Contribution from the Department of Chemistry and the Killgore Research Center,
West Texas State University, Canyon, Texas 79016

Structure of Methyl[hydrotris(1-pyrazolyl)borato](*tert*-butylisocyano)platinum(II)[1]

JOEL D. OLIVER* and NICHOLAS C. RICE

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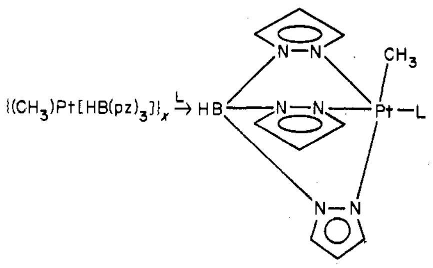
The crystal structure of $(CH_3)[HB(C_3N_2H_3)_3]Pt[CNC(CH_3)_3]$ has been determined from three-dimensional x-ray diffraction data collected by counter methods. The compound crystallizes in the triclinic space group $P\bar{1}$ with $a = 9.352$ (2) Å, $b = 11.280$ (2) Å, $c = 10.710$ (2) Å, $\alpha = 76.08$ (2)°, $\beta = 94.00$ (1)°, and $\gamma = 65.71$ (1)°. A calculated density of 1.71 g cm^{-3} for two formula units per cell agrees with the measured value of 1.71 g cm^{-3}. The coordination about the platinum atom is square planar with the hydrotris(1-pyrazolyl)borate anion functioning as a bidentate ligand. The platinum atom is located 0.033 Å above the plane defined by the four donor atoms. A significant difference in Pt–N bond lengths is observed and is discussed in terms of the trans influence. The isocyanide ligand is coordinated in a linear fashion with a Pt–C bond length of 1.86 (2) Å. The uncoordinated pyrazolyl ring possesses a twofold rotational disorder about the B–N bond. The relation between the solution NMR spectra and the solid-state structure of the compound is discussed. Full-matrix least-squares refinement has yielded a conventional R of 0.065 (0.063 for weighted R) based on the 3417 reflections whose intensities are significantly above background ($I_{net} \geq 10$ counts s^{-1}).

Introduction

The syntheses of a wide variety of five-coordinate Pt(II) complexes stabilized by poly(pyrazolyl)borate ligands have been described by Clark and Manzer.[2,3] These compounds were prepared by reacting neutral ligands with the polymeric complex $\{(CH_3)Pt[HB(pz)_3]\}_x$. The reactions conform to the general equation



where L is a neutral ligand. The ^1H NMR spectrum of the complex where L is carbon monoxide was unusual in that all three pyrazolyl rings were magnetically equivalent at room temperature. The crystal structure of this compound has appeared[4,5] and reveals a bidentate $HB(pz)_3$ ligand.

In order to understand the existence of the four-coordinate complex a series of complexes were prepared by Manzer.[6] The complex with L = *t*-BuNC was particularly interesting. The room-temperature ^1H NMR spectrum indicated a static, five-coordinate complex, whereas at higher temperatures the pyrazolyl rings become magnetically equivalent. The activation energy for the exchange process of this complex (17.1 kcal/mol) is considerably higher than that for the CO complex (14.1 kcal/mol) and suggested that five-coordination may also be present in the crystalline state. An x-ray crystal structure analysis was thus initiated to confirm the stereochemistry of the molecule in the solid state.

Experimental Section

Crystals for the diffraction study were kindly supplied by Dr. L. E. Manzer and were recrystallized from hexane. The data crystal (clear) was mounted with [210] parallel to the ϕ axis of the goniometer. All x-ray studies were performed using a Diano XRD-700 diffractometer equipped with a single-crystal orienter, with Cu Kα radiation and at ambient room temperature (~21 °C).

Intensity-weighted plots of the reciprocal lattice revealed that the diffraction symmetry is $\bar{1}$ with no systematically absent reflections. Cell parameters listed in Table I were obtained by least-squares refinement of 60 independent 2θ measurements with Kα_1 and Kα_2 well resolved. Measurements of ω scans (5° takeoff angle, 0.05° receiving slit) for several reflections showed the peaks to be single, narrow (<0.4° wide from background to background), and symmetrical indicating suitable quality for the stationary-crystal, stationary-counter technique of data collection (5° takeoff angle, 1° receiving slit) using a balanced nickel–cobalt filter pair.

