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The Crystal Structure and Molecular Geometry of Bis[hydrotris(1-pyrazolyl)borato]cobalt(II)

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The crystal structure and molecular geometry of bis[hydrotris(1-pyrazolyl)borato]cobalt(II), $[HB(C_3N_2H_3)_3]_2Co^{II}$, have been elucidated by single-crystal X-ray diffraction studies. The complex crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ (C_{2h}^5; no. 14) with $a = 9.754 \pm 0.006$ Å, $b = 17.650 \pm 0.012$ Å, $c = 15.460 \pm 0.010$ Å, $\beta = 121.60 \pm 0.05°$, $Z = 4$, $\rho_{\text{obsd}} = 1.40 \pm 0.05$ g cm^{-3}, and $\rho_{\text{calcd}} = 1.421$ g cm^{-3}. Data to $\sin \theta = 0.42$ (Mo Kα radiation) were collected with a 0.01°-incrementing Buerger automated diffractometer, and the structure was solved by a combination of Patterson, Fourier, and least-squares refinement techniques. The final discrepancy index is $R_F = 7.28\%$ for 2340 independent nonzero reflections. The crystal is composed of discrete molecular units of $[HB(C_3N_2H_3)_3]_2Co^{II}$ which are separated by normal van der Waals distances. The two hydrotris(1-pyrazolyl)borato ligands adopt a mutually staggered configuration. The central cobalt(II) ion is in trigonally distorted octahedral coordination to six nitrogen atoms, the molecule having approximate (*although not precise*) D_{3d} symmetry. Cobalt-nitrogen distances range from 2.120 (7) to 2.140 (7) Å, averaging 2.129 Å. Mean distances within the hydrotris(1-pyrazolyl)borato ligand are B–N = 1.544 (21), N–N = 1.364 (3), N–C = 1.335 (15), and C–C = 1.386 (24) Å.

Introduction

Trofimenko and coworkers[2-11] have reported the preparation and characterization of a wide variety of transition metal complexes containing poly(1-pyrazolyl)borato, $R_nB(pz)_{4-n}^-$, ligands [where R = H, alkyl, or aryl; pz = pyrazolyl ($C_3N_2H_3$) or substituted pyrazolyl; $0 \leqslant n \leqslant 2$]. The uninegative anions with $n = 2$ are bidentate, while those with $n = 0$ or 1 typically behave as tridentate ligands. The tridentate ligands (of which the parent species is the hydrotris(1-pyrazolyl)borato ion, $HB(C_3N_2H_3)_3^-$) are remarkable in forming a series of complexes analogous to π-cyclopentadienyl or 1,2-dicarbollide species.

We now present the results of the first detailed single-crystal X-ray diffraction study of a poly(1-pyrazolyl)-borato complex—bis[hydrotris(1-pyrazolyl)borato]-cobalt(II), $[HB(C_3N_2H_3)_3]_2Co^{II}$.[12,13] Detailed nuclear magnetic resonance, electron paramagnetic resonance, and optical data on this species have previously been reported.[13-15] Our present study confirms the trigonally distorted octahedral coordination of the cobalt(II) ion and provides precise intramolecular distances and angles which may be used as a basis for more refined calculations on this molecule (*e.g.*, on the dipolar contribution to the isotropic nuclear resonance shift—*cf.* ref 13).

Unit Cell and Space Group

Optical examination and the observed reciprocal lattice symmetry of C_{2h} (2/m) indicated that the crystals belonged to the monoclinic system. A survey of *h*0*l*, *h*1*l*, *hk*0, *hk*1 Weissenberg photographs (taken with Cu Kα radiation; $\bar{\lambda}$ 1.5418 Å) and of 0*kl*, 1*kl*, *hk*0, *hk*1, *h*0*l* precession photographs (Mo Kα radiation; $\bar{\lambda}$ 0.7107 Å) revealed the systematic absences *h*0*l* for $l = 2n + 1$ and 0*k*0 for $k = 2n + 1$, compatible only with space group $P2_1/c$ (C_{2h}^5; no. 14).[16]

Unit cell parameters, calculated from calibrated ($a_{\text{NaCl}} = 5.640$ Å) zero-level precession photographs taken with Mo Kα radiation at room temperature (23 ± 2°) are $a = 9.754 \pm 0.006$ Å, $b = 17.650 \pm 0.012$ Å, $c = 15.460 \pm 0.010$ Å, and $\beta = 121.60 \pm$

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(1) Research Fellow of the Alfred P. Sloan Foundation, 1968–1970.

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TABLE I

OBSERVED AND CALCULATED STRUCTURE FACTOR AMPLITUDES (IN ELECTRONS × 10.00) FOR $[HB(C_3N_2H_3)_3]_2Co^{II}$ [a]

0.05°. [Errors given are the "maximum probable errors" based on the inaccuracies involved in measuring (on precession photographs) the positions of diffraction rows from the crystal under investigation and from our standard sodium chloride crystal.]

The unit cell volume is 2267 Å^3. The observed density (ρ_{obsd} = 1.40 ± 0.05 g cm^{-3}, by flotation in aqueous zinc iodine solution) is consistent with that calculated for mol wt 484.96 and $Z = 4$ (ρ_{calcd} = 1.421 g cm^{-3}).

Collection and Reduction of X-Ray Diffraction Data

The complex crystallizes as large bright yellow parallelepipeds with well-developed (100) faces. Two crystals were used in the course of the analysis. Crystal I was approximately spherical (r = 0.08 mm ± 10%) and was mounted along its unique (b) axis; crystal II, of dimensions 0.20 × 0.28 × 0.31 mm (referred to $\vec{a}$, $\vec{b}$, $\vec{c}$, respectively) was mounted on its c axis.

Intensity data (Mo Kα radiation, $\bar{\lambda}$ 0.7107 Å) were collected on a 0.01°-incrementing Supper-Pace Buerger

TABLE I (*Continued*)

