plane B to plane $D = 130{\cdot}4°$) and a pseudo-symmetry plane through C(16). The oxygen atoms in the molecule are bound by intramolecular hydrogen bonds. Intermolecular van der Waals forces hold the molecules together in the structure.

One of us (P.N.) is a recipient of a Deutscher Akademischer Austauschdienst scholarship, for which he is grateful.

References

COCHRAN, W. (1955). *Acta Cryst.* **8**, 473.

GERMAIN, G. & WOOLFSON, M. M. (1968). *Acta Cryst.* **24**, 91.

HÄNSEL, R., OHLENDORF, D. & PELTER, A. (1970). *Z. Naturforsch.* In the press.

HOPE, H. (1965). *Acta Chem. Scand.* **19**, 217.

International Tables for X-ray Crystallography (1962). Vol. III, p. 202. Birmingham: Kynoch Press.

KARLE, J. & HAUPTMAN, H. (1956). *Acta Cryst.* **9**, 635.

MCDONALD, T. R. R. & BEEVERS, C. A. (1952). *Acta Cryst.* **5**, 654.

SCHOMAKER, V., WASER, J., MARSH, R. E. & BERGMAN, G. (1959). *Acta Cryst.* **12**, 600.

ZECHMEISTER, K. (1969). Dissertation, Technische Hochschule, München.

Acta Cryst. (1971). B**27**, 725

The Crystal and Molecular Structure of Hydrotris(1-pyrazolyl)boratobenzenediazodicarbonyl Molybdenum $HB(pz)_3Mo(CO)_2NNC_6H_5$

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(*Received* 24 *April* 1970)

Hydrotris(1-pyrazolyl)boratobenzenediazodicarbonyl molybdenum, $HB(C_3N_2H_3)_3Mo(CO)_2N_2C_6H_5$, crystallizes in the space group $P\bar{1}$. The unit-cell constants are: $a = 9{\cdot}495 \pm 0{\cdot}010$, $b = 11{\cdot}878 \pm 0{\cdot}014$, $c = 9{\cdot}190 \pm 0{\cdot}009$ Å; $\alpha = 102°56' \pm 5'$, $\beta = 85°56' \pm 3'$, $\gamma = 100°44' \pm 4'$, $Z = 2$; $D_x = 1{\cdot}59$, $D_{\text{meas}} = 1{\cdot}59 \pm 0{\cdot}01$. Data for 2571 reflections were collected at room temperature on a Picker automated diffractometer. The crystal structure was solved by the Patterson method and refined by block-matrix least-squares calculations on 2375 observed reflections to a reliability index of 0·038. Molybdenum and boron lie on the pseudo threefold axis of the molecule and are bonded to adjacent nitrogen atoms on each of the three pyrazole rings. The average B–N bond distance is 1·55 Å. The average Mo–N(pyrazolyl)bond distance is 2·22 Å whereas the Mo–N(diazo) bond distance is 1·83 Å. The geometry about the Mo atom is that of a slightly distorted octahedron. The boron atom exhibits slightly distorted tetrahedral geometry.

Introduction

In the last few years a number of transition metal pyrazolyl borate complexes have been prepared (Trofimenko, 1967, 1968, 1969). In order to gain more insight into the stereochemistry of such compounds we have undertaken the structural determination of the pyrazolyl borate complex hydrotris(1-pyrazolyl)boratobenzenediazodicarbonyl molybdenum.

A similar compound: hydrotris(1-pyrazolyl)boratodicarbonylnitrosyl molybdenum, $HB(pz)_3Mo(CO)_2NO$, has been recently studied (Holt, 1970). However, in the nitrosyl complex a statistical disorder involving the carbonyl and nitrosyl groups has been found. In addition the presence of a disordered solvent molecule has prevented the successful refinement of the structure. The present complex does not show a disordering of the carbonyl and benzenediazo groups because of the very different steric encumbrance of these ligands.

Experimental

Red-orange crystals of the complex were provided by S. Trofimenko. The one chosen was a plate of dimensions 0·45 × 0·24 × 0·04 mm. Weissenberg photographs showed that the crystal was triclinic. Centrosymmetry was assumed and confirmed by the subsequent refinement.

The crystal was mounted on a Picker automated diffractometer with the a axis parallel to the spindle axis. The unit-cell constants were determined from a least-squares fit of the angular positions of twelve independent reflections. Data were taken to a 2θ value

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Table 1. *Comparison between observed and calculated structure factors* ($F_o\times 10$; $F_c\times 10$)

