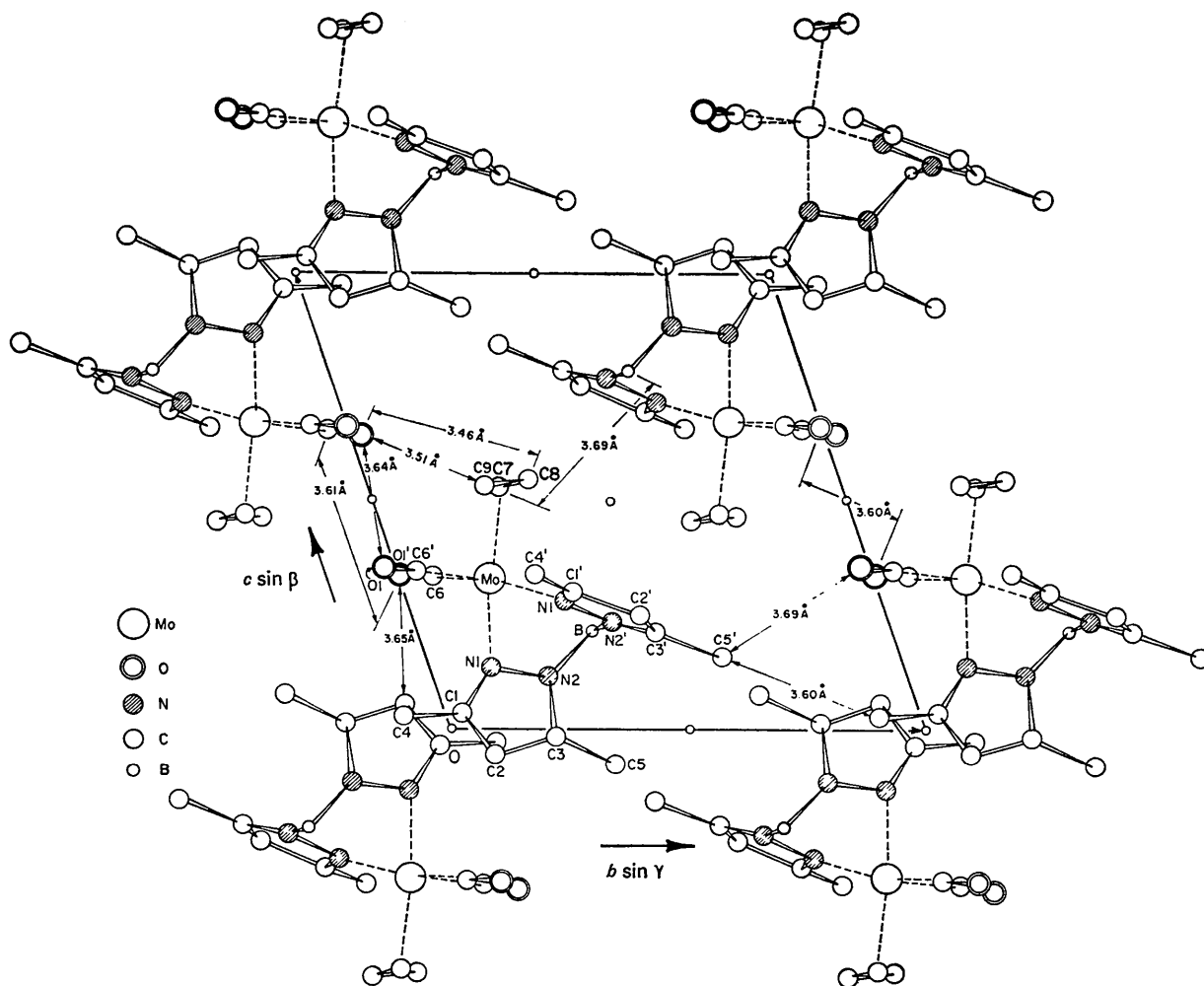|	
Mo—C(6)—O(1)	176·47 (51)°
Mo—C(6')—O(1')	177·50 (42)
Mo—N(1) –N(2)	110·04 (29)
Mo—N(1) –C(1)	142·20 (64)
Mo—N(1')–N(2')	108·51 (27)
Mo—N(1')–C(1')	144·78 (69)
C(6)—Mo—C(6')	79·82 (18)
C(6)—Mo—N(1)	86·21 (15)
C(6)—Mo—N(1')	166·64 (15)

Fig. 3. Projection of the packing on [001]. The shortest intermolecular contact distances are reported.

