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Hydrotris(1-pyrazolyl)borates of Chromium(III)

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Abstract

The preparation and characterization of dichloro-(hydrotris(1-pyrazolyl)borato)pyridinechromium(III), $CrCl_2(HB(PYZ)_3)Py$, (Py = pyridine and $HB(PYZ)_3^{-1}$ is the hydrotris(1-pyrazolyl)borato anion) is described. The structure of the compound was determined by single crystal X-ray diffraction. Crystals were monoclinic, $P2_1/c$, $a = 11.603(2)$, $b = 9.845(1)$, $c = 16.095(2)$ Å, $\beta = 96.04(1)°$ with four formula units in the unit cell. Intensities were measured on a Nicolet P3 diffractometer with use of MoKα radiation. The structure was solved by standard methods and refined to $R_1 = 0.0601$, $R_2 = 0.0397$ based on 3142 independent reflections. Bond lengths and angles are normal. The pyridine molecule is oriented such that the plane bisects the angle between the two *cis* pyrazole rings. The synthesis and preparation of the related Cr(III) species $CrCl_2(HB(PYZ)_3)$pyrazole, $Ph_4As[CrCl_3HB(PYZ)_3]$ and $[Cr(HB(PYZ)_3)_2]PF_6$ are described and the evaluation of the $CrCl_2(HB(PYZ)_3)L$ (L = pyridine or pyrazole) species for genotoxicity is discussed.

Introduction

In recent years, a large number of coordination complexes have been found to possess mutagenic and/or anti-cancer properties [1, 2]. Many of these are six coordinate species (including complexes of Sn(IV), Cr(III) and Ti(IV)) that contain two *cis*-halogen groups in concert with four relatively non-labile ligands [3–6]. In an attempt to find new genetically toxic Cr(III) species we have prepared and characterized complexes of the type $CrCl_2(HB(PYZ)_3)L$ (where L = pyridine or pyrazole). The $HB(PYZ)_3^{-1}$ ligand was chosen because it forces the remaining three ligands into a mutually *cis* configuration. The synthesis of the related Cr(III) species $Ph_4As[CrCl_3(HB(PYZ)_3)$ and $[Cr(HB(PYZ)_3)_2]PF_6$ are also described.

Experimental

Infrared spectra were recorded in the range 4000–300 cm^{-1} on a Perkin-Elmer 283 infrared spectrometer. Spectra were calibrated with polystyrene. Electronic spectra were measured with a Pye Unicam SP8-100 UV Spectrophotometer. Magnetic susceptibility measurements were made on methylene chloride solutions via the Evans NMR method with use of a Varian T-60 Spectrometer [7]. Trichlorotris-(tetrahydrofuran)chromium(III) ($CrCl_3(THF)_3$) was prepared by a literature method and potassium hydrotris (1-pyrazolyl)borate($KHB(PYZ)_3$) was purchased from Columbia Organics, Camden, S.C. [8]. Elemental analyses were performed by Atlantic Microlab, Inc., Atlanta, GA.

Preparation of the Complexes

Tetraphenylarsonium trichloro(hydrotris(1-pyrazolyl)borato)chromate(III) trihydrate

To a solution of 0.20 g of $CrCl_3(THF)_3$ (0.54 mmol) in methylene chloride (20 ml), 0.14 g of $KHB(PYZ)_3$ (0.55 mmol) was added. The green slurry was stirred for 20 min. and the solvent was then removed *in vacuo*. The reaction mixture was dissolved in 2.0 ml of a methanol/12 N HCl mixture (2:1 v/v) which was added dropwise to a stirred solution containing 0.21 g of tetraphenylarsonium chloride hydrate in 1 N HCl (20 ml). The resulting green precipitate was washed with 1 N HCl (2.0 ml) and 2-propanol (2 × 10 ml) and dried *in vacuo*. The product was recrystallized by slow evaporation of a methylene chloride/2-propanol solution yielding green crystals of $Ph_4As[CrCl_3HB(PYZ)_3]\cdot 3H_2O$, 0.11 g, 0.14 mmol, 25% based on Cr. *Anal.* Calcd. for $C_{33}H_{36}N_6Cl_3BO_3AsCr$: C, 49.0; H, 4.5; N, 10.4; Cl, 13.2. Found: C, 49.4; H, 4.1; N, 10.2; Cl, 13.0.

