

## Vanadium(II) and Chromium(II) Complexes with Poly(1-pyrazolyl)borate Ligands. Crystal and Molecular Structures of Potassium Tris[dihydrobis(1-pyrazolyl)borato]vanadium(II) Monoalcoholate and Bis[dihydrobis(1-pyrazolyl)borato]chromium(II)

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Received October 27, 1977

The binding capabilities of polypyrazolylborate ligands toward chromium(II) and vanadium(II) have been studied. Some complexes of these bivalent metals have been isolated and characterized by means of their electronic and magnetic properties. The vanadium(II) and chromium(II) complexes with the ligands hydrotris(1-pyrazolyl)borate ( $\text{HB}(\text{pz})_3^-$ ) and tetrakis(1-pyrazolyl)borate ( $\text{B}(\text{pz})_4^-$ ) have the general formulas  $[\text{M}(\text{HB}(\text{pz})_3)_2]$  and  $[\text{M}(\text{B}(\text{pz})_4)_2]$  ( $\text{M} = \text{Cr}, \text{V}$ ) and are assigned an octahedral geometry on the basis of their electronic spectra. The complexes with the ligand dihydrobis(1-pyrazolyl)borate ( $\text{H}_2\text{B}(\text{pz})_2^-$ ) have the formulas  $[\text{Cr}(\text{H}_2\text{B}(\text{pz})_2)_2]$  and  $\text{K}[\text{V}(\text{H}_2\text{B}(\text{pz})_2)_3] \cdot \text{C}_2\text{H}_5\text{OH}$ . Their crystal structures have been determined by means of x-ray diffraction methods. The compound  $[\text{Cr}(\text{H}_2\text{B}(\text{pz})_2)_2]$  crystallizes in orthorhombic space group  $Pbca$  with  $a = 18.076$  (5) Å,  $b = 14.307$  (4) Å,  $c = 6.130$  (4) Å,  $Z = 4$ , and a final discrepancy factor of  $R = 0.032$ . The coordination about the chromium atom is square planar with four nitrogen atoms from two ligand molecules at a distance of 2.062 (4) Å (average) from the metal. The complex  $\text{K}[\text{V}(\text{H}_2\text{B}(\text{pz})_2)_3] \cdot \text{C}_2\text{H}_5\text{OH}$  crystallizes in the monoclinic space group  $C2/c$  with  $a = 27.626$  (7) Å,  $b = 14.332$  (5) Å,  $c = 18.203$  (5) Å,  $\beta = 123.38$  (10)°,  $Z = 8$ , and a final discrepancy factor of  $R = 0.063$ . The structure consists of discrete potassium ions and tris[dihydrobis(1-pyrazolyl)borato]vanadium(II) anions with a slightly distorted octahedral geometry. The mean V-N bond distance is 2.169 (19) Å. This is the first example of a tris(polypyrazolylborate)metal complex.

### Introduction

The polypyrazolylborate ligands were first described by Trofimenko about a decade ago,<sup>1</sup> but they are still of great interest in coordination chemistry. This new class of ligands, by virtue of their steric and electronic properties, has proved to be capable of forming stable complexes with most transition-metal atoms.<sup>2</sup> In some cases these ligands stabilize otherwise unstable linkages between metal atoms and small molecules, as for example  $\text{Cu-CO}^3$  and  $\text{Pt-C}_2\text{H}_2$ .<sup>4</sup>

Concerning the first-row transition metals, a variety of complexes of manganese through zinc has been described with the ligands  $(\text{H}_n\text{B}(\text{pz})_{4-n})^-$  ( $n = 0, 1, 2$ ).<sup>2</sup> The complexes with bivalent metals are neutral and monomeric, with a metal to ligand ratio of 1:2; their geometry is octahedral, tetrahedral, or square planar.

Dimeric complexes of copper(I) have also been reported with a pyrazole ring symmetrically bridging two metal ions.<sup>5</sup>

