

COMPLEXES OF POLYPYRAZOLYLBORATE LIGANDS

I. CONFORMATIONAL ISOMERISM IN [TETRAKIS(1-PYRAZOLYL)-BORATE] (h^5 -CYCLOPENTADIENYL)DICARBONYLMOLYBDENUM

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SUMMARY

Studies on the structure of $[B(pz)_4](C_5H_5)(CO)_2Mo$, where $B(pz)_4$ represents the tetrakis(pyrazolyl)borate group, have shown that the $B(pz)_4$ ligand is bidentate, while the cyclopentadienyl group is *pentahapto*. The interesting six-membered metallocyclic ring can exist in two conformers in solution, and these interconvert, with an activation energy of the order of 10 kcal/mol, thus giving rise to extensive variations in the proton NMR spectrum as the temperature is varied.

INTRODUCTION

The recent discovery of the polypyrazolylborate class of ligands has resulted in the synthesis of many new complexes¹. Tris and tetrakis(1-pyrazolyl)borate ions, $(HB(pz)_3^-)$ and $B(pz)_4^-$ have the potential to be tridentate or bidentate. To date no example of these ligands being bidentate to a metal atom has been reported. On the contrary, the tris(1-pyrazolyl)borate ligand is tridentate in $[HB(pz)_3]Mo(CO)_2(NN-C_6H_5)_2$ and in $[HB(pz)_3]_2Co^3$. We wish to report our spectroscopic studies on $[B(pz)_4](C_5H_5)(CO)_2Mo$ (I) which, together with preliminary results from a single crystal X-ray crystallographic study, show the $B(pz)_4$ ligand to be bidentate. Our evidence also suggests that the ring formed by the boron and molybdenum atoms and the two bonded pyrazolyl groups can exist in two conformers which interconvert in solution, thus giving rise to proton NMR spectra which vary markedly with temperature.

EXPERIMENTAL

The complex (I) was prepared according to a previously published procedure⁴. Infrared spectra were taken using a Perkin-Elmer 337 grating infrared spectrophotometer and 0.1 mm path-length sodium chloride cavity cells. Variable temperature proton nuclear magnetic resonance spectra were taken on a Varian HA-100.

RESULTS

Infrared spectra

The infrared spectrum of (I) dissolved in toluene- d_8 in the carbonyl region is

shown in Fig. 1. The spectrum consists of two doublets, individual peaks occurring at 1950, 1935, 1865, 1845 cm^{-1} , each with a possible error of $\pm 5 \text{ cm}^{-1}$. Thus a total of four bands is observed rather than the expected two. A similar pattern of bands is also

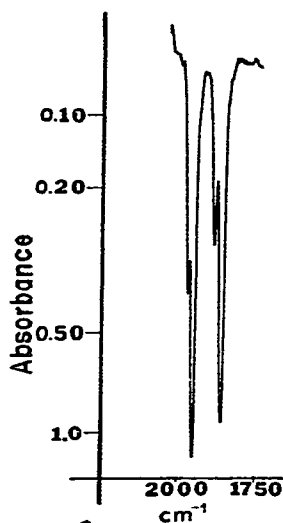


Fig. 1. A portion of the infrared spectrum of $[\text{B}(\text{pz})_4](\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Mo}$ in toluene- d_8 .

observed when other solvents, such as CS_2 , *m*-xylene, CCl_4 and ether, are used. However, the intensities of the less intense bands at 1950 and 1865 cm^{-1} relative to the intensities of the bands at 1935 and 1845 cm^{-1} are extremely solvent dependent. The ratio of intensities ranges from about 1/20 in CCl_4 to about 1/2 in toluene- d_8 . Only one set of bands (*i.e.*, total of two bands) is observed in cyclohexane, in agreement with Trofimenko's report⁴.

Nuclear magnetic resonance spectra

The NMR spectra of (I) at various temperatures in a 3/2/1 mixture of toluene- d_8 , CDCl_3 and TMS are shown in Fig. 2. At room temperature the spectrum consists of a sharp peak at about $\tau 5.2$ which can be assigned to the C_5H_5 group, and a complex group of resonances between $\tau 4.0$ and 2.0 which are due to the protons on the pyrazole rings. Trofimenko pointed out the futility of trying to determine the structure of (I) by NMR⁴. This is especially true in view of our observation of the extreme solvent dependence of the chemical shifts in the pyrazole region. We found the spectrum of (I) to be invariant with temperature from 25° to 150° in DMF- d_7 , but when the solution is cooled a number of changes occur. First, the whole spectrum begins to broaden and eventually to collapse. This is first noticeable at about -69° and becomes maximal at about -92° . On further cooling to about -120° the spectrum again sharpens and two peaks appear in the C_5H_5 region. At temperatures approaching -132° , although viscosity broadening effects may be interfering, it appears that the C_5H_5 resonances have again collapsed while the pyrazole resonances retain some sharpness. Thus, as the temperature is lowered the behavior of the NMR spectrum of (I) may be divided into three stages: (a), broadening and collapse of the whole spectrum; (b), sharpening of the spectrum with concomitant resolution of two C_5H_5 peaks; (c), collapse of the two