Table I. Experimental Summary

Crystal Data for $C_{15}H_{22}N_7BPt$

Fw 506.29	Triclinic
$a = 9.352$ (2) Å	Systematic absences: none
$b = 11.280$ (2) Å	Space group $P\bar{1}$ (No. 2)
$c = 10.710$ (2) Å	$Z = 2$
$\alpha = 76.08$ (2)°	$F(000) = 488$ e
$\beta = 94.00$ (1)°	λ_{Cu}: Kα_1, 1.540 50 Å:
$\gamma = 65.71$ (1)°	Kα_2, 1.544 33 Å
$d_{calcd} = 1.71$ g cm^{-3}	
$d_{measd} = 1.71$ g cm^{-3} (flotation, aqueous $AgNO_3$)	

Data Collection

Crystal dimensions: 0.341 × 0.336 × 0.177 mm
$\mu(Cu\ K\bar{\alpha}) = 137.55\ cm^{-1}$
3709 symmetry-independent reflections for $5 < 2\theta \leq 140°$

At frequent intervals throughout the data collection, the crystal was aligned (1° takeoff angle, 0.05° slit) and the intensities of five standard reflections were monitored. The net intensities for each of these reflections were normalized against their respective original net intensities and their averages were plotted as a function of x-ray exposure hours. This plot revealed a linear isotropic decay of the crystal (13% by the end of data collection) with respect to x-ray exposure hours (the maximum relative deviation of any of the average values from the best fit straight line was 2%). The data were broken into 10 blocks of approximately equal size and the appropriate decay correction factor from the plot was applied to each block.

A correction for absorption as a function of crystal shape was applied,[7] with the correction factors ranging from 4.39 to 25.23. The intensity data were corrected for Lorentz and polarization effects as well as for α_1–α_2 splitting.[8] Standard deviations in the observed structure factor amplitudes, $\sigma(|F_o|)$, were calculated on the basis of counting statistics.[9]

Solution and Refinement of the Structure

The coordinates of the platinum atom were determined from a sharpened three-dimensional Patterson map. A subsequent electron density calculation (space group $P\bar{1}$) revealed the positions of the remaining nonhydrogen atoms of the structure. The identity of the second nitrogen atom of the uncomplexed ring could not be determined from the electron density map; thus the two possible choices, CN(1) and CN(2), were each assigned a scattering factor table corresponding to the average of those of a carbon and a nitrogen atom. Three cycles of full-matrix least-squares refinement of this model yielded $R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.101$ and $R_2 = [\sum(w||F_o| - |F_c||^2)/\sum w\cdot(|F_o|)^2]^{1/2} \doteq 0.152$, where $w = 1/\sigma^2(|F_o|)$. The function minimized in the least-squares calculations was $\sum w(|F_o| - |F_c|)^2$. The isotropic temperature factors for atoms CN(1) and CN(2) refined to similar values (5.7 and 7.3, respectively); thus the ucoordinated ring shows no preferential orientation in the crystal and is disordered.

The pyrazolyl groups were treated as rigid groups in the subsequent least-squares calculations. The individual bond lengths and bond angles within the coordinated pyrazolyl rings are displayed in Figure 1 and

Table II

Fractional Atomic Coordinates and Anisotropic Thermal Parameters (×10⁴) for the Nongroup Atoms of $(CH_3)[HB(pz)_3]Pt[CNC(CH_3)_3]$[a]

