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THE CRYSTAL STRUCTURE OF METHYL[HYDROTRIS(PYRAZOL-1-YL)-BORATO]CARBONYLPLATINUM(II)

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Summary

The crystal structure of methyl[hydrotris(pyrazol-1-yl)borato]carbonylplatinum(II) has been determined by single crystal X-ray diffraction techniques. Crystals of $(CH_3)[HB(C_3N_2H_3)_3]Pt(CO)$ are monoclinic, $P2_1/c$, $a = 14.416(1)$, $b = 7.951(1)$, $c = 12.990(1)$ Å, $\beta = 104.35(1)^\circ$. The observed density (2.04 g cm^{-3}) agrees favorably with that calculated (2.08 g cm^{-3}) on the basis of four molecules per unit cell. The structure was solved by the Patterson method and has been refined by full-matrix least squares techniques to a final R_1 value of 0.041 ($R_2 = 0.039$) for 2124 reflections. The compound is square-planar with only two of the three pyrazolyl groups coordinated to the platinum atom. The platinum atom is located 0.015(1) Å above the plane defined by the four donor atoms. The uncoordinated pyrazolyl group is disordered with the shortest intramolecular distance involving platinum and any non-hydrogen atom of that ring being 3.30(1) Å. The Pt—N distances are 2.036(9) and 2.064(9) Å; Pt—C(methyl) and Pt—C(carbonyl) distances are 2.070(12) and 1.798(16) Å, respectively.

Introduction

Clark and Manzer [1,2] have reported the preparation and structural characterization by NMR techniques of a series of platinum(II) complexes containing the hydrotris(pyrazol-1-yl)borato ligand, $HB(C_3N_2H_3)_3^-$, hereafter referred to as $HB(pz)_3$. These complexes were prepared by cleavage of the polymeric complex, $(CH_3)[HB(pz)_3]Pt$, with various alkenes, alkynes, allenes, and carbon monoxide. The NMR spectrum of each complex was consistent with the formulation of a five-coordinate geometry about the platinum atom. The single crystal X-ray study of the complex $(CH_3)[HB(pz)_3]Pt(CF_3C{\equiv}CCF_3)$ has appeared [3] and reveals a five-coordinate, trigonal bipyramidal structure for the molecule.

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The NMR spectra of the carbonyl complex, $(CH_3)[HB(pz)_3]Pt(CO)$, indicated that the molecule consisted of a stereochemically non-rigid five-coordinate species. In order to determine the stereochemistry of the molecule and thereby gain additional insight into the interpretation of its NMR spectrum, a single crystal X-ray study was initiated (a preliminary account of this study has previously appeared) [4].

Experimental

Clear crystals of the title compound, kindly supplied by Clark and Manzer, were grown from hexane. All X-ray studies were performed with a Diano XRD-700 diffractometer equipped with a single crystal orienter, with Cu-K_α radiation and at ambient room temperature. Crystal Data: $(CH_3)[HB(C_3N_2H_3)_3]Pt(CO)$, mol. wt. 451.2 g/mol, monoclinic, $a = 14.416(1)$, $b = 7.951(1)$, $c = 12.990(1)$ Å, $\beta = 104.35(1)°$, $V = 1442.6$ Å^3, space group $P2_1/c$, D_m (by flotation in $AgNO_3$ solution) 2.04 g cm^{-3}, $D_c = 2.08$ g cm^{-3} (assuming four molecules per cell), $\mu = 186.2$ cm^{-1}, $F(000) = 848$ *e*.

A small platelet (~0.05 × 0.16 × 0.21 mm) was selected for the X-ray study to avoid problems of twinning and poor mosaic quality and was mounted with $[\bar{1}, 0, 2]$ parallel to the φ axis of the goniometer. Intensity weighted plots of the reciprocal lattice revealed diffraction symmetry of $2/m$ (C_{2h}) with systematic absences ($0k0$ for k odd and $h0l$ for l odd) consistent with the space group $P2_1/c$. Lattice parameters were obtained by least-squares refinement of 32 independent 2θ measurements with K_{α_1} (1.54051 Å) and K_{α_2} (1.54433 Å) well resolved.