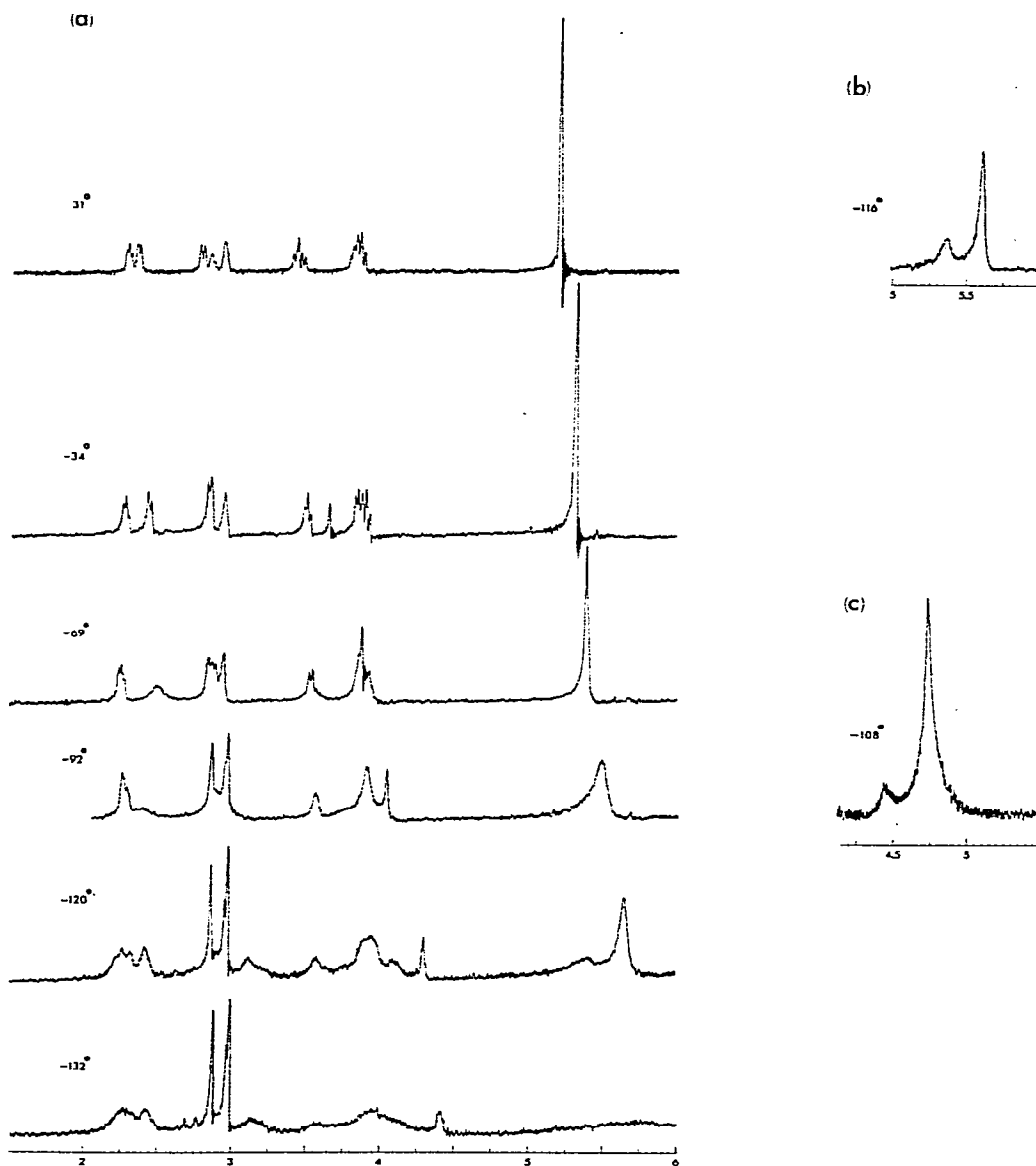


Fig. 2. The PMR spectra of $[B(pz)_4](h^5-C_5H_5)(CO)_2Mo$ in a 3/2/1 mixture of toluene- d_8 , $CDCl_3$ and TMS (a) and (b) and in a 3/2/1 mixture of CCl_2F_2 , $CDCl_3$ and TMS (c). The peaks at τ 2.7 and τ 2.9 in (a) are due to undeuterated solvent. The scale is in τ units.

C_5H_5 peaks. Stages (a) and (b) have been fully observed using a solvent mixture of CCl_2F_2 , $CDCl_3$ and TMS in 3/2/1 volume ratios, but the solution froze in the incipient phase of stage (c).

X-ray crystallographic study

The molecular structure is presented in Fig. 3. This is based on the preliminary

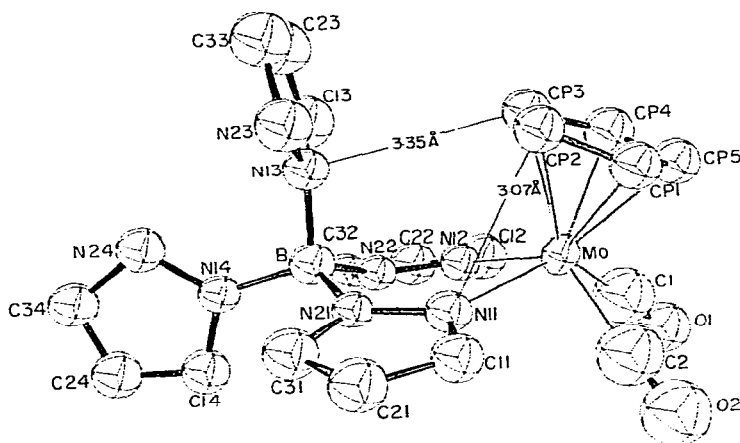


Fig. 3. The $[B(pz)_4](h^5-C_5H_5)(CO)_2Mo$ molecule showing the structure and the atom numbering.