The information so far reported about the behavior of these ligands toward first-row transition metals lying to the left of manganese is still limited.<sup>6</sup> This deficiency as well as the desire to add a new contribution to the still scarcely investigated coordination chemistry of vanadium(II) and chromium(II), prompted us to try to prepare vanadium(II) and chromium(II) complexes with the ligands  $(\text{H}_n\text{B}(\text{pz})_{4-n})^-$  ( $n = 0, 1, 2$ ). The complexes have the formulas  $[\text{ML}_2]$  ( $\text{M} = \text{Cr}, \text{V}$ ,  $\text{L} = \text{HB}(\text{pz})_3, \text{B}(\text{pz})_4$ ;  $\text{M} = \text{Cr}$ ,  $\text{L} = \text{H}_2\text{B}(\text{pz})_2$ ) and  $\text{K}[\text{V}(\text{H}_2\text{B}(\text{pz})_2)_3] \cdot \text{C}_2\text{H}_5\text{OH}$ . All these complexes have been characterized with the usual methods. The x-ray crystal structures of  $[\text{Cr}(\text{H}_2\text{B}(\text{pz})_2)_2]$  and  $\text{K}[\text{V}(\text{H}_2\text{B}(\text{pz})_2)_3] \cdot \text{C}_2\text{H}_5\text{OH}$  have been determined. To date the number of crystal structures of complexes of vanadium(II) and chromium(II) is very limited, mainly due to the extreme sensitivity of these ions toward air oxidation.

### Experimental Section

Anhydrous vanadium(II)<sup>7</sup> and chromium(II)<sup>8</sup> halides and  $\text{K}(\text{HB}(\text{pz})_3)$ ,  $\text{K}(\text{B}(\text{pz})_4)$ , and  $\text{K}(\text{H}_2\text{B}(\text{pz})_2)$  salts<sup>1</sup> were synthesized as already reported.

All preparative operations were carried out in an atmosphere of dry nitrogen using deoxygenated solvents.

$[\text{V}(\text{HB}(\text{pz})_3)_2]$ ,  $[\text{V}(\text{B}(\text{pz})_4)_2]$ . To a hot solution of the appropriate ligand (2 mmol) in ethanol (20 mL), a hot solution of  $\text{VBr}_2$  (1 mmol) in 10 mL of ethanol was added. A mixture of  $\text{KBr}$  and the crystalline

complexes was readily obtained. The mother liquor was then eliminated and the precipitate washed several times by decantation with water and subsequently with ethanol and petroleum ether. The complexes were recrystallized using  $\text{CH}_2\text{Cl}_2$  and  $\text{C}_2\text{H}_5\text{OH}$ . Anal. Calcd for  $\text{C}_{18}\text{H}_{20}\text{B}_2\text{N}_{12}\text{V}$ : C, 45.31; H, 4.23; N, 35.20. Found: C, 45.6; H, 4.33; N, 35.3. Calcd for  $\text{C}_{24}\text{H}_{24}\text{B}_2\text{N}_{16}\text{V}$ : C, 47.32; H, 3.97; N, 36.79. Found: C, 47.0; H, 3.90; N, 36.8.

In the following preparations reactants and solvents were employed in the amounts indicated above.

$\text{K}[\text{V}(\text{H}_2\text{B}(\text{pz})_2)_3] \cdot \text{C}_2\text{H}_5\text{OH}$ . Warm solutions of the reactants in ethanol (the ligand being in excess to the stoichiometric ratio) were mixed and the resulting solution was concentrated by heating. Crystals of the complex precipitated by adding dibutyl ether to the solution. The complex was recrystallized from  $\text{C}_2\text{H}_5\text{OH}$  and  $\text{O}(\text{C}_4\text{H}_9)_2$ . This complex crystallizes with a slightly variable and not fully reproducible amount of solvent (ca. one molecule), depending on the rate of crystallization. Anal. Calcd for  $\text{C}_{20}\text{H}_{30}\text{B}_3\text{KN}_{12}\text{OV}$ : C, 41.63; H, 5.23; N, 29.13. Found: C, 42.5; H, 5.21; N, 28.8.

$[\text{Cr}(\text{HB}(\text{pz})_3)_2]$ ,  $[\text{Cr}(\text{B}(\text{pz})_4)_2]$ . An ethanolic solution of the  $[(\text{C}_2\text{H}_5)_4\text{N}]^+$  salt of the appropriate ligand (obtained by mixing  $[(\text{C}_2\text{H}_5)_4\text{N}]\text{Br}$  and the appropriate ligand and by the elimination of the solid  $\text{KBr}$  by filtration) was used. To a warm ethanolic solution of the appropriate ligand, a warm ethanolic solution of  $\text{CrBr}_2$  was added. Crystals of the complexes immediately precipitated. These were washed several times with cold ethanol and petroleum ether. Anal. Calcd for  $\text{C}_{18}\text{H}_{20}\text{B}_2\text{CrN}_{12}$ : C, 45.22; H, 4.23; Cr, 10.88; N, 35.14. Found: C, 45.0; H, 4.57; Cr, 10.7; N, 34.6. Calcd for  $\text{C}_{24}\text{H}_{24}\text{B}_2\text{CrN}_{16}$ : C, 47.24; H, 3.96; Cr, 8.53; N, 36.72. Found: C, 46.8; H, 4.09; Cr, 8.25; N, 36.9.