Measurements of ω scans (0.5° take-off angle, and an open counter) for several reflections showed the peaks to be single, narrow (< 0.5° wide) and symmetrical indicating suitable crystal quality for the stationary-crystal/stationary-counter technique of data collection (5° take-off angle, 1° receiving slit), using a balanced nickel—cobalt filter pair. Of the 2738 independent reflections measured, 2124 (those with $I_{net} > 7$ counts sec^{-1}) were used in the solution and refinement of the structure. Arbitrary intensities of 3.5 counts sec^{-1} were assigned to those reflections with $I_{net} \leqslant 6$ counts sec^{-1}.

At frequent intervals throughout the data collection, the crystal was aligned (1° take-off angle, 0.05° receiving slit) and the intensities of four standard reflections 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 (18% by the end of data collection) with respect to X-ray exposure hours (the maximum relative deviation of any of the averaged values from the best fit straight line was 2.2%). The data were broken into 10 blocks of approximately equal size and the decay correction factor applied to each block was chosen from this plot.

A correction for absorption as a function of crystal shape was applied with correction factors ranging from 2.28 to 15.43 [5]. The intensity data were corrected for Lorentz and polarization effects as well as $\alpha_1 - \alpha_2$ splitting [6]. Standard deviations in structure factor amplitudes, $\sigma(|F_0|)$, were calculated on the basis of counting statistics [7].

The coordinates of the platinum atom were determined from the Patterson map. A heavy atom map phased by the platinum atoms revealed the positions of the remaining nineteen non-hydrogen atoms in the structure. Due to the proximity of atom A(2) to the inversion center at (1/2, 1/2, 1/2) it was interpreted as the nitrogen atom of the ring in order to prevent the short intermolecular contact distances involving the hydrogen atoms if the atom were a carbon atom.

The structure was refined by full-matrix least-squares methods, including all 20 non-hydrogen atoms of the structure, to an R_1 value of 0.043 ($R_2 = 0.059$). All 13 hydrogen atoms were subsequently located in a difference Fourier map. Continued refinement of these 33 atoms resulted in an R_1 value of 0.039 ($R_2 = 0.033$). Examination of a difference Fourier map at this point revealed a peak (0.5 e/A^3) near the position of a hydrogen atom on A(2) which suggested a rotational disorder in the uncomplexed pyrazolyl ring. This hypothesis was tested by removing the hydrogen atoms of the uncomplexed ring and refining the ring atoms isotropically while holding the remainder of the structure fixed. The atom types for atoms A(1) and A(2) were then reversed and the same process was repeated. Comparison of the isotropic temperature factors for A(1) and A(2) from these two calculations revealed no preferential location of the nitrogen atom in the ring. Scattering factors were then assigned to both the atoms A(1) and A(2) corresponding to the average of those for carbon and nitrogen. Since several of the parameters for the hydrogen atoms were not well behaved in the least squares calculations, the hydrogen atoms of each of the coordinated pyrazolyl groups, as well as the hydrogen atoms of C(9) and C(10) were included in idealized positions and were not refined. The hydrogen atoms of the methyl group were also removed. Additional full-matrix least squares refinement of this model resulted in an R_1 value of 0.041 ($R_2 = 0.039$). A final difference map contained a large peak (1 e/A^3) within 1 Å of the platinum atom, three diffuse peaks (~0.5 e/A^3) near the methyl carbon atom C(2) and two other diffuse peaks (~0.5 e/A^3) in chemically and structurally reasonable positions for the hydrogen atoms of A(1) and A(2). No other peaks in reasonable positions were observed. Scattering factors used for boron, carbon, nitrogen, oxygen, and platinum atoms were those of Cromer and Waber [8]. The anomalous dispersion corrections for the platinum atom were included [9]. Scattering factors for the hydrogen atoms were taken from Stewart, Davidson and Simpson [10].

All calculations were carried out on an IBM 360/40 computer located on the campus of West Texas State University. Structure factor and full-matrix least squares calculations were performed using the ORXFLS3 [11] program. All Fourier calculations were made using a program by Rao [12].

The function minimized in the least squares calculation was $\Sigma w(|F_0|-|F_c|)^2$ where $w = 1/\sigma^2(|F_0|)$. Discrepancy indexes referred to are $R_1 = \Sigma||F_0|-|F_c||/\Sigma|F_0|$ and $R_2 = [\Sigma(w||F_0|-|F_c||^2)/\Sigma w(|F_0|)^2]^{1/2}$. Final atomic parameters are given in Tables 1 and 2. A listing of structure factors is available upon request*.