H	K	FO	FC
L = 0			
-10	1	166	156
-10	3	174	-166
-10	4	196	-187
-9	1	103	-113
-9	2	306	-308
-9	3	163	-153
-9	5	210	208
-9	6	236	232
-8	1	367	-371
-8	2	195	-200
-8	3	196	206
-8	4	343	340
-8	5	209	210
-8	6	100	-85
-8	7	174	-171
-8	8	75	-57
-7	1	249	-236
-7	2	191	195
-7	3	503	504
-7	4	134	112
-7	5	137	-184
-7	6	349	-352
-7	7	158	-152
-7	8	188	185
-7	9	143	139
-7	10	93	94
-6	1	400	368
-6	2	438	438
-6	3	49	52
-6	4	305	-308
-6	5	305	-301
-6	7	114	115
-6	8	511	509
-6	9	118	121
-6	10	202	-211
-6	11	75	-62
-5	1	63	93
-5	3	469	-430
-5	4	159	-186
-5	6	478	461
-5	7	602	600
-5	9	306	-328
-5	10	144	-142
-5	11	74	62
-4	1	516	-483
-4	2	77	-110
-4	3	72	51
-4	5	581	597
-4	6	518	527
-4	7	198	-196
-4	8	361	-370
-4	9	237	-236
-4	10	127	112
-4	11	268	274
-4	12	60	53
-3	1	270	233
-3	2	344	333
-3	3	300	317
-3	4	824	826
-3	5	127	151
-3	6	305	-320
-3	7	376	-364
-3	8	239	-241
-3	9	218	215
-3	10	327	323
-3	11	121	111
-3	12	135	-136
-2	1	259	-227
-2	2	173	190
-2	3	908	939
-2	4	97	-124
-2	5	426	-421
-2	6	45	-64
-2	7	54	-63
-2	8	259	253
-2	9	362	357
-2	10	67	72
-2	11	272	-274
-2	12	199	-204
-1	1	1051	1047
-1	2	518	513
-1	3	266	-263
-1	4	369	296
-1	5	343	-331
-1	6	134	129
-1	7	428	424
-1	8	353	350
-1	9	76	55
-1	10	354	-357
-1	11	177	-178
0	1	511	567
0	2	703	-665
0	3	294	242
0	4	81	-85
0	5	135	-81
0	6	159	188
0	7	186	183
0	8	236	-225
0	9	303	-292
0	10	311	-308
0	12	196	190
1	0	321	280
1	1	1084	-983
1	2	1167	-1341
1	3	68	58
1	4	251	248
1	5	355	368
1	6	276	265
1	7	241	-229
1	8	401	-405
1	9	59	-65
1	11	151	139
2	0	473	-517
2	1	1106	-1134
2	2	157	130
2	3	1001	1011
2	4	436	450
2	5	136	125
2	6	214	-226
2	7	221	-220
2	8	166	-169
2	9	161	170
2	10	258	253
2	11	64	74
3	0	98	62
3	1	479	466
3	2	961	937
3	3	755	742
3	4	481	-459
3	5	627	-599
3	6	348	-358
3	7	145	-136
3	8	132	125
3	9	155	154
3	10	64	-57
4	0	54	-44
4	1	635	624
4	2	183	175
4	3	526	-503
4	4	445	-452
4	5	252	-245
4	6	79	77
4	7	267	274
4	8	160	155
4	9	161	-163
4	10	218	-229
5	0	383	384
5	1	179	179
5	2	395	-389
5	3	422	-415
5	4	53	-49
5	5	217	218
5	6	247	249
5	7	160	164
5	8	188	-191
5	9	196	-194
6	0	100	92
6	1	134	-136
6	2	497	-503
6	3	55	-41
6	4	263	255
6	5	124	129
6	6	136	-157
6	7	209	-220
6	8	161	-167
7	0	266	-275
7	1	148	-150
7	2	188	-181
7	3	222	233
7	4	298	297
7	5	155	-156
7	6	220	-217
7	7	107	-98
8	0	156	-155
8	1	200	200
8	2	160	169
8	3	89	75
8	4	60	-79
8	5	201	-202
9	0	189	187
9	1	175	178
9	3	165	-172
10	0	174	179
L = 1			
-10	2	185	-190
-10	3	76	-32
-9	-3	103	92
-9	-2	127	114
-9	0	134	-132
-9	1	271	-283
-9	2	156	-165
-9	3	218	223
-9	4	214	211
-9	6	157	-155
-9	7	165	-159
-8	-4	185	179
-8	-3	176	172
-8	-2	97	-85
-8	-1	137	-128
-8	0	198	-204
-8	1	45	-6
-8	2	233	230
-8	3	290	286
-8	4	67	61
-8	5	321	-319
-8	6	145	-128
-8	8	236	193
-7	-7	86	-88
-7	-6	165	158
-7	-5	338	346
-7	-4	69	64
-7	-3	45	36
-7	-2	143	-146
-7	-1	231	-232
-7	0	200	194
-7	1	273	274
-7	2	348	353
-7	3	49	35
-7	4	388	-394
-7	5	310	-315
-7	6	257	251
-7	7	195	192
-7	8	51	-36
-7	10	193	-208
-6	-8	49	-75
-6	-7	205	209
-6	-6	344	347
-6	-5	101	91
-6	-4	228	-229
-6	-3	349	-347
-6	-2	79	-56
-6	-1	117	105
-6	0	291	291
-6	1	96	93
-6	2	301	-301
-6	3	464	-461
-6	4	269	-265
-6	5	40	32
-6	6	360	362
-6	7	235	193
-6	8	192	-169
-6	9	170	-161
-6	10	84	-84
-5	-9	63	48
-5	-8	233	240
-5	-7	268	262
-5	-5	342	-344
-5	-4	409	-404
-5	-2	160	172
-5	-1	360	361
-5	0	329	292
-5	1	656	-637
-5	2	489	-477
-5	3	153	126
-5	4	381	384
-5	5	345	347
-5	6	238	229
-5	7	59	-47
-5	8	302	-316
-5	10	147	136
-5	11	217	206
-4	-9	195	196
-4	-8	177	181
-4	-6	318	-316
-4	-5	277	-282
-4	-4	252	246
-4	-3	510	525
-4	-2	467	474
-4	-1	102	-98
-4	0	401	-409
-4	1	471	-469
-4	2	65	68
-4	3	597	594
-4	4	168	183
-4	5	115	100
-4	6	377	-398
-4	7	443	-443
-4	8	74	-72
-4	9	171	174
-4	10	144	142
-3	-11	103	96
-3	-10	160	168
-3	-9	107	111
-3	-8	57	-58
-3	-7	311	-312
-3	-6	241	-238
-3	-5	211	202
-3	-4	550	580
-3	-3	417	411
-3	-2	442	-440
-3	-1	658	-713
-3	0	365	-374
-3	1	331	321
-3	2	225	257
-3	3	250	258
-3	4	85	-104
-3	5	738	-742
-3	6	309	-291
-3	7	130	131
-3	8	298	298
-3	9	267	265
-3	10	55	23
-3	11	185	-179
-2	-11	249	252
-2	-10	71	85
-2	-9	45	-49
-2	-8	198	-195
-2	-6	69	87
-2	-5	467	477
-2	-4	327	329
-2	-3	859	-864
-2	-2	1042	-1043
-2	-1	275	-292
-2	0	613	595
-2	1	224	258
-2	2	634	625
-2	3	340	-358
-2	4	444	-478
-2	5	116	90
-2	6	188	211
-2	7	566	539
-2	8	253	238
-2	9	116	-114
-2	10	239	-237
-2	11	155	-155
-2	12	86	70
-1	-12	144	147
-1	-10	291	-285
-1	-9	238	-243
-1	-8	51	53
-1	-7	398	303
-1	-6	482	478
-1	-5	102	-87
-1	-4	336	-332
-1	-3	579	-606
-1	-2	85	76
-1	-1	192	-173
-1	0	457	492
-1	1	510	569
-1	2	1176	-1245
-1	3	738	-744
-1	4	32	-19
-1	5	378	-382
-1	6	291	303
-1	7	142	146
-1	8	264	-259
-1	9	354	-352
-1	10	72	-63
-1	11	150	157
0	-12	118	-92
0	-11	215	-222
0	-10	151	-156
0	-9	399	403
0	-7	247	248
0	-6	286	-269
0	-5	682	-663
0	-4	325	-334
0	-3	142	113
0	-2	568	582
0	-1	1031	990
0	0	205	196
0	1	760	-711
0	2	645	-735
0	3	271	252
0	4	545	538
0	5	241	259
0	6	87	-58
0	7	147	-147
0	8	430	-418
0	9	51	-28
0	10	348	347
0	11	109	102
1	-12	189	-167
1	-11	101	-96
1	-10	261	260
1	-9	441	436
1	-8	217	213
1	-7	388	-386
1	-6	457	-462
1	-5	85	-105
1	-4	61	59
1	-3	128	-101
1	-2	382	447
1	-1	49	-61
1	0	1341	-1286
1	1	417	-443
1	2	37	20
1	3	1235	1196
1	4	526	526
1	5	261	-238
1	6	377	-385
1	7	123	-121
1	8	112	110
1	9	109	93
1	10	173	169
1	11	69	-41
2	-12	59	-68
2	-11	174	170
2	-10	351	342
2	-9	60	39
2	-8	281	-288
2	-7	432	-445
2	-6	95	83
2	-5	252	273
2	-4	388	424
2	-3	507	486
2	-2	1252	-1232
2	-1	701	-727
2	0	478	-462
2	1	74	-27
2	2	285	298
2	3	414	401
2	4	180	-197