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pt[b]	57 397 (6)	9871 (5)	29 483 (5)	1349 (8)	1162 (7)	1208 (6)	−412 (5)	187 (5)	−227 (5)
B	4 234 (17)	4359 (14)	2 019 (14)	146 (22)	138 (20)	122 (15)	−66 (17)	24 (15)	−37 (14)
C(1)	6 382 (19)	−391 (14)	1 819 (14)	348 (37)	157 (20)	165 (19)	−25 (21)	79 (22)	−88 (17)
C(2)	7 355 (19)	−393 (13)	4 284 (14)	315 (36)	119 (18)	145 (18)	−42 (20)	59 (21)	14 (14)
C(3)	9 879 (17)	−2282 (15)	6 116 (16)	186 (26)	156 (21)	191 (22)	−38 (19)	−47 (19)	32 (17)
C(4)	9 498 (21)	−3459 (18)	6 564 (22)	324 (41)	231 (30)	384 (42)	−159 (29)	−115 (33)	137 (28)
C(5)	10 126 (25)	−1689 (20)	7 259 (18)	480 (56)	345 (40)	168 (24)	−136 (38)	−35 (30)	−60 (26)
C(6)	11 320 (17)	−2516 (18)	5 440 (18)	159 (26)	324 (34)	251 (29)	−63 (24)	59 (22)	−75 (26)
N(1)	8 456 (12)	−1203 (11)	5 114 (12)	185 (20)	138 (15)	174 (16)	−49 (14)	15 (14)	−8 (12)
H[c]	537 (11)	406 (9)	178 (9)	4 (2)					

Group Parameters[d]

Group	x_0	y_0	z_0	ϕ	θ	ρ
pz(1)[e]	0.5002 (8)	0.2351 (7)	0.4046 (7)	−2.745 (19)	1.903 (5)	−1.497 (20)
pz(2)[f]	0.3993 (7)	0.2375 (6)	0.1448 (6)	−1.118 (7)	−2.432 (6)	−3.008 (7)
pz(3)[g]	0.3245 (9)	0.5875 (7)	0.1659 (8)	−1.983 (7)	2.967 (7)	−2.576 (8)

[a] See Figure 3 for the atom-numbering sequence. Numbers in parentheses are the estimated standard deviations in the units of the least significant digits. The temperature factor expression for the nonhydrogen atoms is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. The temperature factor expression for the hydrogen atom is $\exp[-\beta_{11}((\sin\theta)/\lambda)^2]$. [b] Positional and thermal parameters for the Pt atom are presented ×10⁵. [c] Positional parameters are presented ×10³ for the H atom. [d] A description of these group parameters is provided elsewhere.[14] Angular coordinates are in radians. The internal coordinate system of a coordinated pyrazolyl ring was as follows: the ring was defined to lie in the xy plane with atom N(2) at the origin, the vector N(2)-N(1) was coincident with the positive x axis, and the vector from the midpoint of N(1)-N(2) to atom C(4) was parallel to the positive y axis. For the disordered pyrazolyl ring the internal coordinate system contained atom N(6) at the origin, the vector N(6)-CN(2) was coincident with the positive x axis, and the vector from the midpoint of N(6)-CN(2) to atom C(13) was parallel to the positive y axis. [e] Contains atoms N(3), N(2), C(7), C(8), and C(9). [f] Contains atoms N(4), N(5), C(10), C(11), and C(12). [g] Contains atoms CN(1), CN(2), N(6), C(13), and C(14).

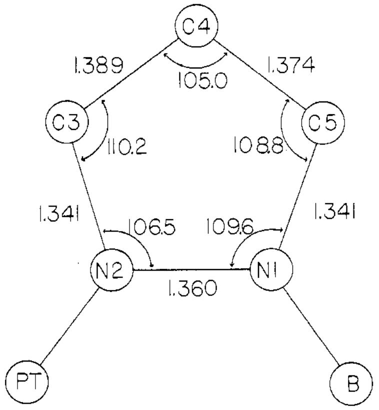


Figure 1. Idealized geometry for the coordinated pyrazolyl rings.

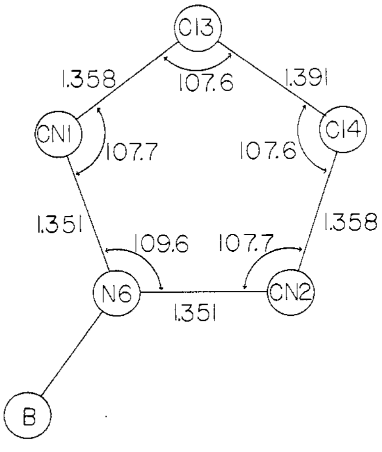


Figure 2. Idealized geometry for the disordered, uncoordinated pyrazolyl ring.