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* The table of structure factors has been deposited as NAPS Document No. MS 2697 (14 pages). Order from ASIS/NAPS, c/o Microfiche Publications, 440 Park Avenue South, New York, N.Y. 10016. A copy may be secured by citing the document number, remitting \$ 5.00 for photocopies or \$ 3.00 for microfiche. Advance payment is required. Make checks payable to Microfiche Publications.

TABLE 1

FINAL POSITIONAL (X 10^4) AND THERMAL PARAMETERS (X 10^4) OF THE NON-HYDROGEN ATOMS FROM THE FULL MATRIX REFINEMENT

(Estimated standard deviations are in parentheses. The temperature factor expression was exp—($h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23}$)

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pt[a]	15318(3)	9287(6)	29690(4)	494(2)	1935(10)	607(4)	—192(5)	116(2)	92(6)
B	3600(8)	2136(16)	4638(11)	45(6)	154(26)	75(11)	18(11)	18(7)	9(14)
O	617(8)	1378(18)	688(8)	130(10)	659(44)	91(10)	—70(17)	—13(8)	1(18)
A(1)	2304(7)	4494(14)	4184(8)	59(6)	216(26)	85(10)	29(11)	8(6)	—1(12)
A(2)	3820(8)	5275(14)	4376(10)	80(8)	176(23)	135(13)	—19(12)	32(9)	46(14)
N(1)	2908(6)	1149(11)	5122(7)	64(5)	135(17)	61(7)	12(8)	20(5)	1(9)
N(2)	2025(6)	577(11)	4563(7)	59(5)	159(19)	62(7)	—20(8)	20(5)	3(9)
N(3)	3683(6)	1270(10)	3630(7)	50(4)	134(17)	61(7)	11(7)	20(5)	9(8)
N(4)	2931(6)	697(10)	2862(7)	63(5)	128(17)	60(7)	2(8)	27(5)	—6(9)
N(5)	3228(6)	3977(11)	4398(7)	59(5)	139(16)	73(7)	—4(9)	15(5)	—12(10)
C(1)	1000(9)	1178(19)	1572(12)	71(8)	309(36)	114(14)	—76(15)	4(9)	—26(20)
C(2)	136(8)	1154(19)	3103(11)	54(7)	360(40)	154(16)	0(15)	31(9)	40(21)
C(3)	1617(9)	—200(15)	5237(10)	93(9)	215(27)	69(10)	—29(13)	42(8)	12(14)
C(4)	2233(11)	—175(16)	6225(10)	112(11)	221(28)	82(11)	9(15)	61(10)	46(15)
C(5)	3038(9)	706(14)	6147(9)	90(8)	167(24)	56(9)	43(12)	23(7)	11(12)
C(6)	3295(9)	86(14)	2086(9)	100(10)	177(24)	62(9)	15(13)	26(8)	18(13)
C(7)	4296(9)	227(16)	2346(10)	83(9)	265(30)	78(11)	53(14)	45(8)	32(15)
C(8)	4504(8)	949(16)	3307(10)	57(7)	223(26)	98(11)	32(12)	36(7)	31(15)
C(9)	2368(9)	6206(16)	4029(9)	87(9)	184(28)	68(10)	50(13)	—4(7)	—11(13)
C(10)	3279(11)	6675(16)	4152(12)	106(12)	136(26)	140(16)	—7(15)	—12(11)	43(16)

[a] Thermal and positional parameters for the Pt atom are presented X 10^5.

TABLE 2

FINAL POSITIONAL PARAMETERS ($\times 10^3$) AND TEMPERATURE FACTORS FOR THE HYDROGEN ATOMS

	x	y	z	$B(A^2)$
H	435(6)	219(10)	543(7)	4(2)
H(3)	96	−81	505	5
H(4)	212	−68	691	5
H(5)	363	98	678	5
H(6)	289	−45	137	5
H(7)	476	−11	191	5
H(8)	521	128	374	5
H(9)	176	704	385	5
H(10)	353	792	408	5

Discussion

The atom labeling scheme for the non-hydrogen atoms and a perspective drawing of the molecule are shown in the stereoscopic drawing [13] in Fig. 1. The hydrogen atom of the carbon atom C(*i*) is labeled H(*i*). Bond distances and bond angles are given in Tables 3 and 4, respectively.