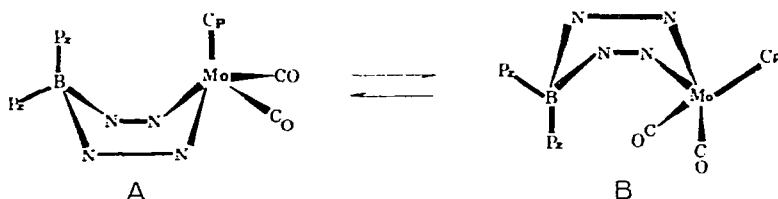


Fig. 4. Possible structures of the conformational isomers of $[B(pz)_4](h^5-C_5H_5)(CO)_2Mo$.

results of a single crystal X-ray study (see Appendix). The C_5H_5 group is *pentahapto* while the $B(pz)_4$ ligand is bidentate and forms a six-membered ring with the molybdenum. This structure had previously been proposed⁴, with some reservations. The plane formed by the ring of one of the unbound pyrazole groups (pz3) is perpendicular to the line formed by the Mo and the boron. The plane formed by the other unbound ring (pz4) is parallel to the Mo-B line. A mirror plane (non-crystallographic) which contains one unbound ring (pz4), the boron atom and the molybdenum atom and which bisects the C_5H_5 ring and the OC-Mo-CO group can be observed. The six-membered ring formed by the molybdenum and boron atoms and edges of pz1 and pz2 has a boat configuration (see Fig. 4).

DISCUSSION

The spectroscopic results can be explained by postulating the presence in solution of conformational isomers similar to A and B in Fig. 4. The infrared spectrum of a mixture of the A and B isomers would be expected to consist of four bands in a pattern of the sort observed. It appears that for the cyclohexane solution the equilibrium between A and B is greatly in favor of one conformer. However, in toluene the equilibrium constant is closer to unity. In view of the very bulky nature of the *B*-substituents on the MoN_4B ring this solvent dependence may not be surprising.

To account for the NMR results, we postulate an interconversion process between A and B. At room temperature the interconversion is rapid with respect to the NMR time scale and an average spectrum is observed; this gives sharp multiplets for

all pz protons and a singlet for C_5H_5 . By cooling the solution, the rate of this interconversion is diminished, which accounts for the broadening and collapse of the *whole* spectrum [stage (a)]. Further cooling reduces the rate of interconversion so much that in stage (b) separate spectra for the isomers A and B can be resolved. The most conspicuous manifestation of this is the occurrence of the two resonances at about τ 5 due to the C_5H_5 rings of the two isomers. The complex pattern of the pyrazole region is due to the superposition of the resonances due to the pyrazole protons in the two isomers. Stage (c) represents a different phenomenon which we feel affects only the C_5H_5 ring since the resonances due to this group are extensively broadened while at the same time the pz resonances remain fairly sharp. This phenomenon may be the slowing of the rotation of the $h^5-C_5H_5$ ring. If the structure of (I) in solution is the same at very low temperature as it is in the crystal then it is clear that the $h^5-C_5H_5$ ring is in a very magnetically asymmetric environment due to the relatively close approach of pz3. Thus the protons of the C_5H_5 ring would have very different chemical shifts if the rotation were stopped which may account for the final broadening of these C_5H_5 resonances as observed in stage (c). We have not yet been able to obtain a low temperature limiting spectrum to test this postulate due to experimental difficulties.

We have considered, but rejected, the possibility that the temperature dependence of the NMR spectrum, to the extent that the details of the low temperature spectra are resolved, might be explainable in another way. In this alternative view, the rotation of the set of ligands, $h^5-C_5H_5$, CO, CO, about a quasi-threefold axis passing through the molybdenum atom is invoked. By a rotation of about 60° one of the CO groups would be brought into the axial position of a square-pyramidal "piano stool" structure with the $h^5-C_5H_5$ group occupying the position of one of the legs. If this structure were in fact the second structure being observed at low temperatures it should, in principle, be possible to identify it because its lack of symmetry would cause it to have a more complex spectrum than that of either of the "ring flip" conformers. However, the overall complexity and poor resolution of the low temperature spectra do not allow such a decision to be made.

We believe that this "rotational conformer" hypothesis is unlikely for several reasons. Among the vast number of $(h^5-C_5H_5)MoL_{4-n}L'_n$ molecules which have been studied there appears to be no case in which the $h^5-C_5H_5$ ring does not form the "seat" of the piano stool and the ligands L and L' the legs⁵. Another consideration is that in the infrared spectrum of (I) there are no significant differences in the splittings or relative intensities of the symmetric and antisymmetric CO stretching modes of the two conformers. If the two species were the "rotational conformers", in one of which the two CO groups are in quite different environments while in the other their environments are symmetry equivalent, such similarity in the spectra would not be likely. Finally, our work on analogous compounds with simpler NMR spectra, which will be reported in a future paper, provide support for the "ring flip conformer" hypothesis.