Electronic spectrum (acetonitrile): 606 nm ($\epsilon = 48$ l mol^{-1} cm^{-1}), 446(222), 272(sh), 264(sh). IR (KBr): 3520(m), 3140(w), 3085(w), 3060(w), 2490(m), 1635(s), 1580(w), 1500(s), 1480(m), 1405(vs), 1390(s), 1310(s), 1185(m), 1160(w), 1115(s), 1095(w), 1075(s), 1070(sh), 1045(vs), 1020(sh), 990(s),

0020-1693/85/$3.30

980(m), 815(w), 790(m), 740(s), 705(s), 685(s), 655(s), 615(s), 475(m), 460(s), 375(s), 340(vs), 330(sh). Magnetic moment: μ_{eff} (300 K): 3.7 B.M.

Dichloro(hydrotris(1-pyrazolyl)borato)pyridine chromium(III) hydrate

To a solution of 0.20 g of $CrCl_3(THF)_3$ in methylene chloride (20 ml), 0.14 g of $KHB(PYZ)_3$ was added. The green slurry was stirred for 20 min. and the solvent was then removed *in vacuo*. The resulting green solid was then dissolved in acetonitrile (25.0 ml), pyridine (5.0 ml) was added and the reaction mixture refluxed for 2 h. Solvent was removed *in vacuo* and the product dissolved in 30 ml of an acetone/water mixture (1:1 v/v). Slow evaporation of this solution yielded red-violet crystals of $CrCl_2(HB(PYZ)_3Py \cdot H_2O$, 0.08 g, 0.20 mmol, 37% based on Cr. *Anal.* Calcd for $C_{14}H_{17}N_7Cl_2BOCr$: C, 38.8; H, 4.0; N, 22.7; Cl, 16.4. Found: C, 38.4; H, 3.6; N, 22.5; Cl, 16.4. The crystals used in the X-ray diffraction study were prepared by slow evaporation of a methylene chloride/toluene solution. The complex can also be prepared in 78% yield by refluxing $Ph_4As[CrCl_3(HB(PYZ)_3)]$ in an acetonitrile/pyridine solution. Electronic spectrum (acetonitrile): 554(48), 412(104), IR(KBr): 3500(w), 3135(m), 3120(m), 2515(m), 1610(s), 1500(s), 1485(m), 1450(s), 1425(w), 1405(vs), 1390(s), 1315(sh), 1310(vs), 1220(sh), 1205(vs), 1185(m), 1155(w), 1115(s), 1095(m), 1070(s), 1045(vs), 1015(m), 985(m), 895(m), 810(m), 790(s), 775(vs), 760(vs), 720(sh), 710(s), 690(s), 655(s), 635(m), 615(s), 610(sh), 440(m), 395(s), 355(vs), 325(s). Magnetic moment: μ_{eff} (300 K) = 3.7 B.M.

Dichloro(hydrotris(1-pyrazolyl)borato)pyrazole chromium(III) hydrate

This complex was prepared in 35% (starting with $CrCl_3(THF)_3$) yield similarly to $CrCl_2(HB(PYZ)_3)Py$ using pyrazole (0.40 g, 5.9 mmol) instead of pyridine. It can also be synthesized in 65% yield using $Ph_4As[CrCl_3(HB(PYZ)_3)]$. *Anal.* Calcd for $C_{12}H_{16}N_8Cl_2BOCr$: C, 34.1; H, 3.8; N, 26.6; Cl, 16.8. Found: C, 34.2; H, 3.6; N, 26.5; Cl, 16.8.

Electronic spectrum (acetonitrile): 546(49), 409(83).