The structure is monomeric and reveals a slightly distorted four-coordinate square-planar geometry about the platinum atom, with the $HB(pz)_3$ moiety acting as a bidentate ligand. The angle formed by the intersection of the plane defined by the atoms Pt, C(1), and C(2), plane A, and that defined by the atoms Pt, N(2), and N(4), plane B, is 1.9° (cf. Table 5 for the equations for planes cited in the text).

The six-membered PtN_4B chelate ring is in the boat conformation with Pt and B being respectively 0.711(1) and 0.530(12) Å above the least-squares plane defined by the four nitrogen atoms. The dihedral angle formed by plane B and the plane defined by the atoms N(1), B, and N(3), plane C, is 114.3°. The Pt—B non-bonded distance, 3.36(1) Å, observed in this compound is significantly

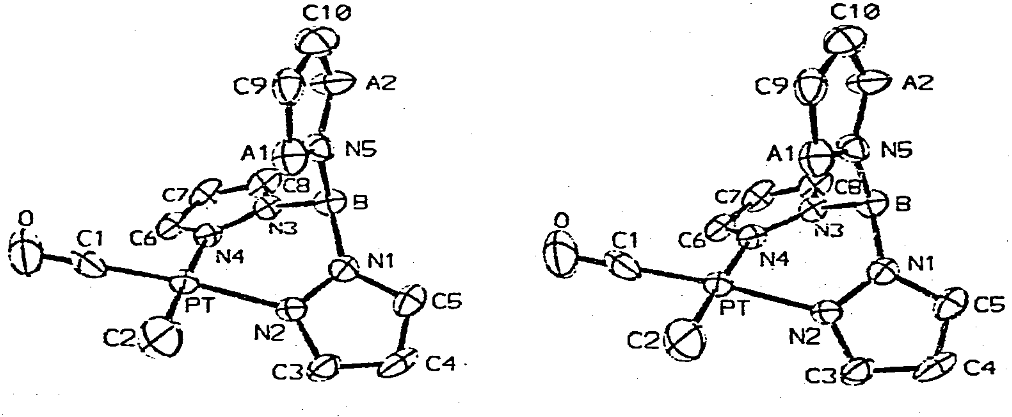

Fig. 1. Stereoscopic view of the molecule employing 30% equiprobability ellipsoids.

longer than the value of 3.201(7) Å observed in the five-coordinate platinum complex [3]. This increase in Pt—B non-bonded distance corresponds to a flattening of the PtN$_4$B boat due to relaxation of steric requirements of a bidentate as opposed to a tridentate polypyrazolylborate.

Each of the three pyrazolyl groups in this compound is planar. The bond distances and bond angles of the two complexed pyrazolyl rings in this work are in good agreement with the values contained in a summary of six X-ray structures containing polypyrazolylborate ligands [14].

A marked tendency for the HB(pz)$_3$ ligand to assume C_{3v} symmetry has been observed [3, 15-17], however in this structure no such tendency is indicated. The angle formed by the intersection of the planes for the two complexed pyrazolyl rings, planes D and E, is 132.6°. The angles between the plane of the uncomplexed pyrazolyl ring, plane F, and the planes D and E are respectively 113.0° and 107.0°. The boron atom and the platinum atom are respectively 0.010(13) and 0.044(1) Å out of plane D and 0.058(13) and 0.043(1) Å out of plane E. The corresponding distances of the boron atom and the platinum atom out of plane F are 0.003(14) and 1.816(1) Å, respectively.

The bonding about the boron atom is tetrahedral with the average of the N—B—N angles being 109.7(8)° and the average of the B—N—H angles being 109(9)°. The mean B—N distance, 1.53(3) Å, is comparable to the average value, 1.54(2) Å, obtained from several other structures [3, 14-20]. The distance B—N(5) is, however, 0.048 Å longer than the average of the two other B—N distances. Using the Cruickshank criteria [21] this difference ($\Delta l/\sigma l = 2.10$) is possibly significant.