H	K	FO	FC
***************			
	L = 10		
-4	5	364	361
-3	5	717	715
-2	5	85	78
-1	5	639	625
2	5	393	394
4	5	139	63
-7	6	272	297
-5	6	284	293
-4	6	457	469
-2	6	553	583
-1	6	233	240
0	6	324	252
3	6	185	205
-9	7	143	195
-8	7	286	297
-5	7	270	259
-4	7	142	128
-3	7	298	291
-1	7	210	205
0	7	242	220
3	7	162	188
-8	8	373	383
-4	8	144	109
-3	8	124	129
-1	8	340	340
0	8	255	182
2	8	198	214
-9	9	225	231
-8	9	174	172
-7	9	109	115
-5	9	110	93
-3	9	118	109
-1	9	334	293
0	9	393	383
1	9	254	244
2	9	233	246
-10	10	261	238
-9	10	195	163
-8	10	[illegible]	207
-7	10	414	426
-5	10	148	89
-4	10	147	124
-1	10	176	157
0	10	307	278
1	10	217	204
3	10	204	213
-7	11	139	162
-6	11	369	394
-5	11	151	158
-4	11	283	310
-3	11	342	366
-1	11	185	191
0	11	375	359
3	11	153	90
-8	12	136	116
-6	12	207	218
-5	12	140	133
-3	12	126	142
-2	12	117	57
-1	12	127	67
0	12	137	126
1	12	160	75
-8	13	132	150
-4	13	142	134
-2	13	285	290
-1	13	140	95
1	13	140	49
-6	14	130	169
-5	14	108	179
-4	14	179	163
-3	14	181	155
-2	14	221	195
-1	14	145	152
0	14	203	212
1	14	211	216
-6	15	147	157
-5	15	131	130
-4	15	153	160
-3	15	153	174
-1	15	300	279
0	15	154	139
-2	16	174	170
***************			
	L = 11		
-9	1	286	273
-6	1	130	99
-5	1	181	165
-4	1	170	175
-3	1	214	215
-1	1	101	98
0	1	128	109
2	1	185	179
-10	2	242	237
-8	2	196	213
-7	2	114	100
-6	2	126	81
-5	2	477	484
-4	2	283	290
-3	2	447	458
-2	2	298	325
-1	2	132	123
1	2	150	165
2	2	239	249
3	2	171	179
-11	3	135	140
-10	3	150	158
-9	3	226	243
-7	3	163	170
-6	3	394	382
-4	3	592	574
-3	3	313	310
-2	3	208	216
-1	3	398	403
1	3	296	286
2	3	341	360
4	3	237	222
-11	4	144	115
-9	4	144	128
-8	4	195	218
-6	4	174	85
-5	4	234	224
-4	4	153	140
-3	4	276	267
-2	4	346	370
-1	4	103	119
0	4	136	72
1	4	161	159
2	4	148	152
3	4	133	116
-7	5	222	211
-2	5	230	247
2	5	123	96
3	5	137	155
-8	6	296	302
-7	6	314	331
-6	6	230	240
-5	6	344	366
-4	6	106	106
-3	6	363	360
-2	6	291	287
-1	6	256	246
1	6	148	81
-9	7	135	195
-7	7	341	327
-6	7	162	155
-4	7	555	572
-3	7	301	305
-2	7	149	147
-1	7	233	242
0	7	194	108
1	7	178	186
2	7	224	241
-10	8	241	233
-8	8	308	281
-7	8	233	250
-3	8	116	104
-1	8	137	83
0	8	366	378
1	8	229	255
2	8	146	183
3	8	198	189
-9	9	252	226
-8	9	225	144
-6	9	147	146
-3	9	107	102
-1	9	292	261
0	9	157	155
-8	10	150	110
-7	10	146	112
-6	10	153	150
-4	10	161	134
-1	10	179	165
1	10	160	189
-8	11	216	221
-6	11	238	256
-4	11	278	269
-3	11	197	169
-1	11	163	153
0	11	212	142
-8	12	129	87
-7	12	231	232
-6	12	165	163
-5	12	532	559
-4	12	150	165
-3	12	225	250
-2	12	278	285
0	12	265	246
-8	13	128	100
-6	13	258	269
-4	13	469	465
-3	13	233	221
-2	13	248	246
-1	13	301	301
1	13	170	155
-7	14	146	149
-6	14	125	112
0	14	234	121
***************			
	L = 12		
-10	0	292	292
-9	0	202	200
-8	0	505	479
-7	0	150	135
-6	0	354	340
-4	0	203	205
-3	0	142	138
-2	0	122	127
-1	0	122	100
2	0	251	232
3	0	163	137
-10	1	166	188
-9	1	385	371
-7	1	282	285
-4	1	227	209
-2	1	199	207
-1	1	129	64
1	1	275	247
2	1	125	108
-8	2	158	112
-5	2	154	83
-4	2	449	446
-3	2	148	135
-2	2	192	203
-1	2	123	123
3	2	162	132
-10	3	153	105
-8	3	185	185
-7	3	165	69
-6	3	110	104
-4	3	197	179
-3	3	237	238
-2	3	176	182
-1	3	185	180
-10	4	212	201
-8	4	293	263
-7	4	146	151
-6	4	147	125
-5	4	360	371
-4	4	169	121
-3	4	428	423
-1	4	252	257
0	4	375	360
1	4	132	65
2	4	178	163
-9	5	164	182
-8	5	123	119
-7	5	210	206
-6	5	179	173
-5	5	372	381
-4	5	596	601
-3	5	106	89
-2	5	448	443
-1	5	225	233
0	5	136	131
1	5	537	535
-10	6	131	130
-8	6	276	286
-7	6	227	185
-6	6	246	223
-5	6	405	441
-3	6	384	396
-2	6	196	202
0	6	203	200
-9	7	167	134
-8	7	157	111
-6	7	163	137
-4	7	192	198
-3	7	233	228
-2	7	155	150
0	7	131	119
-8	8	206	190
-7	8	144	154
-6	8	170	172
-5	8	133	103
-2	8	214	224
-1	8	139	161
-10	9	232	188
-9	9	242	210
-7	9	297	296
-6	9	151	102
-5	9	155	120
-4	9	169	88
-3	9	162	121
-1	9	152	160
0	9	178	152
1	9	248	235
-8	10	173	133
-7	10	145	84
-6	10	301	281
-5	10	222	192
-1	10	290	279
0	10	348	351
-7	11	285	291
-6	11	193	197
-5	11	175	154
-4	11	361	353
-2	11	228	244
-1	11	275	265
-5	12	226	231
-1	12	190	191
-7	13	157	60
-5	13	180	186
-3	14	201	185
-2	15	215	153
***************			
	L = 13		
-10	1	209	184
-9	1	129	121
-8	1	158	150
-7	1	195	189
-6	1	134	162
-5	1	156	162
-4	1	249	243
-3	1	86	79
-2	1	207	211
0	1	115	31
-11	2	186	193
-9	2	283	276
-6	2	253	245
-5	2	148	165
-4	2	138	133
-3	2	390	416
-1	2	172	133
1	2	121	120
4	2	198	114
-10	3	260	248
-7	3	190	179
-5	3	431	440
-4	3	312	299
-3	3	187	197
-2	3	463	473
-1	3	136	140
0	3	438	436
1	3	307	290
-9	4	145	146
-8	4	189	177
-6	4	129	97
-5	4	214	223
-4	4	101	102
-3	4	275	282
-2	4	102	101
-1	4	202	205
0	4	221	203
1	4	153	149
-6	5	159	144
-3	5	133	131
-1	5	238	257
0	5	142	79
-9	6	197	206
-7	6	114	125
-6	6	272	301
-5	6	102	109
-4	6	202	198
-3	6	170	176
-2	6	124	122
-1	6	210	205
-10	7	201	155
-8	7	235	203
-7	7	336	335
-5	7	309	303
-4	7	217	217
-2	7	132	133
0	7	186	184
1	7	129	143
-9	8	230	200
-8	8	310	268
-6	8	318	333
0	8	170	161
1	8	140	122
-8	9	234	199
-7	9	253	251
-6	9	118	121
-5	9	169	115
-4	9	124	90
-3	9	174	128
-1	9	186	194
-7	10	161	120
-2	10	118	116
0	10	146	64
-7	11	187	140
-5	11	210	159
-4	11	181	194
-2	11	202	174
-6	12	214	226
-4	12	210	215
-3	12	334	353
-1	12	203	208
-7	13	258	257
-5	13	124	102
-2	13	242	247
-3	14	136	115
***************			
	L = 14		
-9	0	517	531
-8	0	255	259
-7	0	309	280
-6	0	570	563
-4	0	78	75
-10	1	147	144
-8	1	266	267
-7	1	135	139
-6	1	282	321
-5	1	220	275
-3	1	370	385
-2	1	122	113
0	1	123	116
-9	2	168	139
-4	2	115	113
-2	2	160	162
-1	2	124	84
-10	3	125	83
-7	3	144	78
-5	3	132	116
-2	3	191	202
-1	3	122	77
0	3	166	153
1	3	121	60
-7	4	116	109
-6	4	77	96
-5	4	137	68
-4	4	233	237
-2	4	148	131
-1	4	391	412
1	4	190	176
-10	5	158	139
-7	5	155	162
-6	5	202	184
-5	5	379	376
-4	5	95	82
-3	5	134	115
-2	5	240	233
0	5	327	331
-10	6	128	103
-8	6	211	218
-7	6	128	112
-6	6	347	389
-4	6	225	247
-1	6	319	348
-7	7	253	241
-4	7	131	115
-2	7	135	120
-9	8	142	122
-7	8	205	231
-3	8	103	59
-8	9	168	150
-7	9	234	202
-6	9	154	178
-5	9	239	161
-4	9	111	77
-3	9	168	150
0	9	216	227
-7	10	176	130
-6	10	249	247
-4	10	278	274
-3	10	198	180
-8	11	125	115
-5	11	136	122
-3	11	291	267
-2	11	177	120
***************			
	L = 15		
-8	1	182	208
-6	1	161	189
-5	1	196	234
-3	1	193	158
-2	1	159	156
-7	2	173	145
-4	2	193	222
-2	2	228	228
-8	3	169	132
-3	3	195	210
-2	3	164	159
-7	4	153	159
-2	4	189	169
-7	5	185	169
-7	6	253	261
-6	7	334	318
-5	7	242	253
***************			
	L = 16		
-7	0	225	220
-5	0	464	503
-4	0	188	182
-6	1	199	228
-4	1	193	200