IR(KBr): 3300(m), 3140(w), 3120(w), 3105(w), 2515(w), 1495(m), 1470(m), 1405(s), 1385(m), 1345(m), 1305(sh), 1205(s), 1185(sh), 1160(w), 1125(m), 1120(m), 1110(m), 1070(m), 1055(s), 1045(s), 980(m), 785(sh), 775(s), 760(sh), 755(s), 715(w), 655(w), 650(m), 640(w), 605(m), 385(m), 360(m), 335(m), 315(w). Magnetic moment: μ_{eff} (300 K) = 3.7 B.M.

Bis(hydrotris(1-pyrazolyl)borato)chromium(III) hexafluorophosphate

A solution of $CrCl_3 \cdot 6H_2O$ (0.12 g, 0.45 mmol) in methanol (25 ml) was heated to reflux with 0.1 g of granular Zn. As soon as the solution started to reflux, $KHB(PYZ)_3$ (0.48, 1.9 mmol) was added in one batch. After refluxing 30 min. the reaction mixture was filtered and solvent removed *in vacuo*. The resulting solid was dissolved in acetone (30 ml) and water was added until the solution was cloudy. The reaction mixture was again filtered and NH_4PF_6 (0.5 g) in water (5 ml) was added to the filtrate precipitating a yellow orange solid. This material was collected and recrystallized once by slow evaporation of an acetone/water solution and once by slow evaporation of an acetone/2-propanol solution, yielding orange crystalline $[Cr(HB(PYZ)_3)_2]PF_6$, 0.10 g, 0.16 mmol, 36% yield based on Cr. *Anal.* Calcd. for $C_{18}H_{20}N_{12}B_2PF_6Cr$: C, 34.7; H, 3.2; N, 27.0. Found: C, 34.8; H, 3.3; 27.0.

Electronic spectrum (acetonitrile): 456(35), 370(sh).

IR(KBr): 3170(m), 3155(s), 3135(m), 2510(s), 1515(m), 1505(s), 1440(w), 1405(vs), 1390(s), 1305(vs), 1215(s), 1205(s), 1185(s), 1120(s), 1110(s), 1100(m), 1075(s), 1055(vs), 995(m), 985(m), 920(w), 900(m), 885(s), 840(vs), 820(sh), 810(sh), 780(m), 765(vs), 730(m), 715(sh), 710(sh), 700(s), 660(m), 645(sh), 640(m), 610(m), 600(m), 555(s), 420(s), 370(m), 360(m), 340(w). Magnetic moment: μ_{eff} (300 K) = 3.7 B.M.

Collection of the X-ray Data

A violet prismatic crystal of $CrCl_2Py(HB(PYZ)_3)$ was selected for X-ray studies after examination for perfection under a polarizing microscope. Precession photographs revealed the symmetry of the crystal, and unit cell parameters were obtained from least squares fit of χ, ϕ, and ω for 15 reflections in the range $17.8° < 2\theta < 25.5°$, recorded on a Nicolet P3 diffractometer with use of graphite monochromatized MoKα radiation (λ 0.71069 Å at 22 °C). Crystal data and other numbers related to data collection are summarized in Table I.

Density measurements were obtained by flotation in carbon tetrachloride–hexane. Intensities were also measured on the Nicolet P3 diffractometer with use of a coupled θ(crystal)–2θ(counter) scan. The methods of selection of scan rates and initial data treatment have been described [9, 10]. Corrections were made for Lorentz polarisation effects but not for absorption. This will give a maximum error in F_o of 5.7%.

Solution of the Structure

The position of the chromium atom was determined from a three-dimensional Patterson map and subsequent cycles of refinement and electron density difference syntheses revealed all the atoms. At this stage the temperature factors of all non-hydrogen atoms were made anisotropic and all coordinates were refined and the function minimized was $\Sigma w(|F_o| -$

TABLE I. Crystal Data.