2	5	751	-728
2	6	58	-73
2	7	313	330
2	8	267	264
2	9	87	101
2	11	199	-206
3	-12	177	178
3	-11	234	226
3	-10	45	-13
3	-9	405	-436
3	-8	317	-331
3	-6	36	47
3	-5	495	513
3	-4	127	-124
3	-3	636	-649
3	-2	203	-213
3	-1	24	-11
3	0	838	927
3	1	835	831
3	2	182	170
3	3	392	-392
3	4	444	-445
3	5	74	-72
3	6	324	330
3	7	195	197
3	8	97	91
3	9	74	-79
3	10	259	-260
4	-12	123	123
4	-11	55	-59
4	-10	252	-255
4	-9	213	-218
4	-8	52	-47
4	-7	360	364
4	-6	446	457
4	-5	523	-512
4	-4	450	-464
4	-3	240	-249
4	-2	133	-106
4	-1	523	527
4	0	477	489
4	1	68	52
4	2	469	-479
4	3	363	-344
4	4	220	221
4	5	312	315
4	6	205	207
4	7	52	51
4	8	241	-241
4	9	293	-311
5	-12	84	-65
5	-11	171	-184
5	-10	124	-130
5	-8	487	505
5	-7	333	330
5	-6	345	-345
5	-5	432	-429
5	-4	97	-107
5	-3	318	305
5	-2	56	85
5	-1	127	147
5	0	144	-154
5	1	658	-651
5	2	358	-350
5	3	201	206
5	4	272	281
5	5	211	211
5	7	278	-284
5	8	107	-102
5	9	89	93
6	-10	125	102
6	-9	290	312
6	-8	73	41
6	-7	284	-285
6	-6	460	-459
6	-5	214	-214
6	-4	256	254
6	-3	451	435
6	-2	85	89
6	-1	173	-178
6	0	286	-300
6	1	36	18
6	2	233	239
6	3	247	250
6	4	193	187
6	5	140	-155
6	6	296	-305
6	7	87	-77
6	8	106	112
7	-10	172	182
7	-9	90	-95
7	-8	371	-366
7	-7	249	-249
7	-6	72	-70
7	-5	252	253
7	-4	278	278
7	-3	73	70
7	-2	323	-314
7	-1	221	-210
7	1	144	153
7	2	369	378
7	3	114	129
7	4	216	-214
7	5	243	-252
7	6	50	35
8	-9	92	-86
8	-8	195	-200
8	-7	101	102
8	-6	327	324
8	-5	251	248
8	-4	73	-66
8	-3	321	-315
8	-2	215	-212
8	-1	59	21
8	0	201	207
8	1	150	146
8	3	255	-270
8	4	163	-146
8	5	57	55
9	-8	89	88
9	-7	203	195
9	-6	99	89
9	-5	193	-200
9	-4	256	-248
9	-3	112	-106
9	-2	65	71
9	-1	186	182
9	0	269	278
9	1	66	-60
9	2	296	-305
9	3	133	-104
10	-5	214	-217
10	-3	139	145
10	-2	172	172
10	-1	106	101
L = 2			
-9	-3	92	98
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-9	-1	192	-194
-9	0	84	-72
-9	1	64	19
-9	2	295	305
-9	3	137	135
-9	4	129	-136
-9	5	192	-185
-9	6	121	-122
-8	-5	206	216
-8	-4	73	81
-8	-3	206	-211
-8	-2	106	-80
-8	-1	51	39
-8	0	178	183
-8	1	219	221
-8	2	90	88
-8	3	141	-141
-8	4	328	-339
-8	5	175	-173
-8	6	173	171
-8	7	220	215
-8	8	70	62
-7	-7	200	209
-7	-6	262	275
-7	-4	148	-142
-7	-3	192	-191
-7	-1	347	342
-7	0	204	201
-7	1	65	-50
-7	2	121	-129
-7	3	245	-247
-7	5	251	261
-7	6	151	153
-7	8	270	-269
-7	9	271	-274
-6	-8	222	231
-6	-7	273	269
-6	-6	169	-168
-6	-5	362	-368
-6	-4	59	-31
-6	-2	273	277
-6	-1	231	239
-6	1	309	-310
-6	2	392	-372
-6	3	48	50
-6	4	226	237
-6	5	297	297
-6	6	209	-209
-6	7	290	-289
-6	8	177	-186
-6	10	202	197
-5	-9	165	155
-5	-8	162	152
-5	-7	189	-181
-5	-6	297	-298
-5	-5	223	-208
-5	-4	365	357
-5	-3	533	521
-5	-2	128	144
-5	-1	48	27
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-5	1	307	-315
-5	2	68	86
-5	3	344	350
-5	4	62	54
-5	5	197	-207
-5	6	300	-305
-5	7	205	-198
-5	8	139	138
-5	9	240	234
-5	10	213	215
-4	-10	171	171
-4	-8	124	-127
-4	-7	128	-139
-4	-6	93	-84
-4	-5	539	524
-4	-4	547	540
-4	-2	257	-261
-4	-1	490	-501
-4	0	427	-412
-4	1	277	275
-4	2	622	617
-4	3	251	239
-4	4	339	-341
-4	5	479	-491
-4	6	103	-92
-4	7	167	158
-4	8	115	109
-4	9	50	-53
-4	10	128	-118
-4	11	224	-223
-3	-11	133	132
-3	-10	105	-110
-3	-9	120	-134
-3	-8	158	-160
-3	-6	387	386
-3	-5	250	264
-3	-4	46	39
-3	-3	562	-577
-3	-2	601	-607
-3	-1	251	218
-3	0	432	447
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-3	-4	94	70
-3	-3	297	298
-3	-1	254	-258
-3	0	289	-302
-3	1	127	-121
-3	2	141	158
-3	3	209	211
-3	4	86	99
-2	-8	179	-177
-2	-7	118	-105
-2	-6	74	80
-2	-5	187	179
-2	-4	209	199
-2	-3	44	25
-2	-2	245	-257
-2	-1	272	-287
-2	0	86	75
-2	1	283	283
-2	2	210	198
-2	3	125	112
-2	4	130	-133
-1	-9	190	-189
-1	-8	50	-58
-1	-7	123	101
-1	-6	270	260
-1	-5	200	205
-1	-4	54	-62
-1	-3	209	-212
-1	-2	159	-159
-1	-1	147	134
-1	0	220	223
-1	1	124	130
-1	2	72	-61
-1	3	308	-316
-1	4	280	-277
0	-9	114	-98
0	-8	72	56
0	-7	276	281
0	-6	79	68
0	-5	236	-235
0	-4	286	-282
0	-3	122	-123
0	-2	152	142
0	-1	193	183
0	0	59	51
0	1	60	-75
0	2	281	-289
0	3	205	-201
0	4	135	135
1	-9	149	133
1	-8	317	311
1	-7	65	61
1	-6	240	-240
1	-5	212	-214
1	-3	169	169
1	-2	111	99
1	-1	140	112
1	0	173	-175
1	1	268	-279
1	2	50	-54
1	3	176	180
1	4	268	273
2	-9	182	174
2	-7	219	-217
2	-6	296	-319
2	-5	169	180
2	-4	190	199
2	-3	131	130
2	-2	90	84
2	-1	253	-258
2	0	300	-298
2	2	139	143
2	3	64	26
3	-9	103	-101
3	-8	276	-278
3	-7	137	-130
3	-6	87	65
3	-5	166	170
3	-4	172	122
3	-3	76	-62
3	-2	245	-242
3	-1	229	-232
3	0	92	98
3	1	262	262
3	2	158	158
3	3	78	-84
4	-9	160	-153
4	-7	123	126
4	-6	246	250
4	-5	158	157
4	-4	196	-203
4	-3	318	-326
4	-2	75	-87
4	0	169	166
4	1	137	137
4	2	104	-108
5	-8	88	76
5	-7	154	149
5	-6	74	64
5	-5	239	-238
5	-4	307	-300
5	-2	182	179
5	-1	116	114
5	0	75	72
5	1	160	-155
6	-6	195	-204
6	-5	192	-206
6	-4	65	58
6	-3	204	202
6	-2	179	171
6	-1	55	50
L = 9			
-3	-4	83	69
-3	-3	93	-85
-3	-2	217	-208
-3	-1	173	-162
-2	-6	147	140
-2	-4	178	-167
-2	-3	235	-242
-2	-2	50	-76
-2	-1	65	58
-2	0	258	261
-2	1	192	144
-1	-7	168	159
-1	-6	61	55
-1	-5	227	-224
-1	-4	128	-132
-1	-3	78	92
-1	-2	210	211
-1	-1	248	242
-1	1	153	-150
-1	2	226	-241
0	-7	52	31
0	-6	207	-202
0	-5	195	-187
0	-4	73	48
0	-3	310	320
0	-2	75	56
0	-1	206	-209
0	0	155	-137
0	1	237	-241
0	2	110	-108
1	-7	199	-171
1	-6	209	-217
1	-4	270	269
1	-2	244	-239
1	-1	220	-228
1	0	56	-43
1	1	85	86
1	2	227	219
2	-7	135	-141
2	-6	160	172
2	-5	264	258
2	-4	98	99
2	-3	123	-109
2	-2	155	-158
2	0	208	204
2	1	122	112
3	-7	150	137
3	-6	254	266
3	-5	74	23
3	-4	165	-159
3	-3	239	-245
3	-1	176	182
3	0	128	108
4	-5	213	-207
4	-4	301	-313
4	-2	188	192
4	-1	89	88