Table III. Fractional Atomic Coordinates (×10⁴)[a,b] and Isotropic Thermal Parameters for the Group Atoms of $(CH_3)[HB(pz)_3]Pt[CNC(CH_3)_3]$

	x	y	z	B, Å²
N(3)	5002 (8)	2351 (7)	4046 (7)	5.2 (2)
N(2)	4299 (9)	3727 (7)	3510 (6)	5.0 (2)
C(7)	5005 (10)	2115 (7)	5335 (7)	5.9 (3)
C(8)	4304 (12)	3338 (10)	5631 (7)	7.2 (3)
C(9)	3876 (9)	4329 (6)	4451 (9)	6.5 (3)
N(4)	3416 (9)	3743 (7)	1225 (7)	4.8 (2)
N(5)	3993 (7)	2375 (6)	1448 (6)	4.9 (2)
C(10)	3106 (10)	2193 (6)	541 (8)	5.7 (3)
C(11)	1956 (9)	3443 (9)	−267 (7)	6.1 (3)
C(12)	2194 (9)	4393 (6)	199 (8)	6.0 (3)
N(6)	3245 (9)	5875 (7)	1659 (8)	5.4 (2)
CN(1)	1735 (10)	6462 (10)	1866 (9)	6.0 (3)
CN(2)	3653 (10)	6849 (11)	1037 (10)	8.0 (3)
C(13)	1174 (10)	7831 (9)	1368 (11)	8.1 (4)
C(14)	2383 (15)	8075 (8)	845 (11)	9.5 (5)
H(7)	546 (2)	116 (1)	602 (1)	5.9
H(8)	414 (2)	348 (1)	653 (1)	7.2
H(9)	332 (2)	537 (1)	443 (1)	6.5
H(10)	324 (2)	126 (1)	44 (1)	5.7
H(11)	111 (1)	363 (1)	−104 (1)	6.1
H(12)	153 (1)	544 (1)	−19 (1)	6.0

[a] Fractional coordinates of the hydrogen atoms are presented ×10³. [b] The sequence number of each hydrogen atom is the same as that of the carbon atom to which it is bonded.

correspond to the average values cited by Davies and Payne for several metal complexes with poly(pyrazolyl)borate ligands.[10] The hydrogen atoms were placed in their idealized locations with C–H distances of 1.04 Å. In the least-squares calculations the isotropic temperature factors of the hydrogen atoms of these pyrazolyl rings were constrained to the values for the carbon atoms to which they are bonded.

The geometry of the remaining ring is shown in Figure 2 and is related to those of the other two pyrazolyl rings by averaging the bond lengths and bond angles related by a twofold rotation about the B–N bond. The hydrogen atoms on this pyrazolyl ring were omitted from the structure factor calculations.

A difference electron density map was calculated after two additional cycles of full-matrix least-squares refinement employing anisotropic temperature factors for the nine nongroup atoms were performed and revealed the position of the hydrogen atom bonded to the boron atom. The positions of the methyl hydrogen atoms were poorly defined and were not included in the subsequent least-squares calculations. An additional four cycles of least-squares refinement varying the overall scale factor, the positional and anisotropic thermal parameters of the nine nonhydrogen, nongroup atoms, the positional and isotropic thermal parameters for the single nongroup hydrogen

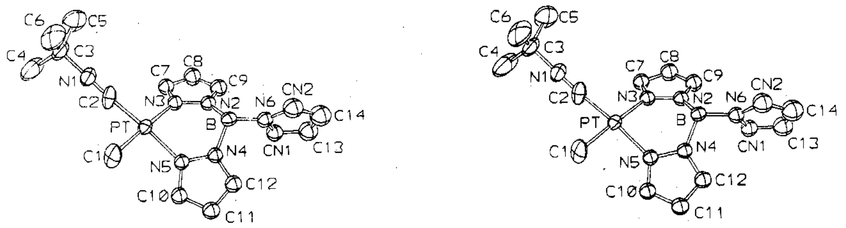


Figure 3. Stereoview of the molecule, illustrating the atom-numbering scheme employed. Ellipsoids of 30% probability are shown.