[a] Table shows h, k, $10|F_o|$, $10|F_c|$ in blocks of constant l.

automated diffractometer, using a "stationary-background, ω-scan, stationary-background" counting sequence.

Experimental details specific to the present analysis include the following. (i) The X-ray generator was operated at 45 kV/17 mA. (ii) The scan angle, ω, was chosen as $\omega = [2.0 + (0.8/L)]°$, where L^{-1} is the Lorentz factor. (iii) The scan speed was 2°/min. (iv) Initial and final backgrounds, $B_1(hkl)$ and $B_2(hkl)$, were each counted for one-fourth the time taken for the appropriate ω scan. (v) $I(hkl)$, the intensity of the reflection hkl, was calculated as: $I(hkl) = C(hkl) - 2[B_1(hkl) + B_2(hkl)]$ (where $C(hkl)$ is the count associated with the ω scan).

All other experimental details and precautions were as described previously.[17]

Using equiinclination Weissenberg geometry, a total of 3075 reflections ($\sin \theta_{\max} = 0.38$) in the quadrants hKl and $\bar{h}Kl$ (K = 0–18) were collected from crystal I; 4126 reflections ($\sin \theta_{\max} = 0.42$) in the quadrants hkL and $\bar{h}kL$ (L = 0–14) were collected from crystal II.

Data for which $I(hkl) < 3[C(hkl) + 4B_1(hkl) + 4B_2(hkl)]^{1/2}$ were rejected as being not significantly different from background at the 3σ level. Data with highly asymmetric backgrounds, *i.e.*, $[B_1(hkl)/B_2(hkl)]$ or $[B_2(hkl)/B_1(hkl)] \geq 3$, were similarly rejected from the subsequent analysis.

All data were corrected for Lorentz and polarization effects. Data from crystal II were corrected for absorption using a locally modified version of Burnham's GNABS (with $\mu = 8.23$ cm^{-1} transmission factors ranged from 0.799 to 0.857); data from the nearly spherical crystal I were not corrected for absorption, but systematic errors due to this omission will be less than 3% in F^2.

Symmetry-equivalent reflections within a zone were averaged and all data were merged to a common scale by a least-squares procedure.[18] The resulting 2340 independent nonzero reflections were used to calculate a Wilson plot,[19] from which were obtained an approximate absolute scale factor and an initial overall isotropic thermal parameter.

Solution and Refinement of the Structure

All crystallographic calculations were, unless otherwise stated, carried out under the CRYRM system[20] using the Harvard University IBM 7094 computers. Scattering factors for neutral nitrogen, carbon, boron, and hydrogen were taken from the compilation of Ibers.[21a] The Thomas–Fermi–Dirac values for neutral cobalt[21b] were corrected to allow for dispersion ($\Delta f'(\text{Co}) = +0.4\ e^-$, $\Delta f''(\text{Co}) = +1.1 e^-$).[21c] The function minimized during least-squares refinement processes was $\Sigma w(|F_o|^2 - |F_c|^2)^2$ where the weighting scheme is that of Hughes,[22] with $4|F_o|_{\min} = 20\ e^-$. Discrepancy indices referred to are $R_F = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_{wF^2} = \Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w|F_o|^4$.

The phase problem was solved by means of a three-dimensional Patterson synthesis which showed a series of peaks consistent with a cobalt atom at $x = 0.810$, $y = 0.151$, $z = 0.162$. A three-dimensional difference Fourier synthesis, phased only by the cobalt atom ($R_F = 0.47$), revealed the positions of all nonhydrogen atoms. Three cycles of full-matrix refinement of positional parameters and individual isotropic thermal parameters for the 33 nonhydrogen atoms led to convergence at $R_F = 11.56\%$ and $R_{wF^2} = 11.12\%$. A second three-dimensional difference Fourier synthesis now showed evidence of anisotropic motion for many atoms and also indicated the location of each of the 20 hydrogen atoms in the molecule, individual peak heights ranging from 0.46 to 1.06 $e^-\ \text{Å}^{-3}$, as compared with peak heights of *ca.* 4 $e^-\ \text{Å}^{-3}$ for carbon atoms on an "observed" Fourier synthesis.

Hydrogen atoms were now included in calculated positions,[23] each being assigned an isotropic thermal parameter of 1.8 Å^2, which was not varied. A structure factor calculation, phased now by all 53 atoms, had discrepancy indices of $R_F = 10.80\%$ and $R_{wF^2} = 10.52\%$.

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(19) A. J. C. Wilson, *Nature*, **150**, 152 (1942).

(20) CRYRM is an integrated sequence of crystallographic routines for the IBM 7094, compiled under the direction of Professor R. E. Marsh at the California Institute of Technology.

(21) "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962: (a) p 202; (b) p 211; (c) p 216.

(22) E. W. Hughes, *J. Amer. Chem. Soc.*, **63**, 1737 (1941).

(23) With d(C–H) = 1.080 Å and the appropriate sp^2 geometry about the carbon atom and with d(B–H) = 1.100 Å and sp^3 geometry about the boron atom. It should be noted that all calculated positions are close (*i.e.*, within *ca.* 0.2 Å) to the centers of the peaks observed on the 11.56% difference Fourier synthesis.