Compound name	Dichloro(hydrotris(1-pyrazolyl)borato)pyridinechromium(III)
Compound formula	$C_{14}H_{15}BCl_2CrN_7$
Formula weight	415.07
Crystal size (mm)	0.16 × 0.26 × 0.56 (mounting axis)
Systematic absences	h0l, l = 2n + 1, 0k0, k = 2n + 1
Space group	$P2_1/c$ (No. 14)
Unit cell (Å, deg)	a = 11.603(2), b = 9.845(1), c = 16.095(2), β = 96.04(1)
Volume (Å^3)	1828.6(5)
Z	4
ρ_{calc}, ρ_{obs} (g cm^{-3})	1.508, 1.50(1)
Max 2θ, reflctns. meas.	55°, h, k, ±l
Standard reflctns. (e.s.d. %)	3 0 6, 1.6; 2 0 –8, 1.6
Temp (°C)	22
No. of independent reflctns.	4224
No. with $I > 2.5\sigma_I$ (used)	3142
No. with $2.5\sigma_I > I > 0$	574
No. with $I < 0$	508
Final R_1, R_2^{a}	0.0601, 0.0397
Final shift/error max(ave)	0.190, (0.021)
Secondary extinction (χ)	0.00022
Final difference map	
Highest peak, lowest valley (eÅ^{-3})	0.42, –0.40
Weighting	$(\sigma_F^2 + 0.000060F^2)^{-1}$
Error in an observation of unit wt.	1.351
No. of variables	287

$^aR_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)^{1/2}$.

TABLE II. Atomic Positional Parameters and Temperature Factors (Å^2).

Atom	×10^4			×10^3
	x	y	z	U_{eq}*
Cr	2562.7(5)	6243.2(5)	3765.2(3)	28(3)
Cl(1)	2266(1)	8547(1)	3568(1)	46(6)
Cl(2)	3219(1)	6547(1)	5166(1)	43(5)
N(1)	871(2)	5991(3)	3979(2)	32(2)
N(2)	211(2)	5014(3)	3573(2)	34(2)
C(1)	174(3)	6658(4)	4457(2)	38(2)
C(2)	–918(3)	6116(4)	4353(3)	45(3)
C(3)	–877(3)	5087(4)	3795(3)	43(3)
N(1′)	2705(2)	4157(3)	3866(2)	33(2)
N(2′)	1812(2)	3360(3)	3523(2)	34(2)
C(1′)	3475(4)	3324(4)	4290(2)	42(2)
C(2′)	3076(4)	1998(4)	4218(3)	52(3)
C(3′)	2034(4)	2055(4)	3745(2)	44(3)
N(1″)	2031(2)	5871(3)	2525(2)	33(2)
N(2″)	1257(2)	4856(3)	2307(2)	37(2)
C(1″)	2309(3)	6408(4)	1801(2)	43(2)
C(2″)	1732(4)	5745(4)	1129(3)	50(3)
C(3″)	1075(4)	4777(4)	1468(3)	49(3)
B	770(4)	4010(4)	3005(3)	38(2)
N	4280(2)	6419(3)	3462(2)	34(2)
C(4)	4936(3)	7477(4)	3741(2)	43(2)
C(5)	6035(4)	7682(5)	3528(3)	56(4)
C(6)	6500(4)	6754(6)	3033(3)	64(4)
C(7)	5857(4)	5657(6)	2749(3)	64(4)
C(8)	4753(4)	5518(4)	2981(2)	46(3)

$*U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33} + 2U_{13}\cos\beta)$.

$|F_c|)^2$. Refinement was terminated when the maximum shift/error dropped to 0.2 Scattering curves were taken from the International Tables [11]. The atom parameters are listed in Tables II and III.

Initial data treatment used programs from the X-RAY package [12]. The structures were solved using programs from SHELX [13]. The least squares planes program was NRC-22 [14] and diagrams were prepared using ORTEP-II [15]. All calculations were carried out on Cyber 170/730 and 170/815 computers.