CONCLUSION

The postulation of conformational isomers for the rather unique six-membered inorganic metallocycle observed in $[B(pz)_4](h^5-C_5H_5)(CO)_2Mo$ appears to account for all the spectroscopic properties observed. The structural conclusions presented here have been extended in the interpretation of a study of two new compounds, [HB-

TABLE I

THE OBSERVED AND CALCULATED STRUCTURE FACTORS IN ELECTRONS ($\times 10$)

M	L	FORS	FCAL	M	L	FORS	FCAL	M	L	FORS	FCAL	M	L	FORS	FCAL	M	L	FORS	FCAL	
2	0	770	1042	0	6	619	793	10	14	68	57	17	5	273	247	0	5	147	134	
4	0	1447	1426	10	6	119	165	12	14	18	58	1	6	1352	1187	2	5	351	332	
6	0	454	558	10	6	564	602	14	14	206	161	3	3	503	432	4	5	932	710	
8	0	2113	2355	14	6	488	411	18	14	31	27	7	6	1147	1133	8	5	746	706	
10	0	208	196	16	6	124	119	20	14	159	175	9	6	1049	1064	10	5	240	272	
12	0	757	850	18	6	456	462	0	16	175	155	11	6	262	277	12	5	155	156	
14	0	608	620	20	6	776	703	2	16	44	64	13	6	183	165	14	5	422	427	
16	0	900	932	22	6	22	15	4	16	32	48	15	6	749	771	16	4	315	30	
18	0	752	295	24	6	173	151	6	16	33	50	1	7	309	307	0	6	452	285	
20	0	1080	1063	26	6	665	648	0	18	227	121	3	7	427	343	2	6	554	540	
22	0	737	758	28	6	566	555	1	18	197	159	5	7	301	256	4	6	1095	1048	
24	0	29	30	30	6	205	240	5	18	126	1210	7	7	256	259	6	6	429	410	
26	0	637	620	32	6	577	509	7	0	487	443	9	7	241	268	8	6	140	177	
28	0	673	652	34	6	290	278	9	0	681	707	11	7	235	273	10	6	701	655	
30	0	299	279	36	6	112	73	11	0	960	1078	1	8	846	752	12	6	478	458	
32	0	288	289	38	6	183	204	13	0	610	634	3	8	163	132	7	7	276	247	
34	0	222	254	40	6	332	332	15	0	140	129	5	8	163	132	2	7	530	456	
36	0	646	559	42	6	234	222	17	0	897	835	0	0	319	181	4	7	642	587	
38	0	208	207	44	6	416	436	19	0	658	633	2	0	1753	1526	6	7	66	28	
40	0	86	78	4	6	630	723	21	0	161	130	4	0	392	348	8	7	295	288	
42	0	475	410	6	6	322	334	23	0	433	446	6	0	1115	1100	0	F	78	33	
44	0	395	276	8	6	276	280	1	1	1248	1121	8	0	524	501	9	9	86	46	
46	0	73	37	10	6	115	110	3	1	153	93	10	0	412	448	0	10	288	278	
48	0	11	0	12	6	694	103	5	1	291	253	12	0	800	767	2	11	189	149	
50	0	1	0	14	6	192	155	7	1	175	169	14	0	1190	1203	0	12	466	413	
52	0	1215	1112	16	6	615	585	9	1	468	501	16	0	678	674	0	13	195	161	
54	0	240	306	18	6	354	369	11	1	302	342	18	0	188	133	0	14	246	183	
56	0	434	609	20	6	386	468	13	1	414	512	20	0	429	435	0	15	110	84	
58	0	154	51	22	6	295	178	15	1	438	395	22	0	768	813	0	16	1	0	
60	0	2246	2513	24	6	497	456	17	1	488	508	0	1	449	466	1	0	234	188	
62	0	246	252	26	6	397	373	19	1	92	76	2	1	1557	1425	3	0	931	876	
64	0	1193	1325	28	6	352	318	21	1	38	17	4	1	742	680	5	0	869	820	
66	0	521	530	30	6	348	304	23	1	134	122	6	1	1113	1055	7	0	447	413	
68	0	328	281	32	6	270	263	1	2	1136	1088	8	1	383	354	9	0	46	52	
70	0	387	470	34	6	235	200	3	2	1769	1663	10	1	454	389	11	0	610	670	
72	0	952	986	36	6	15	19	5	2	1828	1717	12	1	453	420	13	0	660	672	
74	0	255	369	38	6	234	284	7	2	144	114	14	1	381	343	3	0	358	629	
76	0	412	338	40	6	508	455	9	2	909	899	16	1	127	129	17	0	466	501	
78	0	267	241	42	6	210	227	11	2	708	753	18	1	226	236	19	0	543	582	
80	0	523	450	44	6	245	265	13	2	280	278	20	1	39	46	1	1	837	769	
82	0	750	748	46	6	730	793	15	2	936	895	22	1	381	343	3	1	1440	1408	
84	0	105	112	48	6	560	555	17	2	1081	1157	0	2	1216	1158	5	1	662	639	
86	0	606	585	50	6	104	104	19	2	562	570	2	2	455	449	7	1	484	429	
88	0	451	452	52	6	10	293	21	2	206	203	4	2	67	14	4	1	522	503	
90	0	485	768	54	6	10	504	450	1	3	101	108	6	2	1285	1435	11	1	735	719
92	0	378	314	56	6	10	414	334	3	3	206	189	8	2	271	283	13	1	322	37
94	0	326	328	58	6	20	23	52	3	3	103	42	10	2	102	86	15	1	644	687
96	0	245	269	60	6	284	263	7	3	842	833	12	2	832	831	17	1	499	351	
98	0	639	770	62	6	10	72	65	11	3	35	29	14	2	837	879	19	1	389	455
100	0	1078	1205	64	6	153	129	13	3	1146	1138	16	2	260	275	3	2	556	487	
102	0	857	1050	66	6	205	190	15	3	79	80	20	2	814	802	5	2	258	229	
104	0	966	1078	68	6	10	209	159	17	3	116	178	0	3	677	641	7	2	275	173
106	0	573	550	70	6	31	16	19	3	379	380	2	3	126	81	9	2	977	923	
108	0	1066	1114	72	6	119	219	21	3	447	410	4	3	470	429	11	2	478	439	
110	0	522	501	74	6	379	435	1	4	604	558	6	3	1006	967	13	2	198	142	
112	0	489	473	76	6	175	205	3	4	418	475	8	3	589	579	15	2	473	510	
114	0	966	943	78	6	12	299	315	5	4	107	121	10	3	284	255	17	2	618	640
116	0	959	1004	80	6	17	317	299	7	4	1028	977	12	3	317	353	19	2	248	282
118	0	296	224	82	6	195	136	9	4	1072	1052	14	3	258	308	1	3	1249	1125	
120	0	146	232	84	6	81	112	11	4	551	617	16	3	145	154	3	3	1251	1260	
122	0	497	450	86	6	142	158	13	4	79	45	18	3	405	476	5	3	575	552	
124	0	663	610	88	6	12	270	15	4	923	1014	20	3	740	752	7	3	507	450	
126	0	66	91	90	6	18	17	17	4	1015	1056	0	4	878	806	0	4	1231	1151	
128	0	535	519	92	6	12	99	19	4	44	0	2	4	280	267	11	3	550	500	
130	0	478	468	94	6	12	351	325	1	5	436	488	4	4	1158	1063	13	3	89	111
132	0	72	51	96	6	12	221	215	3	5	81	48	6	4	1155	1059	15	3	533	622
134	0	131	122	98	6	4	48	44	3	5	99	60	8	4	135	118	17	3	706	743
136	0	261	277	100	6	12	184	7	5	38	64	10	4	221	200	1	4	574	578	
138	0	311	300	102	6	14	207	272	9	5	222	223	12	4	903	858	3	4	527	518
140	0	14	16	104	6	14	207	231	11	5	158	133	14	4	797	818	4	4	18	4
142	0	79	16	106	6	14	67	27	13	5	257	276	16	4	407	460	7	4	596	562
144	0	951	1102	108	6	14	214	217	15	5	121	112	18	4	561	571	9	4	549	521
146	0	1023	1174	110	6	14	214	217	15	5	121	112	18	4	561	571	9	4	549	521