of 45° with Zr-filtered Mo $K\alpha$ radiation. No attenuators were used. A take-off angle of 3°, a 2θ scan mode and a scan rate of 2° per minute 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 one hundred seconds. Backgrounds on either side of the peak were measured for ten seconds. Data were collected for 2571 reflections of which 2375 were observed. Two standard reflections were measured every forty reflections. The standard deviation of the intensities of these two reflections was ±1·5%.

Crystal data

Space group $P\bar{1}$
$a = 9{\cdot}496 \pm 0{\cdot}011$ Å M.W. 472·12
$b = 11{\cdot}877 \pm 0{\cdot}014$ Cell volume 987 Å^3
$c = 9{\cdot}189 \pm 0{\cdot}009$ Density, observed $1{\cdot}59 \pm 0{\cdot}01$
X-ray $1{\cdot}59$ g.cm^{-3}
$\alpha = 102°56' \pm 5'$
$\beta = 85°56' \pm 1'$ μ(Mo $K\alpha$) 6·9 cm^{-1}
$\gamma = 100°44' \pm 4'$

The background was subtracted and each peak was corrected for Lorentz and polarization factors. 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 minimum value of μR is 0·042 at $2\theta = 0$ perpendicular to the plane of the crystal plate. The maximum value of μR is 0·110 at $2\theta = 40°$ parallel to the plane of the crystal plate.

Determination of the structure and refinement

The structure factors were phased by the heavy atom method. The first Fourier synthesis located all 29 non-hydrogen atoms in the asymmetric unit. The atomic positions and isotropic thermal parameters were refined by six cycles of block-matrix least-squares calculations (Immirzi, 1967) to an R value of 0·079. Three cycles including anisotropic thermal parameters reduced the R value to 0·049.

At this point a difference synthesis showed the positions of the fifteen hydrogen atoms of the asymmetric