TABLE II

FINAL POSITIONAL PARAMETERS FOR $[HB(C_3N_2H_3)_3]_2Co^{II}$ [a,b]

Atom	x	y	z
Co	0.80718 (13)	0.15028 (6)	0.16211 (8)
B(1)	0.7365 (13)	0.3054 (6)	0.0385 (8)
B(2)	0.8859 (14)	−0.0038 (6)	0.2878 (10)
N(1a)	0.6067 (8)	0.2449 (4)	−0.0273 (5)
N(2a)	0.6162 (8)	0.1745 (4)	0.0120 (5)
N(1b)	0.7336 (10)	0.3185 (4)	0.1356 (6)
N(2b)	0.7617 (8)	0.2591 (4)	0.1998 (5)
N(1c)	0.9025 (8)	0.2740 (4)	0.0669 (5)
N(2c)	0.9573 (8)	0.2084 (4)	0.1218 (5)
N(1d)	0.8814 (8)	−0.0188 (4)	0.1902 (5)
N(2d)	0.8448 (9)	0.0394 (4)	0.1234 (5)
N(1e)	0.7226 (8)	0.0288 (4)	0.2648 (5)
N(2e)	0.6651 (9)	0.0938 (4)	0.2098 (6)
N(1f)	1.0206 (9)	0.0563 (4)	0.3519 (5)
N(2f)	1.0088 (8)	0.1257 (4)	0.3104 (5)
C(3a)	0.4973 (12)	0.1350 (5)	−0.0594 (8)
C(4a)	0.4063 (12)	0.1797 (6)	−0.1490 (7)
C(5a)	0.4830 (11)	0.2486 (5)	−0.1223 (7)
C(3b)	0.7388 (12)	0.2854 (5)	0.2734 (8)
C(4b)	0.6926 (13)	0.3618 (5)	0.2551 (8)
C(5b)	0.6915 (11)	0.3798 (5)	0.1673 (7)
C(3c)	1.1000 (11)	0.1957 (5)	0.1306 (7)
C(4c)	1.1373 (11)	0.2505 (6)	0.0839 (7)
C(5c)	1.0111 (12)	0.2992 (6)	0.0438 (7)
C(3d)	0.8508 (13)	0.0116 (6)	0.0456 (8)
C(4d)	0.8929 (14)	−0.0644 (6)	0.0609 (9)
C(5d)	0.9101 (12)	−0.0811 (5)	0.1544 (8)
C(3e)	0.5218 (11)	0.1052 (5)	0.1980 (8)
C(4e)	0.4823 (13)	0.0484 (6)	0.2449 (9)
C(5e)	0.6108 (13)	0.0019 (6)	0.2839 (8)
C(3f)	1.1450 (11)	0.1609 (5)	0.3743 (8)
C(4f)	1.2487 (12)	0.1155 (7)	0.4547 (18)
C(5f)	1.1625 (12)	0.0470 (6)	0.4369 (8)
H(1)	0.7101	0.3589	−0.0040
H(2)	0.9111	−0.0566	0.3305
H(3a)	0.4740	0.0800	−0.0532
H(4a)	0.3088	0.1639	−0.2153
H(5a)	0.4500	0.2949	−0.1679
H(3b)	0.7524	0.2543	0.3321
H(4b)	0.6652	0.3957	0.2964
H(5b)	0.6640	0.4312	0.1335
H(3c)	1.1728	0.1507	0.1680
H(4c)	1.2368	0.2543	0.0796
H(5c)	0.9995	0.3472	0.0042
H(3d)	0.8253	0.0415	−0.0170
H(4d)	0.9071	−0.0991	0.0147
H(5d)	0.9409	−0.1321	0.1900
H(3e)	0.4499	0.1494	0.1604
H(4e)	0.3812	0.0422	0.2469
H(5e)	0.6237	−0.0461	0.3238
H(3f)	1.1688	0.2152	0.3648
H(4f)	1.3612	0.1286	0.5121
H(5f)	1.2016	0.0005	0.4806

[a] Estimated standard deviations, shown in parentheses, are right adjusted to the least-significant digit of the preceding number. [b] Hydrogen atoms are in calculated positions (see ref 23).

Refinement of nonhydrogen atoms was now continued using anisotropic thermal parameters. [Due to the limitation in storage space in the IBM 7094 computer, parameters were blocked into three submatrices. Matrix 1 contained the overall scale factor along with parameters for the cobalt atom and atoms of pyrazolyl ring a; matrix 2 included parameters for B(1) and the atoms of pyrazolyl rings b and c; matrix 3 contained parameters for B(2) and the atoms of pyrazolyl rings d, e, and f. Hydrogen atom positions were not refined, but were up-dated relative to the new carbon and boron positions at the end of each three cycles of refinement.] Six cycles of refinement of positional and anisotropic thermal parameters for the 33 nonhydrogen atoms led to convergence ($\Delta_{\max}/\sigma < 0.05$) at $R_F = 7.28\%$ and $R_{wF^2} = 5.48\%$. It should be noted that (i) inclusion of hydrogen atoms and (ii) anisotropic thermal parameter refinement each constitutes a process significant at a confidence level far greater than 99.5%.[24]

A final difference Fourier synthesis had, as its sole significant feature, a peak of height ~0.7 $e^- Å^{-3}$ in the vicinity of the cobalt atom. The structural analysis was thus judged to be correct and complete.

Observed and calculated structure factors are shown in Table I. Final atomic parameters are collected in Table II. Anisotropic thermal parameters are displayed in Table III, the axes of their associated vibration ellipsoids being defined in Table IV.

The Molecular Structure

Intramolecular distances and their estimated standard deviations (esd's) are shown in Table V; bond angles (with esd's) are colected in Table VI. The stereochemistry of the paramagnetic ($S = ^1/_2$) bis[hydrotris(1-pyrazolyl)borato]cobalt(II) molecule and the system for labeling atoms are depicted in Figure 1, which also illustrates the thermal vibration ellipsoids.

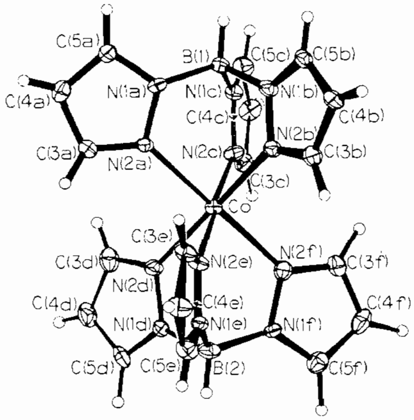

Figure 1.—Numbering of atoms within the $[HB(C_3N_2H_3)_3]_2Co^{II}$ molecule. This diagram also shows the 68% probability envelopes for the atomic vibration ellipsoids [constructed using OTLIPS, an IBM 1620/CALCOMP program written by Dr. P. H. Bird].

[Hydrogen atoms, not labeled in this figure, are numbered similarly to the carbon or boron atoms to which they are attached.]

The central cobalt(II) ion is bonded directly to six nitrogen atoms [N(2a), N(2b), N(2c), N(2d), N(2e), and N(2f)], with individual cobalt–nitrogen bond distances ranging from 2.120 (7) to 2.140 (8) Å, averaging 2.129 (7) Å. The two tridentate hydrotris(1-pyrazolyl)borato ligands adopt a mutually staggered conformation. The coordination sphere about the central

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(24) W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).