The Pt—C(methyl) distance in this compound is 2.07(1) Å. In the five-coordinate complex [3] the corresponding distance is also 2.07(1) Å. The average Pt—C(methyl) distance for several compounds is 2.06 ± 0.06 Å [22-27], thus the bond distance observed in this work is reasonable.

TABLE 3

BOND DISTANCES (Å)

i j	*D(ij)*	*i j*	*D(ij)*
Pt—C(1)	1.798(16)	N(1)—N(2)	1.377(12)
Pt—C(2)	2.070(12)	N(3)—N(4)	1.357(12)
Pt—N(2)	2.036(9)	N(5)—A(1)	1.356(14)
Pt—N(4)	2.064(9)	N(5)—A(2)	1.345(15)
B—N(1)	1.523(15)	B—H	1.30(9)
B—N(3)	1.510(16)	C(3)—H(3)	1.04
B—N(5)	1.564(16)	C(4)—H(4)	1.03
C(1)—O	1.156(19)	C(5)—H(5)	1.05
C(3)—C(4)	1.369(19)	C(6)—H(6)	1.05
C(3)—N(2)	1.324(15)	C(7)—H(7)	1.02
C(4)—C(5)	1.381(19)	C(8)—H(8)	1.07
C(5)—N(1)	1.345(14)	C(9)—H(9)	1.07
C(6)—N(4)	1.339(15)	C(10)—H(10)	1.07
C(6)—C(7)	1.403(19)		
C(7)—C(8)	1.339(18)		
C(8)—N(3)	1.376(14)		
C(9)—A(1)	1.383(17)		
C(9)—C(10)	1.337(21)		
C(10)—A(2)	1.350(18)		

TABLE 4

BOND ANGLES (°)

i *j* *k*	Angle (*ijk*)	*i* *j* *k*	Angle (*ijk*)	*i* *j* *k*	Angle (*ijk*)
C(1)—Pt—C(2)	84.0(6)	C(5)—N(1)—B	126.8(10)	H(3)—C(3)—N(2)	126
C(1)—Pt—N(2)	175.2(5)	C(5)—N(1)—N(2)	108.7(9)	H(3)—C(3)—C(4)	125
C(1)—Pt—N(4)	97.0(5)	N(1)—N(2)—Pt	122.4(6)	H(4)—C(4)—C(3)	127
C(2)—Pt—N(2)	91.6(5)	N(1)—N(2)—C(3)	108.0(9)	H(4)—C(4)—C(5)	126
C(2)—Pt—N(4)	179.0(5)	C(3)—N2—Pt	129.6(8)	H(5)—C(5)—C(4)	126
N(2)—Pt—N(4)	87.4(3)	N(4)—N(3)—B	124.8(8)	H(5)—C(5)—N(1)	127
N(1)—B—N(3)	108.9(9)	N(4)—N(3)—C(8)	107.8(9)	H(6)—C(6)—N(4)	125
N(1)—B—N(5)	109.7(9)	C(8)—N(3)—B	127.4(9)	H(6)—C(6)—C(7)	123
N(3)—B—N(5)	110.5(10)	N(3)—N(4)—Pt	122.5(6)	H(7)—C(7)—C(6)	129
O—C(1)—Pt	176.4(13)	N(3)—N(4)—C(6)	106.5(9)	H(7)—C(7)—C(8)	127
N(2)—C(3)—C(4)	108.8(11)	C(6)—N(4)—Pt	130.9(8)	H(8)—C(8)—C(7)	124
C(3)—C(4)—C(5)	107.5(12)	A(1)—N(5)—B	126.6(9)	H(8)—C(8)—N(3)	125
C(4)—C(5)—N(1)	107.0(10)	A(2)—N(5)—B	122.3(9)	H(9)—C(9)—A(1)	124
N(4)—C(6)—C(7)	111.2(11)	A(2)—N(5)—A(1)	111.1(9)	H(9)—C(9)—C(10)	125
C(6)—C(7)—C(8)	103.8(11)	N(5)—A(1)—C(9)	103.4(10)	H(10)—C(10)—A(2)	126
C(7)—C(8)—N(3)	110.6(10)	N(5)—A(2)—C(10)	107.6(11)	H(10)—C(10)—C(9)	127
A(1)—C(9)—C(10)	110.9(12)	H—B—N(1)	101(4)		
C(9)—C(10)—A(2)	107.1(12)	H—B—N(3)	119(4)		
N(2)—N(1)—B	124.6(9)	H—B—N(5)	108(4)		

The observed Pt—C(carbonyl) distance in this compound is 1.80(2) Å and agrees with the mean value of similar distances for several structures, 1.80 ± 0.04 Å [28-33]. The carbon—oxygen distance is 1.16(2) Å. This value is similar to the C—O distances found in other complexes containing carbonyl ligands [34].