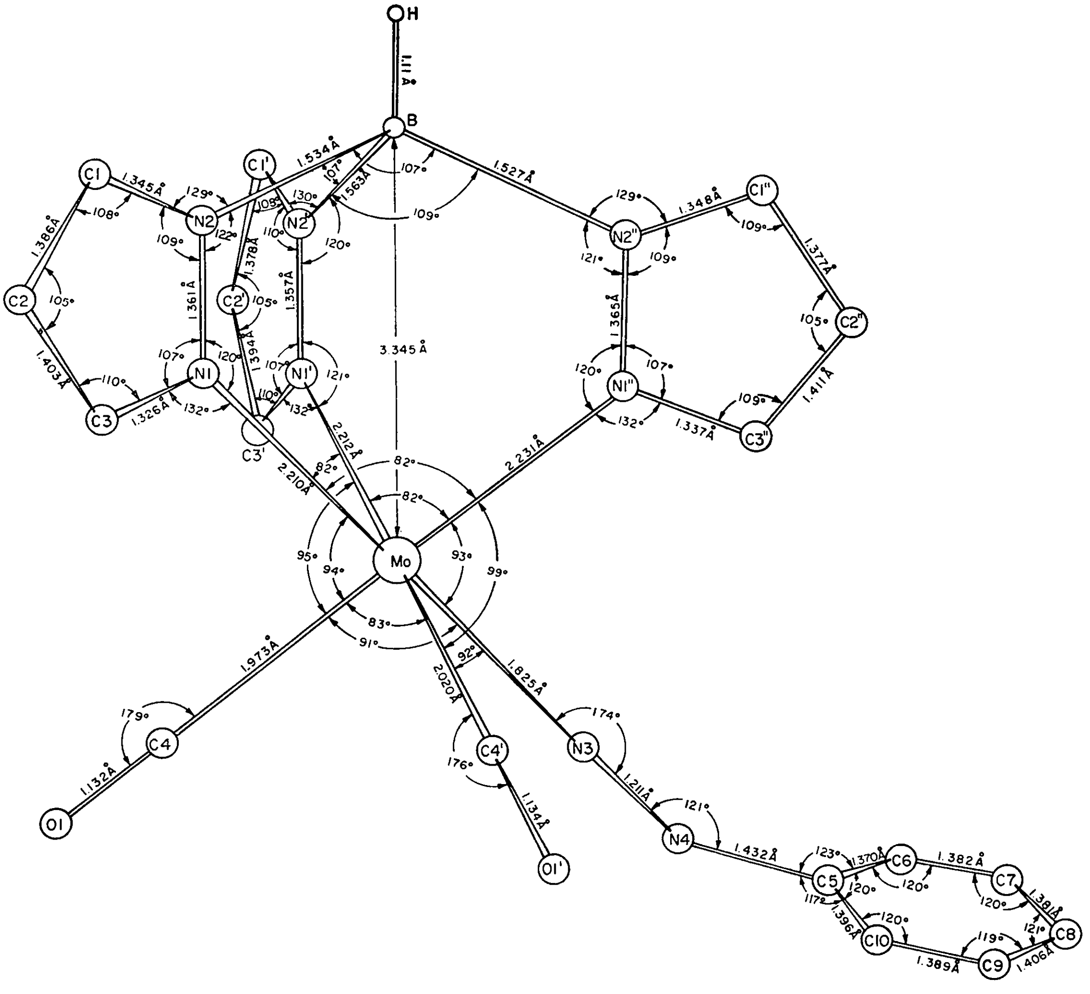


Fig. 1. Molecular geometry of hydrotris(1-pyrazolyl)boratobenzenediazodicarbonyl molybdenum. The most important conformational parameters are shown.

unit. The hydrogen atoms were included in the next refinement with isotropic thermal factors. The R index dropped to 0·038. The function minimized was: $\sum(w|F_c-KF_o|)^2$. The form of Cruickshank's (1949) weighting function was $w=(0{\cdot}77777+0{\cdot}01243\ F_{o_{\min}}+1{\cdot}9888\times10^{-4}(F_o)^2_{\max}$. The standard deviation of each reflection was used as a basis for the weighting function in the earlier stages of the refinement. The list of observed and calculated structure factors is given in Table 1. The atomic scattering factors were taken from Moore (1963). No corrections were included for anomalous scattering.

The final positional and thermal parameters are listed in Table 2 for non-hydrogen atoms. The anisotropic thermal parameters for the non-hydrogen atoms are listed in Table 3. The positional and isotropic thermal parameters for the hydrogen atoms are listed in Table 4. The standard deviations for the positional parameters of the hydrogen atoms are approximately ten times greater than those for the carbon atoms. The standard deviations of the thermal parameters for the hydrogen atoms are approximately ± 1 Å^2.

Table 2. *Positional parameters in fractional coordinates*

Standard deviations are given in parentheses.

Table 2 (*cont.*)

	x	y	z
Mo	0·2091 (1)	0·1638 (1)	0·2708 (1)
O(1)	0·3593 (5)	0·0563 (5)	0·4792 (5)
O(1′)	−0·0441 (5)	−0·0462 (4)	0·3031 (5)
N(1)	0·2860 (5)	0·0562 (4)	0·0608 (5)
N(2)	0·3370 (5)	0·1061 (4)	−0·0560 (5)
N(1′)	0·4014 (4)	0·2938 (4)	0·2298 (4)
N(2′)	0·4393 (5)	0·3089 (4)	0·0896 (5)
N(1″)	0·1146 (5)	0·2388 (4)	0·1084 (5)
N(2″)	0·1933 (5)	0·2651 (4)	−0·0132 (5)
N(3)	0·1417 (4)	0·2620 (4)	0·4333 (5)
N(4)	0·1063 (5)	0·3351 (4)	0·5382 (5)
C(1)	0·3771 (6)	0·0235 (6)	−0·1702 (7)
C(2)	0·3514 (7)	−0·0829 (6)	−0·1267 (7)
C(3)	0·2955 (6)	−0·0570 (5)	0·0204 (7)
C(1′)	0·5618 (7)	0·3904 (6)	0·0941 (8)
C(2′)	0·6052 (7)	0·4293 (6)	0·2408 (8)
C(3′)	0·5014 (6)	0·3675 (5)	0·3226 (7)
C(1″)	0·1160 (7)	0·3137 (5)	−0·0902 (7)
C(2″)	−0·0147 (7)	0·3210 (6)	−0·0172 (8)
C(3″)	−0·0111 (6)	0·2729 (5)	0·1084 (7)
C(4)	0·3057 (6)	0·0957 (5)	0·4026 (6)
C(4′)	0·0447 (6)	0·0293 (5)	0·2874 (6)
C(5)	−0·0423 (6)	0·3372 (5)	0·5755 (6)
C(6)	−0·0729 (7)	0·4413 (5)	0·6608 (7)
C(7)	−0·2133 (7)	0·4500 (6)	0·7045 (7)
C(8)	−0·3229 (7)	0·3533 (7)	0·6631 (7)
C(9)	−0·2930 (7)	0·2459 (7)	0·5755 (9)
C(10)	−0·1514 (7)	0·2382 (6)	0·5326 (8)
B	0·3440 (7)	0·2378 (6)	−0·0470 (7)

Description of the structure

The most important conformational parameters of the molecule are listed in Table 5 and Fig. 1.