$(pz)_3(C_5H_5)(CO)_2Mo$ and $[Et_2B(pz)_2](C_5H_5)(CO)_2Mo$ and the analogous C_7H_7 compounds, reports of which are forthcoming.

ACKNOWLEDGEMENT

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APPENDIX

Tetrakis(1-pyrazolyl)boratecyclopentadienyldicarbonylmolybdenum crystallizes in the monoclinic system, and systematic absences indicate the space group $C2/c$ (No. 15). The unit cell dimensions are: $a = 37.09 \pm 0.01 \text{ \AA}$, $b = 8.742 \pm 0.002 \text{ \AA}$, $c = 12.986 \pm 0.005 \text{ \AA}$, $\beta = 93.79^\circ \pm 0.03^\circ$. A unit cell volume of 4201 \AA^3 and $Z = 8$ gives

H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL								
3	0	421	420	-4.2	2	288	277	-10	10	284	305	-7	3	598	625	-6	3	221	211	-9	4	74	55	5	1	433	463	-10	4	393	399	-11	3	1485	1375	-11	4	457	457
3	0	340	289	-4.4	2	286	290	-10	10	446	449	-9	3	90	95	-3	3	800	747	-10	3	338	399	-11	4	856	839	-11	4	74	41	20	3	1061	1141	-11	5	618	593
3	0	159	160	-4.6	2	132	127	-10	10	300	291	-11	3	806	747	-10	3	718	780	-12	3	115	68	-15	4	74	41	20	3	1061	1141	-11	5	618	593				
0	0	178	174	-2.4	2	150	95	-22	10	92	116	-13	3	718	780	-12	3	235	228	-14	3	396	440	-17	4	74	41	20	3	1061	1141	-11	5	618	593				
11	0	339	290	-4.4	4	864	967	-24	10	262	165	-15	3	235	228	-14	3	396	440	-17	4	74	41	20	3	1061	1141	-11	5	618	593								
1	1	619	624	-6	4	38	11	-26	10	466	375	-17	3	386	341	-16	3	1061	1141	-11	5	618	593	3	1	433	463	-10	4	393	399	-11	3	1485	1375	-11	4	457	457
2	1	904	958	-6	4	812	835	-29	10	344	298	-19	3	278	272	-18	3	247	324	-3	3	467	467	-5	5	1227	1166	-11	4	74	41	20	3	1061	1141	-11	5	618	593
5	1	433	463	-10	4	393	399	-10	10	20	14	-21	3	744	210	-20	3	467	467	-5	5	1227	1166	-11	4	74	41	20	3	1061	1141	-11	5	618	593				
7	1	178	202	-12	4	360	291	-32	10	233	218	-1	4	1535	1416	-2	4	1301	1256	-7	5	610	601	-7	5	610	601	-7	5	610	601	-7	5	610	601	-7	5	610	601
9	1	698	680	-14	4	576	654	-36	10	293	250	-3	4	709	547	-4	4	800	781	-9	5	354	349	-9	5	354	349	-9	5	354	349	-9	5	354	349	-9	5	354	349
1	2	51	29	-16	4	956	985	-36	10	134	104	-5	4	1363	1306	-6	4	612	574	-11	5	642	607	-11	5	642	607	-11	5	642	607	-11	5	642	607	-11	5	642	607
2	2	334	277	-18	4	664	649	-38	10	93	101	-17	4	1387	1310	-6	4	1401	1329	-13	5	591	538	-13	5	591	538	-13	5	591	538	-13	5	591	538	-13	5	591	538
2	2	19	20	-20	4	434	415	-22	12	177	228	-9	4	192	171	-10	4	836	824	-15	5	198	212	-15	5	198	212	-15	5	198	212	-15	5	198	212	-15	5	198	212
7	2	191	125	-22	4	818	817	-4	12	263	309	-11	4	835	869	-12	4	38	9	-1	6	475	459	-1	6	475	459	-1	6	475	459	-1	6	475	459	-1	6	475	459
9	2	285	257	-24	4	976	981	-6	12	373	358	-13	4	835	869	-12	4	262	265	-3	6	740	739	-3	6	740	739	-3	6	740	739	-3	6	740	739	-3	6	740	739
1	3	626	581	-26	4	246	233	-9	12	175	202	-15	4	644	625	-10	4	653	687	-5	6	408	422	-5	6	408	422	-5	6	408	422	-5	6	408	422	-5	6	408	422
3	3	814	799	-28	4	234	183	-10	12	20	0	-17	4	316	385	-18	4	343	350	-7	6	408	422	-7	6	408	422	-7	6	408	422	-7	6	408	422	-7	6	408	422
3	3	351	352	-30	4	475	485	-12	12	376	273	-19	4	974	1004	-20	4	101	74	-9	6	317	257	-9	6	317	257	-9	6	317	257	-9	6	317	257	-9	6	317	257
k = 4	6	***		-32	4	532	553	-14	12	503	585	-21	4	916	821	-2	5	100	77	-11	6	435	430	-11	6	435	430	-11	6	435	430	-11	6	435	430	-11	6	435	430