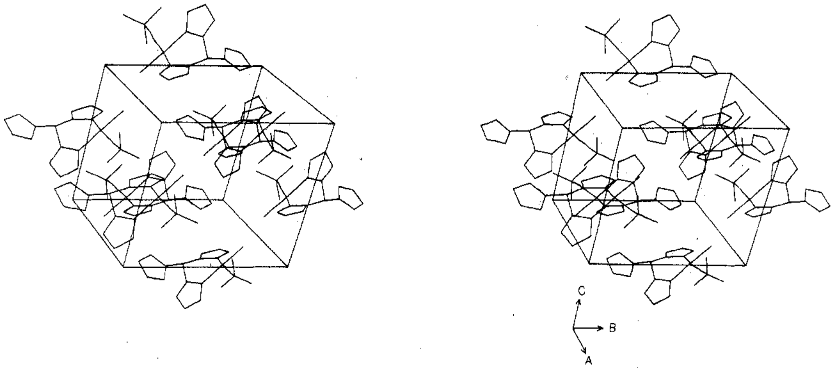


Figure 4. Stereoview of the molecular packing. One unit cell is outlined.

Table IV. Bond Lengths (Å) with Their Standard Deviations in Parentheses

Pt-C(1)	2.117 (15)	B-H	1.05 (11)
Pt-C(2)	1.857 (15)	C(2)-N(1)	1.18 (2)
Pt-N(3)	2.082 (8)	C(3)-N(1)	1.50 (2)
Pt-N(5)	2.006 (7)	C(3)-C(4)	1.49 (3)
B-N(2)	1.57 (2)	C(3)-C(5)	1.58 (3)
B-N(4)	1.56 (2)	C(3)-C(6)	1.53 (2)
B-N(6)	1.50 (2)		

Table V. Bond Angles (deg) with Their Standard Deviations in Parentheses

C(1)-Pt-C(2)	86.6 (6)	N(2)-B-H	113 (6)
C(1)-Pt-N(5)	89.5 (5)	N(4)-B-N(6)	110 (1)
C(1)-Pt-N(3)	177.4 (5)	N(4)-B-H	104 (6)
C(2)-Pt-N(3)	94.8 (5)	N(6)-B-H	114 (6)
C(2)-Pt-N(5)	175.9 (5)	C(2)-N(1)-C(3)	177 (2)
N(3)-Pt-N(5)	89.0 (3)	C(4)-C(3)-N(1)	106 (1)
Pt-N(3)-C(7)	129.9 (6)	C(4)-C(3)-C(5)	112 (2)
Pt-N(3)-N(2)	123.5 (6)	C(4)-C(3)-C(6)	117 (2)
Pt-N(5)-C(10)	129.4 (6)	C(5)-C(3)-N(1)	108 (1)
Pt-N(5)-N(4)	123.9 (5)	C(5)-C(3)-C(6)	107 (2)
Pt-C(2)-N(1)	174 (1)	C(6)-C(3)-N(1)	106 (1)
N(2)-B-N(4)	107 (1)	B-N(6)-CN(1)	123 (1)
N(2)-B-N(6)	108 (1)	B-N(6)-CN(2)	127 (1)

atom, six orientional and positional parameters for each of the rigid groups, and the isotropic thermal parameters of the nonhydrogen atoms of the pyrazolyl rings served to complete refinement at $R_1 = 0.065$ and $R_2 = 0.063$.