Table 5 (cont.)

Angles

C(6')–Mo–N(1)	98·92 (16)
C(6')–Mo–N(1')	105·33 (15)
N(1) –Mo–N(1')	80·87 (16)
N(1) –Mo–H1(B)	73·2
C(6)–Mo–H1(B)	98·9
B——N(2) –N(1)	113·72 (47)
B——N(2) –C(3)	136·24 (41)
B——N(2')–N(1')	114·21 (28)
B——N(2')–C(3')	134·53 (44)
N(2) –B——N(2')	107·90 (39)
N(1) –N(2) –C(3)	110·01 (26)
N(2) –C(3) –C(2)	107·08 (52)
C(3)–C(2)–C(1)	106·83 (33)
C(2)–C(1)–N(1)	108·78 (40)
C(1)–N(1) –N(2)	107·17 (25)
N(2) –C(3)–C(5)	121·67 (35)
C(2)–C(3)–C(5)	131·21 (42)
N(1) –C(1)–C(4)	121·14 (30)
C(2)–C(1)–C(4)	130·03 (45)
N(1')–N(2')–C(3')	110·80 (28)
N(2')–C(3')–C(2')	106·44 (52)
C(3')–C(2')–C(1')	106·86 (48)
C(2')–C(1')–N(1')	109·32 (31)
C(1')–N(1')–N(2')	106·59 (26)
N(2')–C(3')–C(5')	123·00 (32)
C(2')–C(3')–C(5')	130·59 (45)
N(1')–C(1')–C(4')	120·37 (33)
C(2')–C(1')–C(4')	130·78 (42)
C(7)–C(8)–C(9)	118·38 (36)

The allyl group is compelled by steric reasons to assume the position shown in Fig. 1. Very short contact distances from the two carbonyl groups (2·46–2·55 Å), as well as from one pyrazolyl group (3·07 Å), hinder rotation of the allyl group. For the same reason, the distances of C(7) and C(9) from Mo (2·33 and

2·36 Å) are considerably longer than the Mo–C(8) distance (2·21 Å).

As for the other geometrical parameters (Fig. 2), there are no remarkable differences between this and the similar compund hydrotris-(1-pyrazolyl)boratobenzenediazodicarbonylmolybdenum (Avitabile, Ganis & Nemiroff, 1970). Bond lengths and angles are quite normal. The greater distance Mo–N(1') (2·25 Å) with respect to Mo–N(1) (2·18 Å) can be due to the non-bonded interaction C(9)–N(1') and C(8)–N(1'), both about 3·07 Å.

Fig. 3 shows the packing of dihydro-(3,5-dimethyl-1-pyrazolyl)boratodicarbonylmolybdenum-π-allyl on [100]. The shortest intermolecular contact distances are reported.

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The Crystal Structure of a Pyrrhotite (Fe₇S₈)

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The structure of a pyrrhotite exhibiting a hexagonal ($a = 2A$, $c = 3C$) supercell has been determined from analysis of three-dimensional single-crystal intensity data. The symmetry of the structure is trigonal, space group $P3_1$; the hexagonal symmetry shown by single crystals possibly results from twinning, in which platy domains stacked normal to c are related by 180° rotations about c. The structure is composed of 12 subcell units stacked in three layers of four. The vacancies in the Fe sites are ordered, confined to alternate layers of Fe atoms normal to c. The distortions observed in the structure are analogous to those in the structure of troilite. Three Fe atoms in each Fe layer are displaced toward an enlarged tetrahedral site; the displacements from the ideal positions are 0·22 Å in both the vacancy layers and the full Fe layers.

Introduction

Pyrrhotites have the general composition $Fe_{1-x}S$. Below 370°C most pyrrhotites exhibit some degree of

superstructure development; the B-8 (NiAs) type structure of the subcell was assigned by Alsen (1925). Compositions at, or near, stoichiometric FeS have the hexagonal troilite superstructure with $a = A\sqrt{3}$, $c = 2C$, where