$[\text{Cr}(\text{H}_2\text{B}(\text{pz})_2)_2]$ . Warm solutions in ethanol of the reactants in the stoichiometric ratio were mixed, and the solid  $\text{KBr}$ , which formed, was eliminated by filtration. The volume of the solution was then reduced on boiling until crystals were formed. These were washed as above. All the chromium(II) complexes could not be recrystallized due to their easy decomposition in solution, in spite of the care taken to prevent oxidation. Anal. Calcd for  $\text{C}_{12}\text{H}_{16}\text{B}_2\text{CrN}_8$ : C, 41.67; H, 4.65; Cr, 15.03; N, 32.39. Found: C, 40.8; H, 4.66; Cr, 14.5; N, 31.9.

The complexes were filtered on a sintered-glass frit and dried by standing in a stream of dry nitrogen at 100 °C. Magnetic and spectrophotometric measurements were performed with the apparatus already described on samples contained in suitable airtight containers (Gouy tube, UV cells) filled in a drybox under inert atmosphere.<sup>9</sup>

**X-Ray Study of  $[\text{Cr}(\text{H}_2\text{B}(\text{pz})_2)_2]$ .** Crystals suitable for diffraction crystallize as red-orange hexagonal prisms, one of which, with maximum dimensions along direct crystal axes of  $0.08 \times 0.18 \times 0.25$  mm, was chosen for the preliminary work of orientation, for lattice constant and space group determination, and finally for data collection. These routines<sup>10</sup> were executed by a Philips PW 1100 automated

**Table I.** Atomic<sup>a</sup> Parameters for the Structure of [Cr(H<sub>2</sub>B(pz)<sub>2</sub>)<sub>2</sub>] (All Quantities × 10<sup>3</sup>)<sup>b</sup>

Atom	x	y	z	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>12</sub>	U <sub>13</sub>	U <sub>23</sub>
Cr1	0	0	0	288 (7)	376 (7)	434 (8)	-38 (7)	62 (7)	-112 (8)
N1	205 (2)	-875 (3)	-2590 (8)	166 (29)	382 (27)	386 (33)	12 (22)	41 (27)	-34 (26)
N2	908 (2)	-1180 (3)	-3013 (8)	409 (34)	310 (27)	277 (32)	-37 (25)	-2 (27)	-52 (27)
N3	1031 (2)	606 (3)	-384 (8)	312 (29)	304 (27)	487 (38)	12 (24)	13 (27)	-110 (28)
N4	1599 (2)	110 (3)	-1229 (7)	252 (26)	378 (28)	363 (27)	-49 (31)	38 (23)	38 (31)
C1	-200 (3)	-1148 (4)	-4301 (10)	289 (36)	358 (34)	431 (46)	-37 (29)	-71 (33)	-1 (32)
C2	226 (4)	-1633 (4)	-5786 (9)	639 (49)	379 (35)	240 (40)	-50 (34)	-33 (36)	-107 (30)
C3	922 (3)	-1627 (3)	-4902 (11)	432 (41)	355 (33)	351 (42)	-41 (28)	43 (39)	-39 (42)
C4	1244 (3)	1504 (4)	-426 (11)	352 (36)	337 (35)	634 (51)	-7 (30)	-81 (38)	-65 (38)
C5	1934 (3)	1586 (4)	-1344 (11)	331 (42)	464 (40)	703 (51)	-138 (32)	-30 (39)	146 (40)
C6	2145 (3)	687 (5)	-1820 (10)	307 (37)	600 (44)	455 (51)	-19 (37)	65 (33)	104 (38)
B1	1537 (4)	-972 (4)	-1389 (12)	441 (49)	425 (43)	477 (52)	109 (37)	-35 (42)	-31 (45)

<sup>a</sup> The form of the thermal ellipsoid is  $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + \dots)]$ . <sup>b</sup> *F* relative scale factor = 22 018.