A final difference electron density map contained three large peaks with densities of −1.3, −1.5, and +2.4 e Å^{-3} within 1.5 Å of the platinum atom and one large peak (−1.2 e Å^{-3}) within 0.9 Å of atom C(14). Several smaller peaks with densities 0.25–0.60 e Å^{-3} were scattered throughout the unit cell. Some of these peaks apparently correspond to methyl hydrogen atoms. Single peaks were found in chemically sensible locations to be associated with each of the atoms CN(1), CN(2), C(13), and C(14). The remaining peaks are too far from remaining portions of the structure to be significant.

Scattering factors for boron, carbon, nitrogen, and platinum atoms were taken from Cromer and Waber.[11] The anomalous dispersion corrections for the platinum atom were included.[12] Scattering factors for the hydrogen atoms were those of Stewart, Davidson, and Simpson.[13]

Discussion

The molecular geometry and the atom-labeling scheme for $(CH_3)[HB(C_3N_2H_3)_3]Pt[CNC(CH_3)_3]$ are shown in the stereoscopic drawings in Figure 3. Figure 4 is a stereoscopic view of the molecular packing. Final atomic parameters are listed in Tables II and III. Bond lengths and bond angles are given in Tables IV and V, respectively. Table VI contains the equations for selected least-squares planes.

The structure is monomeric and shows great similarity to the structure of $(CH_3)[HB(pz)_3]Pt(CO)$.[4,5] Again the solid-state structure reveals a bidentate $HB(pz)_3^-$ ligand. In this structure the noncoordinated pyrazolyl ring occupies the equatorial position on the boron atom of the PtN_4B moiety, whereas in the complex with carbon monoxide[4,5] the similar ring occupies the axial position on the boron atom. The platinum atom is 0.033 Å above the plane defined by the four donor atoms (plane A).

The six-membered PtN_4B chelate ring is in the boat conformation with Pt and B being respectively 0.604 and 0.664 Å above the plane defined by the four nitrogen atoms (plane B). The plane defined by the atoms Pt, N_3, and N_5 (plane

Table VI. Selected Least-Squares Planes[a]

Plane	Atoms defining the plane	*A*	*B*	*C*	*D*
A	C(1), C(2), N(3), N(5)	0.9039	0.2644	−0.3364	−4.536
B	N(2), N(3), N(4), N(5)	0.9652	−0.1192	−0.2326	−3.875
C	Pt, N(3), N(5)	0.8972	0.2864	−0.3361	−4.576
D	B, N(2), N(4)	−0.6394	0.7669	−0.0546	−0.086
E	N(2), N(3), C(7), C(8), C(9)	0.9881	0.0478	0.1465	−6.183
F	N(4), N(5), C(10), C(11), C(12)	0.7690	−0.1690	−0.6165	−2.235
G	N(6), CN(1), CN(2), C(13), C(14)	0.3457	0.3178	0.8829	−5.529

[a] The equations of the planes are of the form: $Ap + Bq + Cr + D = 0$. p, q, and r are the Cartesian coordinates (Å) relative to the crystallographic directions a, $c^* \times a$, and c^*.

C) intersects the plane defined by the atoms B, N_2, and N_4 (plane D) to form an angle of 109.6°. The Pt–B nonbonded distance, 3.32 (2) Å, is consistent with the value found in a similar complex containing a carbonyl ligand.[4,5]

The angle formed by the intersection of the two complexed pyrazolyl rings, planes E and F, is 131.4°. The plane of the uncomplexed ring (plane G) intersects planes E and F to form angles of 119.1 and 109.4°, respectively. The boron atom and the platinum atom are respectively 0.13 and 0.11 Å out of plane E, 0.11 and 0.11 Å out of plane F, and 0.07 and 0.32 Å out of plane G.

The bonding about the boron atom is tetrahedral. The distance B–N(6) is 0.06 Å shorter than the average of the two other B–N bond lengths. Applying the Cruickshank criteria[15] this difference ($\Delta l/\sigma l = 2.30$) is possibly significant.

The Pt–C(methyl) distance in this compound is 2.12 Å, whereas the corresponding values in the other two cleavage products from $(CH_3)[HB(C_3N_2H_3)_3]Pt$ whose structures have been reported[4,5,10] are 2.07 Å in each case. The average Pt–C(methyl) distances in several compounds is 2.06 ± 0.06 Å (cf. ref 5 and references contained therein). Thus the value observed in this work falls within an acceptable range.