TABLE III

ANISOTROPIC THERMAL PARAMETERS FOR $[HB(C_3N_2H_3)_3]_2Co^{II}$ [a,b]

Atom	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Co	103.5(1.7)	18.2(0.3)	38.7(0.7)	5.1(1.3)	67.6(1.7)	9.6(0.8)
B(1)	145(18)	21(3)	47(7)	−19(12)	87(18)	7(7)
B(2)	163(19)	21(3)	67(8)	42(12)	114(21)	18(8)
N(1a)	124(12)	27(2)	37(5)	14(9)	69(12)	23(6)
N(2a)	114(12)	21(2)	42(4)	−7(8)	47(12)	16(5)
N(1b)	169(13)	19(2)	51(5)	17(9)	119(14)	0(6)
N(2b)	138(12)	21(2)	45(5)	9(9)	99(13)	0(6)
N(1c)	125(12)	20(2)	46(5)	9(8)	72(13)	7(5)
N(2c)	90(11)	26(3)	46(4)	26(8)	74(12)	20(5)
N(1d)	113(11)	19(2)	40(4)	9(8)	63(12)	−3(5)
N(2d)	178(14)	21(2)	41(5)	15(9)	114(14)	6(6)
N(1e)	98(11)	19(2)	42(4)	−10(8)	50(12)	11(5)
N(2e)	132(13)	19(2)	61(5)	4(9)	113(14)	14(6)
N(1f)	156(13)	20(2)	33(5)	28(9)	55(13)	15(5)
N(2f)	92(11)	25(2)	44(5)	−5(8)	50(13)	4(6)
C(3a)	154(16)	24(3)	56(6)	−22(11)	89(18)	0(7)
C(4a)	149(17)	41(4)	44(6)	−6(13)	84(17)	−3(8)
C(5a)	144(14)	26(3)	43(6)	11(11)	77(16)	1(7)
C(3b)	169(18)	29(3)	56(6)	6(12)	109(18)	−10(8)
C(4b)	181(18)	20(3)	72(7)	35(11)	125(19)	−5(7)
C(5b)	130(15)	21(3)	59(7)	9(10)	82(17)	−10(7)
C(3c)	134(16)	29(3)	45(6)	21(11)	77(16)	−5(7)
C(4c)	120(14)	40(4)	59(7)	8(13)	107(17)	10(9)
C(5c)	171(18)	32(4)	59(7)	−30(12)	138(19)	2(8)
C(3d)	165(17)	38(4)	64(7)	2(14)	118(19)	−26(9)
C(4d)	214(21)	33(4)	69(8)	−1(14)	133(22)	−38(9)
C(5d)	135(16)	21(3)	75(8)	−26(11)	83(19)	−29(8)
C(3e)	106(14)	24(3)	77(7)	3(10)	103(18)	13(8)
C(4e)	149(17)	38(4)	93(9)	0(14)	165(22)	23(10)
C(5e)	192(19)	33(4)	68(8)	−18(14)	160(21)	1(8)
C(3f)	118(14)	32(3)	62(7)	−42(12)	110(17)	−15(8)
C(4f)	136(17)	53(5)	45(6)	54(15)	43(18)	−7(9)
C(5f)	141(17)	39(4)	57(7)	36(13)	85(19)	6(8)

[a] Estimated standard deviations are shown in parentheses. [b] The anisotropic thermal parameter (T) is defined as: $T = \exp[-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - \beta_{12}hk - \beta_{13}hl - \beta_{23}kl]$.

cobalt(II) ion is thus essentially octahedral rather than trigonal prismatic. However, intraligand N(2)–Co–N(2′)[25] bond angles are each significantly lower than the ideal octahedral angle of 90°, individual angles lying between 84.6 (3) and 86.3 (3)°. The cobalt(II) ion is thus in a trigonally distorted octahedral (D_{3d}) coordination environment and lies 1.316 (3) Å below the plane defined by N(2a), N(2b), N(2c) [equation: $-0.094X - 0.854Y + 0.512Z = -3.107$;[26] see Table VII] and 1.328 (3) Å above the plane defined by N(2d), N(2e), N(2f) [equation: $-0.087X - 0.855Y + 0.526Z = -0.363$].

Figure 2 shows the molecule projected onto the plane defined by N(2a), N(2b), N(2c). It is immediately apparent that (in the solid state, at least) the molecule *as a whole* is distorted significantly from ideal D_{3d} symmetry—probably as a result of *inter*molecular repulsions. The atoms B(1), Co, B(2)—which define the S_6 axis in a species of regular D_{3d} symmetry—are essentially collinear [$\angle B(1)\cdots Co\cdots B(2) = 178.8\ (3)°$], the major distortion from D_{3d} symmetry appearing to involve slight rotations of the pyrazolyl rings about their appropriate N(1)–N(2) axes.[25] This is particularly pronounced for ring f (see Figure 2). The net result of these distortions is that the cobalt(II) ion is not coplanar with any of the pyrazolyl rings; rather, it lies 0.062 Å from plane a (the least-squares plane through the atoms of ring a), 0.205 Å from plane b, 0.123 Å from plane c, 0.138 Å from plane d, 0.042 Å from plane e, and 0.277 Å from plane f. The boron atoms B(1) and B(2) similarly are displaced from the least-squares planes defined by the pyrazolyl rings (see Table VII).

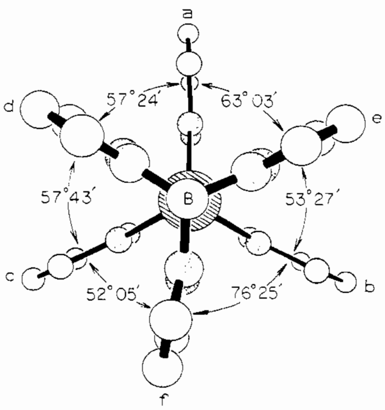

Figure 2.—The $[HB(C_3N_2H_3)_3]_2Co^{II}$ molecule, projected onto the plane defined by N(2a), N(2b), N(2c). Note the distortion of the molecule from precise D_{3d} symmetry.

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(25) N(2) and N(2′) are used as generic names for the atoms N(2a), N(2b), N(2c), N(2d), N(2e), N(2f)—with the proviso that N(2) ≠ N(2′). This nomenclature is used for convenience throughout this paper.

(26) Cartesian coordinates—see Table VII, footnote *a*.

TABLE IV

ATOMIC VIBRATION ELLIPSOIDS FOR $[HB(C_3N_2H_3)_3]_2Co^{II}$ [a,b]

Atom	B_{max}, Å^2	B_{med}, Å^2	B_{min}, Å^2
Co	2.97	2.83	1.96
B(1)	4.40	3.36	2.05
B(2)	5.21	4.39	2.03
N(1a)	4.08	3.56	1.75
N(2a)	4.68	2.83	1.95
N(1b)	4.77	3.00	2.16
N(2b)	3.88	2.74	2.33
N(1c)	3.69	3.30	2.32
N(2c)	4.16	2.52	2.00
N(1d)	3.51	2.76	2.18
N(2d)	5.00	2.49	2.13
N(1e)	4.02	2.54	2.02
N(2e)	4.48	3.14	2.07
N(1f)	5.18	3.06	1.66
N(2f)	3.80	2.97	2.46
C(3a)	4.86	3.90	2.67
C(4a)	5.17	4.21	3.02
C(5a)	4.33	3.11	2.98
C(3b)	4.76	4.26	3.00
C(4b)	5.44	4.99	1.79
C(5b)	4.65	3.60	2.32
C(3c)	4.62	3.23	2.69
C(4c)	5.17	3.91	2.68
C(5c)	5.35	4.18	2.30
C(3d)	5.95	4.58	2.94
C(4d)	6.54	5.89	2.31
C(5d)	6.27	4.07	1.98
C(3e)	5.68	2.92	2.60
C(4e)	6.98	4.55	2.59
C(5e)	5.72	4.27	2.89
C(3f)	5.15	3.72	2.08
C(4f)	8.15	3.85	2.73
C(5f)	5.64	4.10	3.20

[a] Axes dimensions for the vibration ellipsoids are presented in terms of the isotropic thermal parameter, *B*. The transformation to root-mean-square displacement is $(\overline{U^2})^{1/2} = (B/8\pi^2)^{1/2}$. [b] The vibration ellipsoids are illustrated in Figure 1.