C	0	509	505	-34	4	173	112	-16	12	27	51	-1	5	171	178	-4	5	137	120	-3	7	119	145	-3	7	119	145	-3	7	119	145	-3	7	119	145	-3	7	119	145
0	1	823	834	-36	4	423	352	-18	12	346	369	-3	5	28	15	-8	5	423	336	-5	7	202	190	-5	7	202	190	-5	7	202	190	-5	7	202	190	-5	7	202	190
0	2	116	111	-38	4	412	350	-20	12	300	321	-5	5	28	15	-8	5	423	336	-5	7	202	190	-5	7	202	190	-5	7	202	190	-5	7	202	190	-5	7	202	190
0	3	511	504	-40	4	281	230	-22	12	180	167	-7	5	49	15	-10	5	522	545	-11	7	100	90	-11	7	100	90	-11	7	100	90	-11	7	100	90	-11	7	100	90
0	4	90	44	-42	4	169	161	-24	12	244	224	-9	5	452	533	-12	5	337	379	-4	1	670	605	-4	1	670	605	-4	1	670	605	-4	1	670	605	-4	1	670	605
0	5	347	347	-44	4	366	366	-26	12	271	238	-12	5	464	464	-14	5	337	379	-4	1	670	605	-4	1	670	605	-4	1	670	605	-4	1	670	605	-4	1	670	605
0	6	156	115	-2	6	769	945	-28	12	315	279	-13	5	522	524	-16	5	534	527	-6	1	593	651	-6	1	593	651	-6	1	593	651	-6	1	593	651	-6	1	593	651
0	7	133	147	-4	6	797	891	-30	12	167	125	-15	5	17	1	-18	5	370	420	-8	1	854	832	-8	1	854	832	-8	1	854	832	-8	1	854	832	-8	1	854	832
0	8	21	1	-6	6	542	627	-32	12	180	178	-17	5	126	98	-2	6	743	688	-10	1	111	149	-10	1	111	149	-10	1	111	149	-10	1	111	149	-10	1	111	149
0	9	237	220	-8	6	673	801	-34	12	14	85	-70	5	237	260	-4	6	1249	1203	-12	1	355	384	-12	1	355	384	-12	1	355	384	-12	1	355	384	-12	1	355	384
0	10	19	19	-10	6	1464	1549	-36	14	155	165	-1	6	653	534	-6	6	489	514	-14	1	891	887	-14	1	891	887	-14	1	891	887	-14	1	891	887	-14	1	891	887
0	11	201	180	-12	6	65	27	-6	14	281	310	-3	6	45	68	-8	6	683	717	-16	1	683	650	-16	1	683	650	-16	1	683	650	-16	1	683	650	-16	1	683	650
0	12	100	106	-14	6	375	403	-8	14	17	185	-5	6	339	472	-10	6	916	944	-12	2	862	838	-12	2	862	838	-12	2	862	838	-12	2	862	838	-12	2	862	838
0	13	176	197	-16	6	598	640	-10	14	54	34	-7	6	1479	1424	-12	6	635	679	-14	2	105	100	-14	2	105	100	-14	2	105	100	-14	2	105	100	-14	2	105	100
k = 4	14	***		-18	6	466	641	-12	14	168	189	-9	6	462	445	-14	6	335	370	-6	2	623	548	-6	2	623	548	-6	2	623	548	-6	2	623	548	-6	2	623	548
0	15	312	435	-20	6	570	554	-14	14	209	177	-11	6	553	599	-2	7	600	552	-8	2	192	183	-8	2	192	183	-8	2	192	183	-8	2	192	183	-8	2	192	183
0	1	340	384	-22	6	385	436	-16	14	132	160	-13	6	469	491	-4	7	665	647	-10	2	250	272	-10	2	250	272	-10	2	250	272	-10	2	250	272	-10	2	250	272
0	2	315	364	-24	6	754	781	-18	14	41	70	-15	6	407	386	-6	7	77	26	-12	2	160	153	-12	2	160	153	-12	2	160	153	-12	2	160	153	-12	2	160	153
0	3	458	340	-26	6	290	358	-20	14	25	259	-17	6	56	52	-8	7	290	315	-14	2	437	443	-14	2	437	443	-14	2	437	443	-14	2	437	443	-14	2	437	443
0	4	178	174	-26	6	102	76	-22	14	246	201	-1	7	832	836	-10	7	220	186	-10	2	437	443	-10	2	437	443	-10	2	437	443	-10	2	437	443	-10	2	437	443
0	5	153	176	-30	6	619	539	-24	14	36	31	-3	7	150	131	-11	7	150	131	-11	2	3100	1647	-11	2	3100	1647	-11	2	3100	1647	-11	2	3100	1647	-11	2	3100	1647
0	6	27	5	-32	6	600	519	-26	14	137	156	-5	7	795	745	-12	1	5	91	-4	3	575	565	-4	3	575	565	-4	3	575	565	-4	3	575	565	-4	3	575	565
0	7	26	21	-34	6	316	274	-28	14	101	159	-7	7	20	78	-3	1	87	52	-6	3	651	678	-6	3	651	678	-6	3	651	678	-6	3						