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

$$\exp\left[-\tfrac{1}{4}(B_{11}a^{*2}h^2+B_{22}b^{*2}k^2+B_{33}c^{*2}l^2+2B_{12}a^*b^*hk+2B_{13}a^*c^*hl+2B_{23}b^*c^*kl)\right]$$

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mo	2·866 (0·019)	3·051 (0·020)	2·546 (0·019)	0·067 (0·015)	0·017 (0·015)	0·449 (0·015)
O(1)	4·899 (0·227)	6·784 (0·268)	5·669 (0·251)	1·879 (0·202)	−0·389 (0·187)	2·844 (0·212)
O(1′)	5·045 (0·236)	3·953 (0·208)	6·122 (0·259)	−0·514 (0·178)	0·624 (0·196)	0·413 (0·185)
N(1)	3·279 (0·202)	2·806 (0·187)	2·555 (0·187)	0·835 (0·157)	0·067 (0·151)	−0·055 (0·150)
N(2)	2·800 (0·190)	4·159 (0·218)	2·305 (0·185)	0·999 (0·167)	−0·039 (0·147)	0·176 (0·159)
N(1′)	2·987 (0·190)	2·479 (0·178)	2·413 (0·178)	0·396 (0·150)	−0·077 (0·144)	0·425 (0·142)
N(2′)	2·684 (0·188)	3·533 (0·207)	3·398 (0·209)	0·433 (0·158)	0·146 (0·156)	1·116 (0·167)
N(1″)	2·853 (0·191)	3·235 (0·199)	3·048 (0·199)	0·763 (0·158)	−0·361 (0·153)	0·682 (0·158)
N(2″)	3·587 (0·208)	3·349 (0·205)	2·539 (0·189)	0·754 (0·167)	−0·412 (0·156)	0·695 (0·158)
N(3)	2·541 (0·177)	2·886 (0·184)	2·266 (0.175)	0·581 (0·146)	−0·129 (0·138)	−0·238 (0·142)
N(4)	3·226 (0·203)	3·070 (0·199)	3·271 (0·204)	0·441 (0·163)	0·131 (0·160)	0·095 (0·161)
C(1)	3·279 (0·258)	5·145 (0·313)	3·227 (0·260)	1·517 (0·232)	−0·123 (0·203)	−0·777 (0·228)
C(2)	4·014 (0·285)	4·208 (0·286)	3·968 (0·287)	1·258 (0·231)	−1·005 (0·227)	−1·123 (0·228)
C(3)	3·029 (0·243)	3·014 (0·244)	4·322 (0·284)	0·286 (0·197)	−0·719 (0·207)	−0·407 (0·209)
C(1′)	3·511 (0·272)	4·319 (0·294)	5·630 (0·343)	0·443 (0·228)	0·399 (0·240)	2·090 (0·260)
C(2′)	3·791 (0·188)	3·759 (0·207)	5·627 (0·209)	−0·241 (0·158)	−0·713 (0·156)	0·764 (0·167)
C(3′)	3·817 (0·263)	3·325 (0·247)	3·686 (0·266)	0·658 (0·207)	−0·950 (0·209)	0·608 (0·206)
C(1″)	4·668 (0·301)	3·801 (0·265)	3·598 (0·272)	0·554 (0·228)	−1·642 (0·229)	1·286 (0·218)
C(2″)	4·276 (0·297)	4·063 (0·284)	4·990 (0·319)	1·112 (0·238)	−1·421 (0·243)	0·658 (0·242)
C(3″)	2·504 (0·230)	3·683 (0·253)	4·467 (0·288)	0·641 (0·197)	−0·701 (0·204)	0·397 (0·216)
C(4)	3·226 (0·243)	3·984 (0·263)	3·094 (0·243)	0·773 (0·204)	−0·305 (0·190)	0·956 (0·203)
C(4′)	3·855 (0·265)	3·543 (0·257)	3·239 (0·251)	0·858 (0·213)	0·274 (0·203)	0·252 (0·203)
C(5)	2·967 (0·228)	3·440 (0·237)	2·489 (0·218)	0·818 (0·190)	0·076 (0·177)	0·635 (0·184)
C(6)	4·415 (0·296)	3·231 (0·256)	3·832 (0·281)	0·703 (0·221)	0·460 (0·222)	0·022 (0·213)
C(7)	5·307 (0·335)	4·353 (0·302)	4·323 (0·302)	2·102 (0·263)	0·499 (0·250)	0·780 (0·241)
C(8)	4·125 (0·296)	7·028 (0·392)	3·487 (0·285)	2·576 (0·284)	0·835 (0·230)	1·534 (0·266)
C(9)	3·859 (0·303)	5·315 (0·344)	6·273 (0·389)	0·780 (0·260)	0·200 (0·269)	0·904 (0·293)
C(10)	3·924 (0·290)	4·157 (0·295)	5·033 (0·328)	0·908 (0·236)	0·673 (0·240)	−0·281 (0·247)
B	3·247 (0·285)	4·366 (0·314)	2·826 (0·268)	0·472 (0·241)	0·061 (0·216)	0·809 (0·234)

Table 4. *Positional and thermal parameters for the hydrogen atoms*

	x	*y*	*z*	*B*
H(C1)	0·4125 (78)	0·0425 (66)	−0·2649 (86)	4·3 (0·9) Å^2
H(C2)	0·3673 (69)	−0·1614 (56)	−0·1857 (72)	2·6 (0·7)
H(C3)	0·2629 (76)	−0·1079 (61)	0·0861 (81)	3·5 (0·8)
H(C1′)	0·6064 (64)	0·4158 (52)	0·0070 (68)	1·7 (0·6)
H(C2′)	0·6858 (21)	0·4903 (61)	0·2832 (87)	4·6 (0·9)
H(C3′)	0·3857 (75)	0·2599 (61)	−0·1543 (79)	3·6 (0·8)
H(C1″)	0·1519 (73)	0·3339 (60)	−0·1824 (78)	3·2 (0·8)
H(C2″)	−0·0910 (81)	0·3576 (67)	−0·0334 (86)	4·3 (0·9)
H(C3″)	−0·0886 (67)	0·2591 (55)	0·1902 (71)	2·6 (0·7)
H(C6)	0·0088 (80)	0·5184 (65)	0·6953 (85)	4·6 (0·9)
H(C7)	−0·2384 (82)	0·5336 (66)	0·7654 (87)	4·9 (0·9)
H(C8)	−0·4201 (78)	0·3575 (64)	0·6964 (84)	4·2 (0·9)
H(C9)	−0·3676 (90)	0·1732 (73)	0·5455 (96)	5·6 (1·0)
H(C10)	−0·1293 (75)	0·1614 (60)	0·4674 (80)	3·6 (0·8)
H(B)	0·4923 (81)	0·3681 (67)	0·4237 (83)	3·6 (0·9)

Table 5. *Conformational parameters of the structural unit*

Standard deviations are given in parentheses.