Results and Discussion

The new Cr(III) anion, $[CrCl_3(HB(PYZ)_3]^{-1}$ has been prepared by the reaction of $CrCl_3(THF)_3$ and $KHB(PYZ)_3$ in methylene chloride and isolated as its tetraphenylarsonium ($[Ph_4As]^+$) salt. This complex reacts with the ligands L (L = pyridine or pyrazole) in refluxing acetonitrile to yield new complexes of the type $CrCl_2(HB(PYZ)_3L$. $KHB(PYZ)_3$ also reacts with $CrCl_3\cdot6H_2O$ in refluxing methanol in the presence of granular Zn to form the Cr(III) cation $[Cr(HB(PYZ)_3)_2]^+$, which can be isolated as its hexafluorophosphate salt. This preparation is very similar to the one used by Gillard to form species of the type $[CrL_3]^{3+}$ (L = ethylenediamine) [16]. The $[Cr(HB(PYZ)_3)_2]^+$ cation was mentioned in a 1971 review article by Trofimenko but no synthetic details or

TABLE III. Selected Interatomic Distances (Å) and Angles (deg).

Cr–Cl(1)	2.311(1)	Cr–N(1)	2.043(3)	Cr–N(1′)	2.065(3)
Cr–Cl(2)	2.312(1)	Cr–N(1″)	2.060(3)	Cr–N	2.108(3)
N(1)–N(2)	1.354(3)	N(1′)–N(2′)	1.368(4)	N(1″)–N(2″)	1.365(3)
N(1)–C(1)	1.345(4)	N(1′)–C(1′)	1.345(4)	N(1″)–C(1″)	1.349(4)
C(1)–C(2)	1.369(5)	C(1′)–C(2′)	1.385(5)	C(1″)–C(2″)	1.375(5)
C(2)–C(3)	1.358(5)	C(2′)–C(3′)	1.361(6)	C(2″)–C(3″)	1.369(6)
C(3)–N(2)	1.350(4)	C(3′)–N(2′)	1.351(4)	C(3″)–N(2″)	1.347(5)
N(2)–B	1.537(5)	N(2′)–B	1.534(5)	N(2″)–B	1.552(5)
N–C(4)	1.340(4)	C(4)–C(5)	1.379(6)	C(5)–C(6)	1.360(6)
N–C(8)	1.333(4)	C(8)–C(7)	1.379(6)	C(7)–C(6)	1.364(7)
Cl(1)–Cr–Cl(2)	94.2(0)	Cl(1)–Cr–N	91.1(1)	Cl(1)–Cr–N(1)	90.6(1)
Cl(1)–Cr–N(1′)	175.0(1)	Cl(1)–Cr–N(1″)	90.9(1)	Cl(2)–Cr–N	89.8(1)
Cl(2)–Cr–N(1)	94.1(1)	Cl(2)–Cr–N(1′)	92.1(1)	Cl(2)–Cr–N(1″)	174.8(1)
N–Cr–N(1)	175.7(1)	N–Cr–N(1′)	91.7(1)	N–Cr–N(1″)	89.1(1)
N(1)–Cr–N(1′)	86.3(1)	N(1)–Cr–N(1″)	86.9(1)	N(1′)–Cr–N(1″)	85.0(1)
Cr–N(1)–N(2)	120.7(2)	Cr–N(1′)–N(2′)	119.2(2)	Cr–N(1″)–N(2″)	120.1(2)
Cr–N(1)–C(1)	133.1(2)	Cr–N(1′)–C(1′)	133.6(3)	Cr–N(1″)–C(1″)	133.9(3)
N(2)–N(1)–C(1)	106.2(3)	N(2′)–N(1′)–C(1′)	106.8(3)	N(2″)–N(1″)–C(1″)	106.0(3)
N(1)–C(1)–C(2)	110.2(4)	N(1′)–C(1′)–C(2′)	109.5(4)	N(1″)–C(1″)–C(2″)	110.6(4)
C(1)–C(2)–C(3)	105.9(4)	C(1′)–C(2′)–C(3′)	106.1(4)	C(1″)–C(2″)–C(3″)	105.2(4)
C(2)–C(3)–N(2)	108.3(3)	C(2′)–C(3′)–N(2′)	108.7(4)	C(2″)–C(3″)–N(2″)	109.0(4)
C(3)–N(2)–N(1)	109.4(3)	C(3′)–N(2′)–N(1′)	108.9(3)	C(3″)–N(2″)–N(1″)	109.2(3)
C(3)–N(2)–B	131.1(3)	C(3′)–N(2′)–B	131.1(3)	C(3″)–N(2″)–B	131.6(3)
N(1)–N(2)–B	119.4(3)	N(1′)–N(2′)–B	120.0(3)	N(1″)–N(2″)–B	119.2(3)
N(2)–B–N(2′)	107.6(3)	N(2)–B–N(2″)	107.1(3)	N(2′)–B–N(2″)	106.9(3)
Cr–N–C(4)	120.3(3)	Cr–N–C(8)	122.5(3)	C(4)–N–C(8)	117.3(3)
N–C(4)–C(5)	122.8(4)	C(4)–C(5)–C(6)	119.0(4)	C(5)–C(6)–C(7)	119.5(4)
N–C(8)–C(7)	122.8(4)	C(8)–C(7)–C(6)	118.6(5)		