The two observed Pt—N distances in this work do not differ significantly from their mean value of 2.050 Å and compare favorably to the average value of Pt—N distances for several other structures, 2.02 ± 0.03 Å [35-39]. These distances are, however, 0.083 Å shorter than the average Pt—N distance found in the five-coordinate complex of platinum [3]. The non-bonded distance Pt—A1 is 3.30 Å. The observed "bite" angle of the chelating ligand (i.e., the angle subtended at the metal atom by the donor nitrogen atoms) in the five-coordinate compound is 83.1(3)°, whereas the "bite" angle observed in this work is 87.4(3)°. These structural differences may be explained by the reduced steric requirements of the bidentate versus the tridentate $HB(pz)_3$ ligand.

The shortest non-bonded contact distances involving the platinum atom and either atoms A(1) or A(2), the two possibilities for donor atoms on the un-

TABLE 5

SELECTED LEAST SQUARES PLANES (The equations of the planes are of the form: $Ax + By + Cz + D = 0$)

Plane	Atoms defining the plane	*A*	*B*	*C*	*D*
A	Pt, C(1), and C(2)	−0.0940	−0.9911	−0.0947	1.2035
B	Pt, N(2), and N(4)	−0.0971	−0.9870	−0.1279	1.3283
C	N(1), B, and N(3)	−0.6502	0.5493	−0.5249	4.5351
D	N(1), N(2), C(3), C(4), and C(5)	0.4764	−0.8590	−0.1874	0.7817
E	N(3), N(4), C(6), C(7), and C(8)	0.0284	0.8991	−0.4369	0.9759
F	N(5), A(1), A(2), C(9), and C(10)	0.1573	−0.1543	−0.9754	5.3771

coordinated pyrazolyl ring, are 5.39 and 5.61 Å. These distances are considerably greater than the sum of the Van der Waals radii for the respective atoms. The fractional coordinates of the hydrogen atoms in idealized positions on A(1) and A(2) are (0.170, 0.123, 0.915) and (0.456, −0.023, 0.951), respectively. The hydrogen atom on A(1) is 2.61 Å from the platinum atom, while the hydrogen atom on A(2) is 1.60 Å from itself through the inversion center at (1/2, 1/2, 1/2). A minor rotation of the uncomplexed ring about the B—N(5) bond would increase both these contact distances simultaneously, therefore these contact distances are not significantly shorter than expected. The shortest Pt—Pt intermolecular distance is 5.84 Å. No other intermolecular contact distances are shorter than the sum of their respective Van der Waals radii.

In conclusion, the existence of the four-coordinate complex rather than the expected five-coordinate species allows for an alternate interpretation of the NMR spectrum of this compound. Fluctionality of $RB(pz)_3$ ligands in similar compounds has been observed [19,40]. Extension of the "tumbling" mechanism of Tromfimenko [40] to this case would require a dissociation of one coordinated pyrazolyl group followed by coordination of the previously unattached group. A rapid inversion of the PtN_4B boat, as postulated by Calderon, et al. [19], constitutes a second dynamic exchange process available to a bidentate $RB(pz)_3$ ligand. The exchange rate in any case must be rapid on the NMR time scale in order to retain the ^{195}Pt coupling to the protons of the pyrazolyl groups.