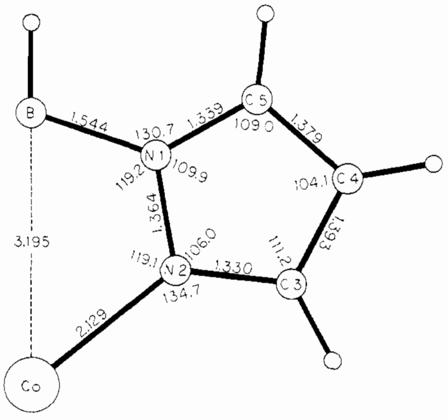

Figure 3.—Mean bond distances and angles for the "asymmetric unit" of the $[HB(C_3N_2H_3)_3]_2Co^{II}$ molecule. *Individual* bond distances and angles are listed in Tables V and VI.

TABLE V

DISTANCES WITHIN THE $[HB(C_3N_2H_3)_3]_2Co^{II}$ MOLECULE, WITH ESTIMATED STANDARD DEVIATIONS[a]

Atoms	Distance, Å		Atoms	Distance, Å
(a) Distances from Cobalt				
Co---N(2a)	2.123 (7)		Co---N(2d)	2.133 (8)
Co---N(2b)	2.120 (7)		Co---N(2e)	2.128 (8)
Co---N(2c)	2.130 (7)		Co---N(2f)	2.140 (7)
		Av	Co---N	2.129 (7)[b]
Co···B(1)	3.198 (11)		Co···B(2)	3.192 (13)
		Av	Co···B	3.195 (4)[b]
(b) Distances within Hydrotris(1-pyrazolyl)borato ligands				
B(1)---N(1a)	1.558 (14)		B(2)---N(1d)	1.510 (15)
B(1)---N(1b)	1.533 (14)		B(2)---N(1e)	1.549 (15)
B(1)---N(1c)	1.541 (14)		B(2)---N(1f)	1.571 (15)
		Av	B---N(1)	1.544 (21)[b]
N(1a)---N(2a)	1.363 (10)		N(1d)---N(2d)	1.363 (11)
N(1b)---N(2b)	1.368 (11)		N(1e)---N(2e)	1.361 (11)
N(1c)---N(2c)	1.367 (10)		N(1f)---N(2f)	1.359 (11)
		Av	N(1)---N(2)	1.364 (3)[b]
N(2a)---C(3a)	1.307 (13)		N(2d)---C(3d)	1.329 (14)
N(2b)---C(3b)	1.351 (13)		N(2e)---C(3e)	1.326 (13)
N(2c)---C(3c)	1.343 (12)		N(2f)---C(3f)	1.324 (13)
		Av	N(2)---C(3)	1.330 (15)[b]
C(3a)---C(4a)	1.428 (15)		C(3d)---C(4d)	1.386 (17)
C(3b)---C(4b)	1.403 (15)		C(3e)---C(4e)	1.403 (16)
C(3c)---C(4c)	1.364 (15)		C(3f)---C(4f)	1.375 (16)
		Av	C(3)---C(4)	1.393 (23)[b]
C(4a)---C(5a)	1.373 (15)		C(4d)---C(5d)	1.397 (16)
C(4b)---C(5b)	1.388 (15)		C(4e)---C(5e)	1.347 (17)
C(4c)---C(5c)	1.355 (15)		C(4f)---C(5f)	1.415 (16)
		Av	C(4)---C(5)	1.379 (25)[b]
C(5a)---N(1a)	1.327 (12)		C(5d)---N(1d)	1.326 (13)
C(5b)---N(1b)	1.339 (13)		C(5e)---N(1e)	1.356 (14)
C(5c)---N(1c)	1.358 (13)		C(5f)---N(1f)	1.328 (14)
		Av	C(5)---N(1)	1.339 (15)[b]
(c) Intramolecular Contacts				
N(1a)···N(1b)	2.509 (11)		N(2a)···N(2b)	2.891 (10)
N(1a)···N(1c)	2.511 (10)		N(2a)···N(2c)	2.897 (10)
N(1b)···N(1c)	2.507 (11)		N(2b)···N(2c)	2.881 (10)
N(1d)···N(1e)	2.511 (10)		N(2d)···N(2e)	2.869 (11)
N(1d)···N(1f)	2.508 (11)		N(2d)···N(2f)	2.897 (11)
N(1e)···N(1f)	2.529 (11)		N(2e)···N(2f)	2.918 (11)
N(2a)···N(2d)	3.097 (11)		N(2a)···N(2e)	3.175 (11)
N(2b)···N(2e)	3.094 (11)		N(2b)···N(2f)	3.155 (10)
N(2c)···N(2d)	3.056 (11)		N(2c)···N(2f)	3.182 (11)

[a] Esd's, shown in parentheses, are right adjusted to the last digit of the preceding number. [b] Esd's for average bond lengths are calculated from

$$\sigma = \left[\left\{\sum_{i=1}^{i=N}(\chi_i - \bar{\chi})^2\right\} \Big/ (N-1)\right]^{1/2}$$

where χ_i is the *i*th bond length and $\bar{\chi}$ is the mean of the *N* equivalent bond lengths.

As shown in Figure 2, angles between the least-squares planes of successive (relative to the psuedo-S_6 axis) pyrazolyl rings vary from 52° 05′ to 76° 25′. Each of the two hydrotris(1-pyrazolyl)borato ligands is individually distorted from idealized C_{3v} symmetry, dihedral angles between the appropriate least-squares planes being: a–b = 116° 31′, b–c = 128° 55′, c–a = 115° 04′; d–e = 120° 23′, e–f = 129° 49′, d–f = 109° 46′.

Individual cobalt–boron distances are Co···B(1) = 3.198 (11) Å and Co···B(2) = 3.192 (13) Å. The average value of 3.195 (4) Å is thus significantly lower than the distance of 3.4 Å used by Jesson[13] in his calculations of the dipolar contribution to the isotropic nuclear resonance shifts in poly(1-pyrazolyl)borato complexes of Co(II).

Individual $B(sp^3)$–$N(sp^2)$ distances in the present molecule range from 1.510 (15) to 1.571 (15) Å, averaging 1.544 (21) Å—a value consistent with $B(sp^3)$–$N(sp^3)$ distances of 1.59 (4) Å (av) in $[H_2B(NH_3)_2]^+Cl^-$ [27] and 1.56 (5) Å in $H_3B \cdot NH_3$.[28,29]

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(27) C. E. Nordman and C. R. Peters, *J. Amer. Chem. Soc.*, **81**, 3551 (1959).

(28) E. W. Hughes, *ibid.*, **78**, 503 (1956).

(29) E. L. Lippert and W. N. Lipscomb, *ibid.*, **78**, 503 (1956).