characterizations were included [17]. The analogous Cr(II) species was recently prepared by Dapporto, *et al.* [18]. All of these complexes have been characterized by elemental analysis, IR and electronic spectroscopy and magnetic susceptibility. In addition, the structure of $CrCl_2(HB(PYZ)_3)Py$ was determined by X-ray crystallography (*vide infra*).

In their infrared spectra, all of the complexes have many bands in the range 3200–300 cm^{-1} caused by the $HB(PYZ)_3^{-1}$ ligand [19]. The intense peaks at 340 cm^{-1} and 330 cm^{-1} found in the IR spectrum of $Ph_4As[CrCl_3(HB(PYZ)_3)]$ are assignable to ν(Cr–Cl). Two peaks are consistent with the molecule having C_{3v} symmetry. In their visible spectra in acetonitrile solution all of the complexes have two bands caused by the expected ${}^4A_{2g} \rightarrow {}^4T_{2g}$ and ${}^4A_{2g} \rightarrow {}^4T_{1g}$ d–d transitions of an octahedral Cr(III) complex [20]. The magnetic susceptibilities of the complexes (3.7 B.M. at 300 K) are consistent with their formulation as monomeric Cr(III) species [21].

An interesting aspect of the reaction of $[CrCl_3(HB(PYZ)_3)]^{-1}$ with pyridine is the ease with which it occurs. This is in marked contrast to the lack of reaction of *mer*-$CrCl_3(Py)_3$ with boiling pyridine [22]. This lack of reaction is hardly surprising since the steric needs of aromatic amine rings bound to metals are highly restrictive [23]. One cannot obtain even the expected product, [*trans*-$Cr(Py)_4Cl_2]^+$, which has been reported, although no synthetic details were given [24]. In particular, one would not expect to obtain a [*cis*-$Cr(Py)_4Cl_2]^+$ cation which is the analogue of the complex $CrCl_2(HB(PYZ)_3Py$ reported here. The complex exists because the steric requirements for five membered rings are less than those of pyridine and, because the rings are bound to boron, they are bent away from the 'normal' octahedral positions as shown by the reduction of the N–B–N angles (85.0(1)°–86.9(1)°) from 90°. Further, the pyrazole rings are oriented such that the

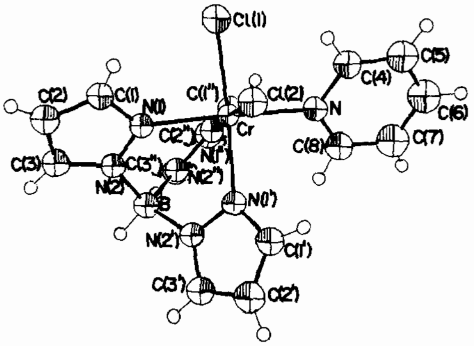

Fig. 1. The molecule $CrCl_2(HB(PYZ)_3)Py$ showing the atom numbering.