TABLE 2

FINAL ATOMIC POSITIONAL (Å) AND THERMAL PARAMETERS^a

Atom	x	y	z	B(Å ²)
Mo	0.17994(5)	0.04593(29)	0.21638(15)	^b
N11	0.1309(5)	-0.0607(29)	0.1463(14)	3.6(4)
C11	0.1232(7)	-0.2122(37)	0.1491(19)	3.9(6)
C21	0.0882(7)	-0.2394(38)	0.1062(21)	4.7(7)
C31	0.0743(7)	-0.0985(38)	0.0690(19)	4.6(6)
N21	0.1008(5)	0.0057(26)	0.0985(14)	2.7(4)
N12	0.1632(5)	0.2362(26)	0.1090(13)	3.2(4)
C12	0.1862(7)	0.3477(40)	0.0846(21)	5.4(7)
C22	0.1665(7)	0.4446(37)	0.0153(20)	5.2(7)
C32	0.1310(7)	0.3889(37)	-0.0016(20)	4.8(6)
N22	0.1311(5)	0.2591(26)	0.0600(14)	3.1(4)
N13	0.0835(5)	0.2446(29)	0.1896(16)	3.8(4)
C13	0.0633(7)	0.1785(37)	0.2595(22)	5.1(7)
C23	0.0523(7)	0.2986(43)	0.3245(22)	5.9(7)
C33	0.0698(8)	0.4207(42)	0.2903(25)	6.3(8)
N23	0.0888(6)	0.4027(35)	0.2054(20)	6.5(7)
N14	0.0651(5)	0.2137(24)	0.0035(14)	3.1(4)
C14	0.0677(5)	0.1638(26)	-0.0952(15)	4.2(5)
C24	0.0359(7)	0.2065(35)	-0.1405(19)	4.5(6)
C34	0.0145(6)	0.2045(34)	-0.0798(20)	4.3(6)
N24	0.0336(6)	0.2893(33)	0.0158(18)	4.1(6)
B	0.0950(9)	0.1821(46)	0.0841(25)	3.8(8)
C1	0.2231(9)	0.0819(41)	0.1640(25)	7.7(9)
O1	0.2525(5)	0.0960(25)	0.1211(15)	7.0(5)
C2	0.2014(9)	-0.1481(50)	0.1679(26)	7.8(10)
O2	0.2149(6)	-0.2578(32)	0.1455(17)	8.2(7)
CP1	0.1783(7)	-0.0500(35)	0.3822(18)	4.3(6)
CP2	0.1465(6)	0.0463(37)	0.3703(18)	4.1(6)
CP3	0.1570(7)	0.1969(36)	0.3499(18)	4.2(6)
CP4	0.1967(7)	0.2023(38)	0.3525(20)	4.9(7)
CP5	0.2092(7)	0.0487(39)	0.3747(19)	4.5(6)