Bond distances

Mo—N(1)	2·210 (4) Å
Mo—N(1′)	2·212 (4)
Mo—N(1″)	2·231 (5)
Mo—N(3)	1·825 (4)
Mo—C(4)	1·973 (6)
Mo—C(4′)	2·020 (6)
B—N(2)	1·534 (9)
B—N(2′)	1·563 (8)
B—N(2″)	1·525 (8)
N(1)—N(2)	1·361 (6)
N(2)—C(1)	1·345 (8)
C(1)—C(2)	1·386 (10)
C(2)—C(3)	1·403 (9)
C(3)—N(1)	1·326 (7)
N(1′)-N(2′)	1·357 (6)
N(1′)-C(3′)	1·346 (7)
C(2′)-C(3′)	1·394 (9)
C(1′)-C(2′)	1·378 (10)
N(1″)-N(2″)	1·365 (6)
C(2″)-C(3″)	1·411 (9)
N(2″)-C(1″)	1·348 (8)
N(3)—N(4)	1·211 (6)
N(4)—C(5)	1·432 (7)

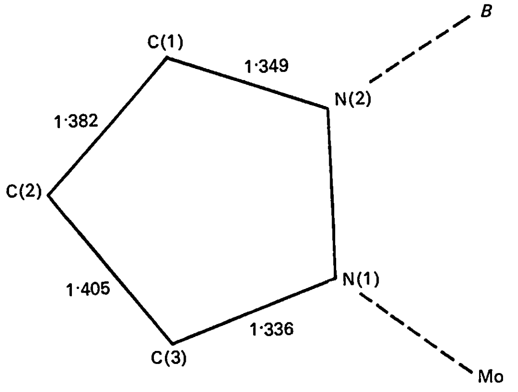


Fig. 2. Representation of a pyrazolyl ring in the molecule. Average parameters of the three pyrazolyl rings are given which shows that the twofold symmetry is lacking in the rings.

Table 5 (*cont.*)

C(5)—C(10)	1·396 (9)
C(9)—C(10)	1·389 (10)
C(8)—C(9)	1·406 (11)
C(7)—C(8)	1·381 (10)
C(6)—C(7)	1·382 (9)
O(1′)-C(4′)	1·134 (8)
O(1)—C(4)	1·132 (8)
C(1″)-C(2″)	1·377 (9)
N(2′)-C(1′)	1·350 (8)
N(1″)-C(3″)	1·337 (7)
C(5)—C(6)	1·370 (8)

Mo–B (non-bonded distance) = 3·345 (7)

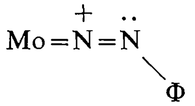
Bond angles

Mo—C(4′)—O(1′)	176·34 (15)°
Mo—C(4)—O(1)	179·05 (62)
Mo—N(3)—N(4)	174·21 (12)
Mo—N(1)—C(3)	131·81 (07)
Mo—N(1)—N(2)	120·51 (06)
Mo—N(1′)-N(2′)	121·24 (06)
Mo—N(1′)-C(3′)	131·90 (06)
Mo—N(1″)-N(2″)	120·43 (06)
N(1)—Mo—N(1′)	82·20 (08)
N(1)—Mo—N(1″)	81·60 (08)
N(1′)-Mo—N(1″)	81·66 (08)
N(1)—Mo—C(4)	94·49 (12)
N(1′)-Mo—C(4)	95·36 (09)
N(1′)-Mo—C(4′)	172·44 (79)
N(1″)-Mo—C(4′)	99·08 (09)
C(4)—Mo—C(4′)	83·41 (13)
C(4′)—Mo—N(3)	91·78 (12)
C(4)—Mo—N(3)	90·80 (09)
N(1′)-Mo—N(3)	95·70 (10)
N(1″)-Mo—N(3)	93·03 (11)
B—N(2)—N(1)	121·78 (26)
B—N(2)—C(1)	128·76 (29)
B—N(2′)-N(1′)	120·58 (23)
B—N(2′)-C(1′)	129·67 (28)
B—N(2″)-N(1″)	121·29 (24)
B—N(2″)-C(1″)	129·29 (28)
N(2)—B—N(2′)	107·07 (21)
N(2)—B—N(2″)	108·88 (22)
N(2′)-B—N(2″)	107·38 (21)
N(1)—N(2)—C(1)	109·46 (24)
N(2)—C(1)—C(2)	108·20 (26)
C(1)—C(2)—C(3)	104·99 (26)
C(2)—C(3)—N(1)	109·66 (25)
C(3)—N(1)—N(2)	107·68 (21)
N(2′)-N(1′)—C(3′)	106·84 (23)
N(1′)-C(3′)—C(2′)	109·83 (25)
C(3′)—C(2′)—C(1′)	105·24 (28)

Table 5 (*cont.*)

C(2′)—C(1′)—N(2′)	108·34 (27)
C(1′)—N(2′)-N(1′)	109·74 (21)
N(2″)-N(1″)-C(3″)	107·47 (22)
N(1″)-C(3″)-C(2″)	109·35 (24)
C(3″)-C(2″)-C(1″)	105·08 (27)
C(2″)-C(1″)-N(2″)	108·68 (25)
C(1″)-N(2″)-N(1″)	109·41 (21)
N(3)—N(4)—C(5)	121·09 (21)
N(4)—C(5)—C(10)	116·44 (27)
C(10)-C(9)—C(8)	118·99 (31)
C(9)—C(8)—C(7)	120·49 (32)
C(8)—C(7)—C(6)	119·97 (30)
C(7)—C(6)—C(5)	120·10 (27)
Torsion angle	
N(3)—N(4)—C(5)-C(6)	159·75

The coordinations of the molybdenum and boron atoms are slightly distorted octahedral and tetrahedral respectively. The hydrotris(1-pyrazolyl)borate ligand has nearly C_{3v} symmetry as foreseen by Trofimenko (1969). The average B–N bond distance is 2·22 Å, whereas the Mo–N(diazo) bond distance is 1·83 Å. The bond distances Mo–N(pyrazolyl) have nearly the value expected for neutral nitrogen atoms bonded to Mo. In fact the formal charge of these nitrogen atoms is only $-\frac{1}{3}$ because the uninegative charge on the $\mathrm{HB(pz)_3^-}$ ion must be shared among three nitrogen atoms. The shorter Mo–N(diazo) bond distance may be explained in terms of a substantial contribution of the resonance structure



$$\mathrm{Mo}=\overset{+}{\mathrm{N}}=\overset{\cdot\cdot}{\mathrm{N}}\diagdown\Phi$$

which also justifies the collinearity of the Mo–N–N atoms. The torsion angle around the bond N(4)–C(5) is approximately 20°; a similar torsion angle has been found for *trans*-azobenzene (~17°) (DeLeange, Robertson & Woodward, 1939).

The conformation of each pyrazole ring is not characterized by C_2 symmetry and is in agreement with resonance between the two limiting structures *A* and *B*, with *A* given double weight:

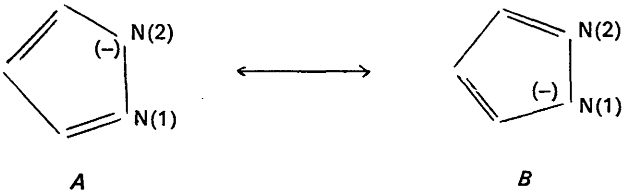


Fig. 2 shows the geometrical parameters of the pyrazolyl ligand averaged among all the three rings. Fig. 3 shows a projection of the structure on (001). The shortest intermolecular contact distances are reported.