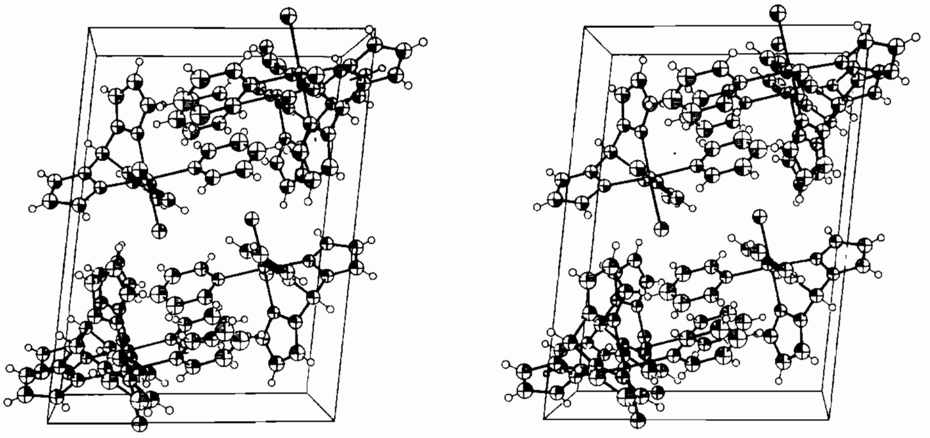

Fig. 2. The packing of the molecules within the unit cell *a* and *c** are parallel to the bottom and sides of the page and the view is down *b*.

pyridine ring can bisect the angle between the two pyrazole rings to which it is *cis.* This means that the pyridine ring is roughly coplanar with the trans pyrazole ring (dihedral angle 9.5(4)°) and all other inter-ring acute dihedral angles are roughly 60° (range 56.9(4)–63.7(4)°). Pyridine and the pyrazole rings are planar and the boron and chromium atoms lie close to the plane of each bound ring (range 0.020(4)–0.089(1) Å) except for ring N(1′)N(2′)C(1)C(2′)C(3′), where the chromium atom lies 0.206(1) Å out of the plane. There is no obvious reason why only this ring shows the effect; on symmetry grounds the N(1′)N(2′)C(1)C(2′)C(3′) ring should show the same effect but the corresponding distance is only 0.068(1) Å. The cause may be crystal packing. The packing is shown in Fig. 2 and as can be seen there is no strong interaction between the molecules. In particular there is no evidence of ring–ring π–π interactions. The Cr–Cl and Cr–N bond lengths in $\mathrm{CrCl_2(HB(PYZ)_3)Py}$ are similar to those in other octahedral Cr(III) complexes contaning chloride and N donor ligands, *e.g.* *mer*-trichloro(dimethylformamide)(1,10-phenanthroline)chromium(III) and *fac*-trichloro(diethylenetriamine)chromium(III) [25, 26]. The bond lengths and angles found in the $\mathrm{HB(PYZ)_3}^{-1}$ ligand are typical of those found in other metal complexes of that ion [27, 28].

Preliminary work indicates that neither $\mathrm{CrCl_2(HB(PYZ)_3)Py}$ or $\mathrm{CrCl_2(HB(PYZ)_3)}$(Pyrazole) are active in the Ames assay for mutagenicity using the *Salmonella* strains TA98 and TA102 [29]. This result is interesting in light of recent work by Warren *et al.* who have shown that cationic complexes of the type [*Cis*-$\mathrm{CrL_2Cl_2}$]$^{+1}$ (L = 2,2′-bipyridine or 1,10-phenanthroline) are mutagenic while the analogous complex where L = ethylenediamine is not [4]. Many cationic complexes of 2,2′-bipyridine and 1,10-phenanthroline are known to intercalate DNA and DNA intercalation is a known cause of mutagenesis [30–32]. Although the $\mathrm{CrCl_2(HB(PYZ)_3)L}$ complexes have the same *cis*-$\mathrm{CrCl_2N_4}$ (N = an aromatic amine ligand) configuration as the mutagenic Cr(III) species they cannot act as DNA intercalators because of the structural constraints of the ligands. The above results suggest that the active Cr(III) complexes are mutagenic because of their ability to intercalate DNA.

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