^a Numbers in parentheses are the estimated standard deviations occurring in the last digit listed. ^b The molybdenum atom was assigned an anisotropic thermal tensor of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. The tensor components with their e.s.d.'s in parentheses are: $\beta_{11} = 0.00046(1)$, $\beta_{22} = 0.00911(53)$, $\beta_{33} = 0.00564(15)$, $\beta_{12} = 0.00004(11)$, $\beta_{13} = 0.00010(3)$, $\beta_{23} = 0.00034(27)$.

multiplied by 10, for $[(C_3H_3N_2)_4B]Mo(CO)_2(C_5H_5)$ is presented as Table 1. The molecular structure and atom numbering system are shown in Fig. 3. Final atomic positions and thermal parameters are given in Table 2, with the listed standard deviations being derived from the inverse matrix of the final least-squares refinement cycle. Intramolecular distances and bond angles are given in Table 3 and 4, respectively.

The most significant result of this investigation is the unequivocal demonstration that in the crystalline state the $[B(pz)_4](C_5H_5)(CO)_2Mo$ molecule has a structure which contains a bidentate tetrakis(1-pyrazolyl) ligand, this being the first structural characterization of the ligand acting in this manner. There is also a slightly tilted *pentahapto*-cyclopentadienyl ring, and two carbonyl groups of the normal terminal type.

The six-membered ring formed by the molybdenum atom, the nitrogen atoms

TABLE 3

INTRAMOLECULAR BOND DISTANCES^a (Å)

<i>Atoms</i>	<i>Distance</i>	<i>Atoms</i>	<i>Distance</i>
Mo-CP1	2.31(2)	N13-C13	1.35(3)
Mo-CP2	2.42(2)	C12-C23	1.42(3)
Mo-CP3	2.38(2)	C23-C33	1.34(3)
Mo-CP4	2.29(2)	C33-N23	1.36(3)
Mo-CP5	2.26(2)	N23-N13	1.40(3)
Mo-C1	1.80(4)	CP1-CP2	1.44(3)
Mo-C2	1.99(4)	CP2-CP3	1.40(3)
Mo-N11	2.18(2)	CP3-CP4	1.47(3)
Mo-N12	2.23(2)	CP4-CP5	1.44(3)
N11-C11	1.36(3)	CP5-CP1	1.44(3)
C11-C21	1.40(3)	C1-O1	1.26(3)
C21-C31	1.40(3)	C2-O2	1.13(3)
C31-N21	1.37(3)	B-N21	1.56(3)
N21-N11	1.37(3)	B-N22	1.54(3)
N12-C12	1.35(3)	B-N13	1.56(3)
C12-C22	1.40(3)	B-N14	1.50(3)
C22-C32	1.40(3)	N14-C14	1.36(3)
C32-N22	1.39(3)	C14-C24	1.34(3)
N22-N12	1.33(3)	C24-C34	1.34(3)
		C34-N24	1.39(3)
		N24-N14	1.36(3)

^a Numbers in parentheses are the estimated standard deviations occurring in the last digit listed.

TABLE 4

BOND ANGLES^a

<i>Atoms</i>	<i>Angle (Deg.)</i>	<i>Atoms</i>	<i>Angle (Deg.)</i>
N12-Mo-N11	82.5(8)	CP1-CP2-CP3	109(2)
Mo-N11-N21	129(2)	CP2-CP3-CP4	109(2)
N11-N21-B	125(2)	CP3-CP4-CP5	106(2)
N21-B-N22	110(2)	CP4-CP5-CP1	109(2)
B-N22-N12	126(2)	CP5-CP1-CP2	107(2)
N22-N12-Mo	128(2)	N14-B-N13	108(2)
Cl-Mo-C2	69(1)		
N11-Mo-Cl	130(1)		
N11-Mo-C2	81(1)		
N12-Mo-Cl	81(1)		
N12-Mo-C2	123(1)		

^a Numbers in parentheses are the estimated standard deviations occurring in the last digit listed.

on the bonded pyrazole rings, and the boron atom is in a rather flattened boat conformation. The angle subtended at the molybdenum atom is much more acute than the one at the boron atom; this presumably helps to minimize non-bonded repulsions.

The (h^5 -C₅H₅) group is somewhat unusual. The molybdenum to carbon distances fall in the range 2.26 to 2.42 Å; a tilt on the Mo-(h^5 -C₅H₅ centroid) vector can account for the variations in the bond lengths. Although the variations are large, this situation is not to be confused with the one found in (C₅H₅)₃MoNO where the Mo-C distances to two of the rings vary from 2.32 to 2.68 Å, a range of almost 0.40 Å. In this case a form of bonding basically different from that of a true (h^5 -C₅H₅) is believed to exist.

The coordination around the boron atom is roughly tetrahedral as anticipated. This type of structure is consistent with the temperature-dependent NMR spectrum of this substance in solution.

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