TABLE VI

ANGLES WITHIN THE $[HB(C_3N_2H_3)_3]_2Co^{II}$ MOLECULE[a]

Atoms	Angle, deg	Atoms	Angle, deg
	(a) Angles around Cobalt		
B(1)···Co···B(2)	178.8 (3)		
N(2a)–Co–N(2b)	85.9 (3)	N(2b)–Co–N(2f)	95.5 (3)
N(2a)–Co–N(2c)	85.8 (3)	N(2c)–Co–N(2d)	96.6 (3)
N(2a)–Co–N(2d)	93.4 (3)	N(2c)–Co–N(2e)	177.2 (3)
N(2a)–Co–N(2e)	96.6 (3)	N(2c)–Co–N(2f)	91.4 (3)
N(2a)–Co–N(2f)	176.8 (3)	N(2d)–Co–N(2e)	84.6 (3)
N(2b)–Co–N(2c)	85.3 (3)	N(2d)–Co–N(2f)	85.3 (3)
N(2b)–Co–N(2d)	177.9 (3)	N(2e)–Co–N(2f)	86.2 (3)
N(2b)–Co–N(2e)	93.5 (3)		
	(b) Angles around Boron Atoms		
N(1a)–B(1)–N(1b)	108.5 (8)	N(1d)–B(2)–N(1e)	110.3 (9)
N(1a)–B(1)–N(1c)	108.2 (8)	N(1d)–B(2)–N(1f)	109.0 (9)
N(1b)–B(1)–N(1c)	109.3 (8)	N(1e)–B(2)–N(1f)	108.3 (9)
	Av	N–B–N	108.9 (8)
	(c) Angles from Cobalt Atom		
Co–N(2a)–N(1a)	119.1 (6)	Co–N(2d)–N(1d)	119.6 (6)
Co–N(2b)–N(1b)	119.0 (6)	Co–N(2e)–N(1e)	118.7 (6)
Co–N(2c)–N(1c)	118.9 (6)	Co–N(2f)–N(1f)	119.3 (6)
	Av	Co–N(2)–N(1)	119.1 (3)
Co–N(2a)–C(3a)	134.2 (7)	Co–N(2d)–C(3d)	133.5 (7)
Co–N(2b)–C(3b)	133.9 (7)	Co–N(2e)–C(3e)	135.4 (7)
Co–N(2c)–C(3c)	136.4 (7)	Co–N(2f)–C(3f)	134.7 (7)
	Av	Co–N(2)–C(3)	134.7 (11)
	(d) Angles from Boron Atoms		
B(1)–N(1a)–N(2a)	119.4 (8)	B(2)–N(1d)–N(2d)	118.9 (8)
B(1)–N(1b)–N(2b)	119.7 (8)	B(2)–N(1e)–N(2e)	119.6 (8)
B(1)–N(1c)–N(2c)	119.4 (8)	B(2)–N(1f)–N(2f)	118.4 (8)
	Av	B–N(1)–N(2)	119.2 (7)
B(1)–N(1a)–C(5a)	130.2 (8)	B(2)–N(1d)–C(5d)	131.3 (9)
B(1)–N(1b)–C(5b)	130.3 (9)	B(2)–N(1e)–C(5e)	131.9 (9)
B(1)–B(1c)–C(5c)	131.0 (9)	B(2)–N(1f)–C(5f)	129.4 (9)
	Av	B–N(1)–C(5)	130.7 (9)
	(e) Angles within Pyrazole Rings		
C(5a)–N(1a)–N(2a)	110.4 (8)	C(5d)–N(1d)–N(2d)	109.8 (8)
C(5b)–N(1b)–N(2b)	109.7 (8)	C(5e)–N(1e)–N(2e)	108.4 (8)
C(5c)–N(1c)–N(2c)	109.6 (8)	C(5f)–N(1f)–N(2f)	111.3 (8)
	Av	C(5)–N(1)–N(2)	109.9 (11)
N(1a)–N(2a)–C(3a)	106.7 (8)	N(1d)–N(2d)–C(3d)	106.8 (8)
N(1b)–N(2b)–C(3b)	106.8 (8)	N(1e)–N(2e)–C(3e)	105.9 (8)
N(1c)–N(2c)–C(3c)	104.5 (7)	N(1f)–N(2f)–C(3f)	105.5 (9)
	Av	N(1)–N(2)–C(3)	106.0 (9)
N(2a)–C(3a)–C(4a)	110.4 (9)	N(2d)–C(3d)–C(4d)	110.6 (11)
N(2b)–C(3b)–C(4b)	109.8 (9)	N(2e)–C(3e)–C(4e)	112.0 (10)
N(2c)–C(3c)–C(4c)	112.2 (9)	N(2f)–C(3f)–C(4f)	112.1 (10)
	Av	N(2)–C(3)–C(4)	111.2 (10)
C(3a)–C(4a)–C(5a)	103.5 (9)	C(3d)–C(4d)–C(5d)	104.2 (11)
C(3b)–C(4b)–C(5b)	104.7 (10)	C(3e)–C(4e)–C(5e)	102.9 (11)
C(3c)–C(4c)–C(5c)	105.1 (10)	C(3f)–C(4f)–C(5f)	104.0 (10)
	Av	C(3)–C(4)–C(5)	104.1 (8)
C(4a)–C(5a)–N(1a)	109.9 (9)	C(4d)–C(5d)–N(1d)	108.6 (10)
C(4b)–C(5b)–N(1b)	109.1 (9)	C(4e)–C(5e)–N(1e)	110.8 (10)
C(4c)–C(5c)–N(1c)	108.6 (10)	C(4f)–C(5f)–N(1f)	107.0 (10)
	Av	C(4)–C(5)–N(1)	109.0 (13)

[a] See footnotes to Table V.

The Pyrazolyl Rings

Each of the six five-membered pyrazolyl rings is planar within the limits of experimental error, root-mean-square deviations from planarity each being less than 0.009 Å (see Table VII).

Mean bond lengths and angles obtained from the six crystallographically independent pyrazolyl systems in $[HB(C_3N_2H_3)_3]_2Co^{II}$ are shown in Figure 3. They are in good agreement with values obtained from the pyrazole rings in *trans*-dichlorotetrakis(pyrazole)nickel(II),[30] $(C_3N_2H_4)_4NiCl_2$, in which average bond distances (with N(2) bonded directly to the nickel(II) ion) are N(1)–N(2) = 1.344 Å, N(2)–C(3) = 1.325 Å, C(3)–C(4) = 1.391 Å, C(4)–C(5) = 1.364 Å, and C(5)–N-

TABLE VII

IMPORTANT LEAST-SQUARES PLANES WITHIN THE $[HB(C_3N_2H_3)_3]_2Co^{II}$ MOLECULE[a,b]