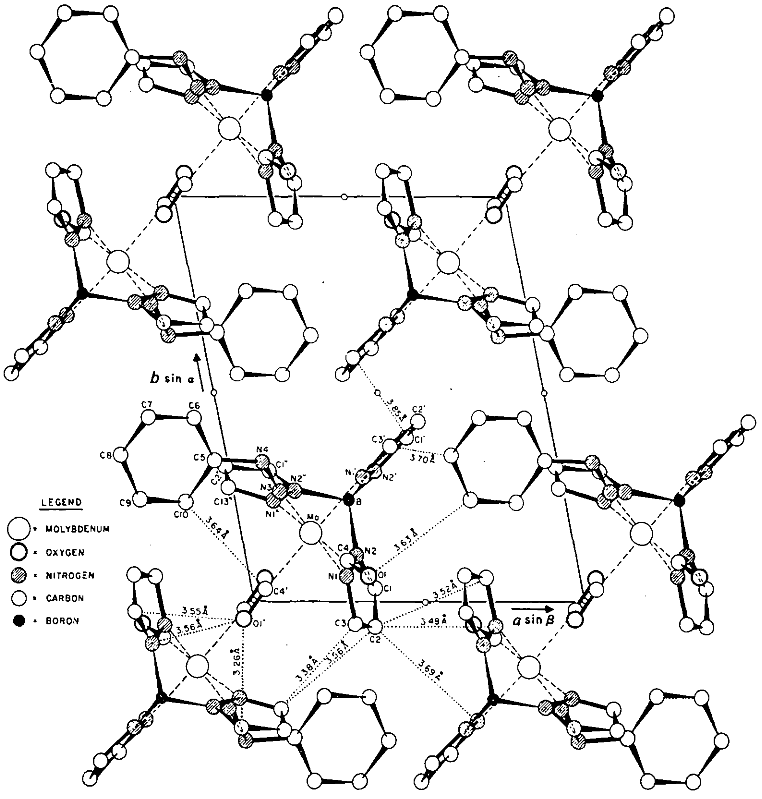


Fig. 3. Projection of the packing on (001). The shortest intermolecular contact distances are reported.

The authors are grateful to Prof. S. Holt for suggesting this research and to Dr S. Trofimenko for supplying samples of the compound. We are also deeply indebted to Prof. M. Goodman for encouraging this research.

References

CRUICKSHANK, D. W. J. (1949). *Acta Cryst.* **2**, 1965.
DELEANGE, J. J., ROBERTSON, J. M. & WOODWARD, I. (1939). *Proc. Roy. Soc.* A **1 71**, 398.
HOLT, S. (1970). Private communication.
IMMIRZI, A. (1967). *Ric. Sci.* **37**, 743.
MOORE, F. H. (1963). *Acta Cryst.* **16**, 1169.
TROFIMENKO, S. (1967). *J. Amer. Chem. Soc.* **89**, 3170.
TROFIMENKO, S. (1968). *J. Amer. Chem. Soc.* **90**, 4754.
TROFIMENKO, S. (1969). *J. Amer. Chem. Soc.* **91**, 588.

Acta Cryst. (1971). B**27**, 731

Double Oxides Containing Niobium, Tantalum, or Protactinium. IV. Further Systems Involving Alkali Metals

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(*Received* 2 *June* 1970)

The binary systems A_2O–B_2O_5 (where A = Rb or Cs and B = Nb or Ta) and A_2O–Pa_2O_5 (where A = Li, Na or K) have been partially examined. Unit-cell data are reported for most of the compounds prepared. In the Na_2O–Pa_2O_5 system, $NaPaO_3$ having a rhombohedrally distorted perovskite structure, and $NaPa_3O_8$ with a hexagonal unit cell have been observed. A value of 0·86 Å has been calculated for the ionic radius of protactinium from the cell parameters of $KPaO_3$ and $RbPaO_3$. The formation of $A$$PaO_3$ compounds is discussed.

Introduction

Double oxides containing niobium or tantalum and alkali metals lithium to potassium, and some of those with caesium were reported on in the first paper of the present series (Whiston & Smith, 1965). This study is extended in the present paper to include the remaining rubidium and caesium compounds with niobium and tantalum, and also those of protactinium with the lighter alkali metals. These latter compounds have also been extensively studied by Keller in recent years.

Experimental

Preparative and X-ray techniques were outlined in part I (Whiston & Smith, 1965) and part III (Iyer & Smith, 1967). Fuller details of the experimental conditions are given by Iyer (1965).

The system Rb_2O–Nb_2O_5

Reisman & Holtzberg (1960) identified eight intermediate phases in the system Rb_2O–Nb_2O_5. The compositions and melting points are given in Table 1. None of the complex X-ray powder diffraction patterns were indexed by these authors. We have not been able to prepare single crystals of rubidium-rich phases (including $RbNbO_3$) for X-ray examination because of their highly hygroscopic nature. We obtained crystals of '$Rb_4Nb_6O_{17}$' and the lattice was found to be orthorhombic with

$$a = 6{\cdot}42,\ b = 7{\cdot}68,\ c = 38{\cdot}55\ \text{Å}\ .$$

The density measured (4·45 g.cm.$^{-3}$) does not agree with the calculated value (4·09 g.cm.$^{-3}$) with $Z = 4$ for the above composition. However the calculated density (4·56 g.cm.$^{-3}$) for $Rb_8Nb_{14}O_{39}$ with $Z = 2$ agrees quite well with the measured density.

Table 1. *Compositions and melting points*

Compound	Melting point	
$Rb_4Nb_{30}O_{77}$	1351 °C	(incongruent)
$Rb_2Nb_8O_{21}$	1315	(congruent)
$Rb_8Nb_{22}O_{59}$	1319	(congruent)
$Rb_2Nb_4O_{11}$	1185	(incongruent)
$Rb_4Nb_6O_{17}$	1148	(incongruent)
$RbNbO_3$	964	(incongruent)
$Rb_8Nb_6O_{19}$	830	(congruent)
$Rb_8Nb_2O_9$	1300	(congruent)

Crystals of $Rb_2Nb_4O_{11}$ suitable for X-ray examination were prepared by firing a mixture of carbonate and oxide, containing slight excess of the carbonate, over extended periods. The lattice was found to be monoclinic with

$$a = 12{\cdot}95,\ b = 7{\cdot}48,\ c = 14{\cdot}92\ \text{Å},\ \beta = 106{\cdot}4^\circ\ .$$

The space group was Cm, $C2$, or $C2/m$. The density measured (4·86 g.cm^{-3}) shows rather poor agreement

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