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References

1 H.C. Clark and L.E. Manzer, J. Amer. Chem. Soc., 95 (1973) 3812.
2 H.C. Clark and L.E. Manzer, Inorg. Chem., 13 (1974) 1996.
3 B.W. Davies and N.C. Payne, Inorg. Chem., 13 (1974) 1843.
4 J.D. Oliver and P.E. Rush, Chem. Commun., 23 (1974) 966.
5 J.M. Williams, Argonne National Laboratory Program MET 176X.
6 A. Tulinsky, C.R. Worthington and E. Pignataro, Acta Crystallogr., 12 (1959) 623.
7 H.T. Evans, Acta Crystallogr., 14 (1961) 689.
8 D.T. Cromer and J.T. Waber, Acta Crystallogr., 18 (1965) 104.
9 D.T. Cromer, Acta Crystallogr., 18 (1965) 17.
10 R.F. Stewart, E.R. Davidson and W.T. Simpson, J. Chem. Phys., 42 (1965) 3175.
11 W.R. Busing, K.O. Martin, H.A. Levy, G.M. Brown, R.D. Ellison, W.C. Hamilton, J.A. Ibers, C.K. Johnson and W.E. Theissen, ORXFLS3 Crystallographic Structure Factor Least-Squares Program, Oak Ridge National Laboratory, Oak Ridge, Tenn., 37830, Dec. 1973 version.
12 S.T. Rao, private communication to R.E. Davis (1964).
13 C.K. Johnson, Oak Ridge National Laboratory Program ORTEP, ORNL-3794.
14 L.O. Guggenberger, C.T. Prewitt, P. Meakin, S. Trofimenko and J.P. Jesson, Inorg. Chem., 12 (1973) 508.
15 F.A. Cotton, B.A. Frenz and A. Shaver, Inorg. Chim. Acta, 7 (1973) 161.
16 G. Avitabile, P. Ganis and M. Nemiroff, Acta Crystallogr., B27 (1971) 725.
17 M.R. Churchill, K. Gold and C.E. Maw, Jr., Inorg. Chem., 9 (1970) 1597.
18 F.A. Cotton, M. Jeremic and A. Shaver, Inorg. Chim. Acta, 6 (1972) 543.
19 J.L. Calderon, F.A. Cotton and A. Shaver, J. Organometal. Chem., 37 (1972) 127.
20 C.A. Kosky, P. Ganis and G. Avitabile, Acta Crystallogr., B27 (1971) 1859.
21 D.W.J. Cruickshank, Acta Crystallogr., 2 (1949) 65.

22 A. Robson and M.R. Truter, J. Chem. Soc., (1965) 630.
23 L.N. Hargreaves and M.R. Truter, J. Chem. Soc., A (1969) 2282.
24 J.E. Lydon and M.R. Truter, J. Chem. Soc., (1965) 6899.
25 T.G. Spiro, D.H. Templeton and A. Zalkin, Inorg. Chem., 7 (1968) 2165.
26 M.R. Truter and R.C. Watling, J. Chem. Soc. A, (1967) 1955.
27 H.S. Preston, J.C. Mills and C.H.L. Kennard, J. Organometal. Chem., 14 (1968) 447.
28 V.C. Albano, G.M.B. Ricci and P.L. Bellon, Inorg. Chem., 8 (1969) 2109.
29 J.C. Calabrese, L.F. Dahl, P. Chini, G. Longoni and S. Matinengo, J. Amer. Chem. Soc., 96 (1974) 2614.
30 L. Manojlović-Muir, K.W. Muir and R. Walker, J. Organometal. Chem., 66 (1974) 621.
31 V.G. Albano, P.L. Bellon and M. Sansoni, J. Chem. Soc. D, (1969) 899.
32 M. Orchin and P.J. Schmidt, Coord. Chem. Rev., 3 (1968) 345.
33 H.C. Clark, P.W.R. Corfield, K.R. Dixon and J.A. Ibers, J. Amer. Chem. Soc., 89 (1967) 3360.
34 J.D. Oliver and R.E. Davis, unpublished results.
35 R.S. Osborn and D. Rogers, J. Chem. Soc. Dalton Trans., 9 (1974) 1002.
36 D. Moras, J. Dehand and R. Weiss, C.R. Acad. Sci. France Ser. C, 267 (1968) 1471.
37 J.W. Charmichael, N. Chan, A.W. Cordes, C.K. Fair and D.A. Johnson, Inorg. Chem., 11 (1972) 1117.
38 J.S. Anderson, J.W. Charmichael and A.W. Cordes, Inorg. Chem., 9 (1970) 143.
39 G. Ferraric and D. Viterbo, Acta Crystallogr., B25 (1969) 2066.
40 S. Tromfimenko, J. Amer. Chem. Soc., 91 (1969) 3183.