The Pt–C(isocyano) distance is normal and the terminally bonded *tert*-butylisocyano ligand possesses the expected geometry. The average C–C–C angle centering on atom C(3) is 112 (5)° and reflects the large thermal motions associated with the three methyl groups.

The two independent Pt–N distances in this structure are highly significantly different based upon the Cruickshank criteria,[15] $\Delta l/\sigma l = 7.15$. The sense of this difference is consistent with the σ-bonded methyl group's exerting a stronger *trans* influence than the isocyano ligand, as predicted by Appleton, Clark, and Manzer.[16]

The observed "bite" angle of the bidentate chelating ligand in this work is 89.0 (3)° and is consistent with the value (87.4 (3)°) observed in a related four-coordinate complex.[4,5]

The shortest intermolecular contact distance involving the platinum atom and any atom of the uncoordinated pyrazolyl ring is Pt···CN(2) (4.58 Å). The shortest intermolecular contact distance involving two nonhydrogen atoms is 3.35 Å (C9···C9). Thus no intermolecular contact distances are significantly shorter than the sum of their respective van der Waals radii.

In conclusion, an attempt to correlate the solid-state structure and the solution NMR spectra of this compound is appropriate. The NMR spectra of $Pt(CH_3)[HB(pz)_3](CN\text{-}t\text{-}Bu)$ have been recorded over a wide temperature range[6] and indicate stereochemical nonrigidity. The high-temperature limiting spectra showed the presence of three equivalent pyrazolyl rings, each showing coupling to ^{195}Pt. At low temperatures the spectra showed the presence of two sets of pyrazolyl rings in the ratio of 2:1, each showing ^{195}Pt satellites and confirming the five-coordinate stereochemistry. Detailed NMR line shape analyses of the variable-temperature spectra of the CN-*t*-Bu and other complexes were consistent only with five-coordinate trigonal-bipyramidal structures in solution. The differences in structure in the solution and in the solid state must reflect the similarities in energy between the four- and five-coordinate species.

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Registry No. $(CH_3)[HB(pz)_3]Pt[CNC(CH_3)_3]$, 60104-27-0.

Supplementary Material Available: Listing of structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.

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Contribution from the Institute of Materials Science and the Department of Chemistry,
University of Connecticut, Storrs, Connecticut 06268

Crystal Structure of Cobalt(II) Orthophosphate Monohydrate, $Co_3(PO_4)_2 \cdot H_2O$

J. B. ANDERSON, E. KOSTINER,* and F. A. RUSZALA

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A new monohydrate of cobalt(II) orthophosphate has been prepared and its crystal structure determined and refined by full-matrix least-squares procedures using automatic diffractometer data to a residual $R = 0.048$ ($R_w = 0.065$) with a data/parameter ratio of 13. The space group is $P2_1/c$ with $a = 9.516$ (6), $b = 7.904$ (4), $c = 9.277$ (6) Å, and $\beta = 114.22$ (4)°. Divalent cobalt ions occupy three distinct coordination polyhedra: Co(1) and Co(2) are surrounded by six oxygens while Co(3) is five-coordinated. The water oxygen bridges an edge shared by a pair of Co(2) polyhedra across a center of symmetry. Details of the structure are presented as well as the probable location of hydrogen bonds.

Introduction

We have found that single crystals of hydroxyphosphates of the type $M_5(PO_4)_2(OH)_4$,[1] $M_5(PO_4)_3(OH)$,[2] and $M_2(PO_4)(OH)$[1] can be grown hydrothermally from solutions containing a slight excess of phosphoric acid. During the investigation of the preparation of a hydroxyphosphate of the type $Co_2(PO_4)(OH)$ by hydrothermal reaction of $Co_3(PO_4)_2$ in phosphoric acid solutions, we observed the formation of a new phase which proved to be a monohydrate of cobalt orthophosphate.

Very little has been reported on the hydrates of cobalt(II)

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* To whom correspondence should be addressed at the Institute of Materials Science.