Atom	Dev, Å	Atom	Dev, Å
Plane a:	N(1a), N(2a), C(3a), C(4a), C(5a)		
Equation:	$-0.896X + 0.300Y + 0.327Z = -4.320$		
N(1a)	+0.000 (8)	Co	−0.062 (1)
N(2a)	−0.002 (8)	B(1)	−0.052 (12)
C(3a)	+0.002 (11)		
C(4a)	−0.002 (11)		
C(5a)	+0.001 (10)		
Plane b:	N(1b), N(2b), C(3b), C(4b), C(5b)		
Equation:	$0.790X + 0.269Y + 0.551Z = 7.277$		
N(1b)	+0.004 (8)	Co	−0.205 (1)
N(2b)	−0.006 (8)	B(1)	−0.119 (12)
C(3b)	+0.006 (11)		
C(4b)	−0.003 (11)		
C(5b)	−0.001 (10)		
Plane c:	N(1c), N(2c), C(3c), C(4c), C(5c)		
Equation:	$0.015X + 0.532Y + 0.847Z = 3.438$		
N(1c)	+0.001 (8)	Co	−0.123 (1)
N(2c)	−0.000 (8)	B(1)	−0.041 (12)
C(3c)	−0.001 (10)		
C(4c)	+0.002 (11)		
C(5c)	−0.002 (11)		
Plane d:	N(1d), N(2d), C(3d), C(4d), C(5d)		
Equation:	$0.852X + 0.245Y + 0.462Z = 7.090$		
N(1d)	+0.000 (8)	Co	+0.138 (1)
N(2d)	+0.002 (8)	B(2)	+0.022 (13)
C(3d)	−0.004 (12)		
C(4d)	+0.004 (13)		
C(5d)	−0.002 (11)		
Plane e:	N(1e), N(2e), C(3e), C(4e), C(5e)		
Equation:	$-0.019X + 0.528Y + 0.849Z = 3.133$		
N(1e)	+0.005(8)	Co	−0.042(1)
N(2e)	−0.001 (8)	B(2)	−0.067 (13)
C(3e)	−0.003 (11)		
C(4e)	+0.007 (13)		
C(5e)	−0.008 (12)		
Plane f:	N(1f), N(2f), C(3f), C(4f), C(5f)		
Equation:	$-0.779X + 0.351Y + 0.519Z = -2.795$		
N(1f)	+0.012 (8)	Co	−0.277 (1)
N(2f)	−0.013 (8)	B(2)	−0.180 (13)
C(3f)	+0.010 (11)		
C(4f)	−0.002 (12)		
C(5f)	−0.006 (12)		
Plane g:	N(2a), N(2b), N(2c)		
Equation:	$-0.094X - 0.854Y + 0.512Z = -3.107$		
Co	+1.316 (1)		
Plane h:	N(2d), N(2e), N(2f)		
Equation:	$-0.087X - 0.855Y + 0.526Z = -0.363$		
Co	−1.328 (1)		

Angles between Planes

a–b	116° 31′	b–c	128° 25′	c–e	184° 31′
a–c	115° 05′	b–d	186° 26′	c–f	52° 05′
a–d	57° 24′	b–e	53° 27′	d–e	120° 23′
a–e	63° 03′	b–f	76° 25′	d–f	109° 46′
a–f	193° 14′	c–d	57° 43′	e–f	129° 49′
g–h	1° 08′				

[a] Planes are defined as $c_1X + c_2Y + c_3Z = d$, where X, Y, Z are Cartesian coordinates which are related to the natural monoclinic cell coordinates (x, y, z) by the transformations: $X = xa + zc \cos \beta$; $Y = yb$; $Z = zc \sin \beta$. [b] Estimated standard deviations, shown in parentheses, are right adjusted to the least significant digit of the preceding number.

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[30] C. W. Reimann, A. D. Mighell, and F. A. Mauer, *Acta Crystallogr.*, **23**, 123 (1967).

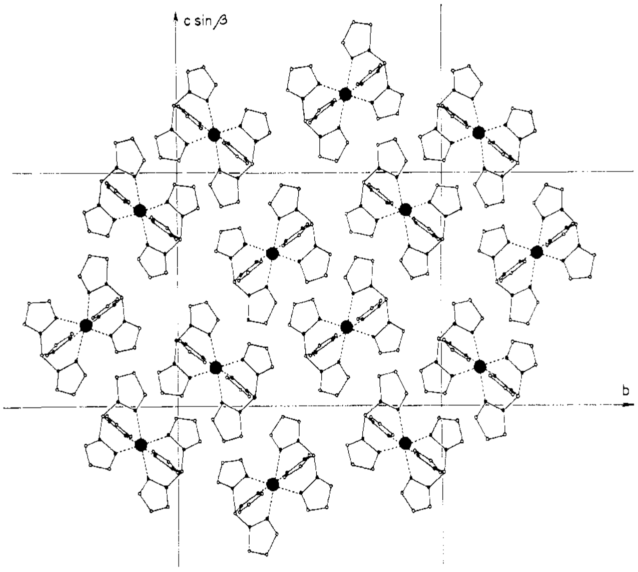

Figure 4.—Packing of $[HB(C_3N_2H_3)_3]_2Co^{II}$ molecules within the unit cell, as viewed down *a*.

(1) = 1.345 Å. [Bond distances obtained from an X-ray structural analysis of pyrazole itself[31] are N(1)–N(2) = 1.36 Å, N(2)–C(3) = 1.31 Å, C(3)–C(4) = 1.41 Å, C(4)–C(5) = 1.34 Å, and C(5)–N(1) = 1.35 Å;[32] this structural analysis is, however, of limited accuracy, since only *hk*0, *h*0*l*, and 0*kl* diffraction data were used.]

Finally, it may be noted that the N(1)–N(2)[25] bonds of the pyrazolyl rings are not parallel to the B(1)···Co···B(2) axis but are canted toward the boron atoms, due to the B–N bond distances being shorter than the Co–N distances. Thus, the average intraligand N(1)···N(1′) distance[25] is 2.513 Å, while the mean intraligand N(2)···N(2′) contact is 2.892 Å.

Intermolecular Contacts

The packing of molecules within the crystal lattice (viewed down *a*) is illustrated in Figure 4. The individual $[HB(C_3N_2H_3)_3]_2Co^{II}$ molecules are separated by normal van der Waals distances, closest approaches (of each type) being: hydrogen···hydrogen, 2.57 Å; carbon···hydrogen, 2.84 Å; nitrogen···hydrogen, 3.00 Å; boron···hydrogen, 3.26 Å.

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[31] H. W. W. Ehrlich, *Acta Crystallogr.*, **13**, 946 (1960).

[32] We have followed the suggestion of Reimann, *et al.*,[30] that Ehrlich's[31] original assignment of N(1) and N(2) should be reversed.

CONTRIBUTION NO. 3986 FROM THE ARTHUR AMOS NOYES LABORATORY OF CHEMICAL PHYSICS,
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The Structure of μ-Amido-μ-nitro-bis[tetraamminecobalt(III)] Tetrachloride Tetrahydrate

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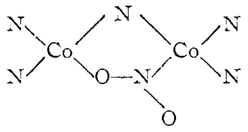
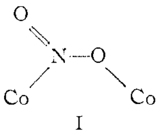
μ-Amido-μ-nitro-bis[tetraamminecobalt(III)] tetrachloride tetrahydrate, $[(NH_3)_4Co(NH_2)(NO_2)Co(NH_3)_4]Cl_4\cdot 4H_2O$, crystallizes in the monoclinic system, space group $P2_1/m$, with $a = 10.328$ (2), $b = 15.103$ (2), $c = 7.756$ (1) Å, $\beta = 124.10$ (2)°, and $Z = 2$. The crystal structure has been determined from three-dimensional X-ray data using the heavy-atom method and refined by least squares to an R index of 0.048. The cation has mirror symmetry and contains the planar group of atoms



The *exo*-N–O bond length (1.23 ± 0.01 Å) is about equal to the N–O distance in the nitrite ion. The bridging N–O bond, however, is considerably longer (1.31 ± 0.01 Å), approaching the N–O single-bond length. The ions and the water molecules are linked by a network of hydrogen bonds, in which most of the hydrogen atoms take part.

Introduction

Binuclear cobalt complexes containing one or two bridging NO_2 groups were discovered and formulated by Werner[1] more than 50 years ago. However, the arrangement of the bridging NO_2 group could not be decided at that time. Three possible arrangements are



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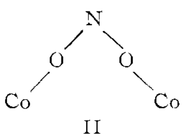

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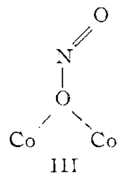

III

[1] A. Werner, *Justus Liebigs Ann. Chem.*, **375**, 1 (1910).