diffractometer. The compound was found to be orthorhombic with space group *Pbca* and with cell parameters  $a = 18.076$  (5),  $b = 14.307$  (4), and  $c = 6.130$  (3) Å using Mo K $\alpha$  radiation, monochromatized by a flat graphite crystal ( $\lambda$  0.7093 Å). The values of the lattice constants were obtained by least-squares refinement of 16 reflections automatically found and centered by the machine. The density value obtained by flotation is in agreement with the calculated value for four molecules of formula C<sub>12</sub>H<sub>16</sub>N<sub>8</sub>B<sub>2</sub>Cr in the unit cell ( $d_{\text{measd}} = 1.43$ ,  $d_{\text{calcd}} = 1.449$  g/cm<sup>3</sup>). The crystal chosen had faces of the forms {100}, {010}, {012}. Intensity data were collected using the  $\theta$ - $2\theta$  scan technique with a scan range of 0.70° in  $\theta$  at a scan rate of 0.07°/s. The background measuring time at each side of the scan was determined as scan time/2. A total of 906 independent reflections were measured in the  $\theta$  range 3–20°. The intensities of three standard reflections, measured every 90 min, showed deviations from the mean in no case greater than 5%. Data processing was carried out as previously described,<sup>11</sup> a value of 0.03 being assigned to the instability factor *R*, used in the formula to derive the  $\sigma(I)$ 's. Only 501 reflections had intensities greater than three times their standard deviations and were considered observed. The usual corrections were carried out including one for absorption. The transmission factors varied between 0.89 and 0.95 using a linear absorption coefficient  $\mu = 7.12$  cm<sup>-1</sup>.

A Patterson map was used to locate the positions of the Cr and N atoms in the asymmetric unit. The other nonhydrogen atoms were found in a subsequent *F<sub>o</sub>* Fourier synthesis. Refinement of the structure was by full-matrix least-squares methods. The course of the refinement, as indicated by values of *R* and *R<sub>w</sub>* in parentheses, was as follows: complete isotropic refinement of all the nonhydrogen atoms (0.103, 0.109), three cycles of anisotropic refinement, including a fixed contribution for the eight hydrogen atoms and the effect of anomalous dispersion for Cr species (0.032, 0.044). The pyrazole ring C–H distances were assumed to be 0.95 Å, whereas the B–H distances were fixed at 1.05 Å. The isotropic thermal parameters of the hydrogen atoms were fixed about 1 Å<sup>2</sup> greater than those of their bonded heavier atoms.

The final positional and thermal parameters obtained from the last cycle of least-squares refinement are given in Table I along with their standard deviations as estimated from the inverse matrix.

**X-Ray Study of K[V(H<sub>2</sub>B(pz)<sub>2</sub>)<sub>3</sub>]·C<sub>2</sub>H<sub>5</sub>OH.** A green crystal of the compound with a parallelepiped shape was chosen for diffraction studies. Its dimensions were 0.40 × 0.04 × 0.04 mm. A preliminary study of the lattice enabled us to determine the direct cell parameters as  $a = 27.626$  (7) Å,  $b = 14.332$  (5) Å,  $c = 18.203$  (5) Å, and  $\beta = 123.38$  (10)°, using Mo K $\alpha$  radiation. The monoclinic space group *C2/c* was assigned to the structure. The routines used were those belonging to the Philips PW 1100 diffractometer package.<sup>10</sup> The calculated density for eight unit formulas C<sub>20</sub>H<sub>30</sub>N<sub>12</sub>O<sub>8</sub>VK in the cell is 1.275 g/cm<sup>3</sup>, which agrees with the value of 1.26 g/cm<sup>3</sup> measured by flotation. The crystal chosen had faces of the forms {100}, {010}, {001}. Data were collected as described above for the chromium complex. Differences were a scan width of 0.08° in  $\theta$  (corrected for Mo K $\alpha$  dispersion) and a scan rate of 0.08°/s. A total of 2998 independent reflections were measured in the  $\theta$  range 3–20°. The decay of the intensities of three standard reflections, measured every 100 min, summed up to 12% of the initial values at the end of data collection. The intensities were corrected for this effect. The calculated transmission factors fell in the range 0.92–0.95 using a linear absorption coefficient for Mo K $\alpha$  radiation of 4.97 cm<sup>-1</sup> and were not applied

to correct the intensities. For structure solution a total of 918 reflections with  $I > 3\sigma(I)$  were used.

A three-dimensional Patterson map was sufficient to locate the V and K atoms in the asymmetric unit; a subsequent *F<sub>o</sub>* Fourier map clearly showed all nonhydrogen atoms except the solvent atoms. Three isotropic cycles for all 35, already found, atoms gave *R* = 0.132 and *R<sub>w</sub>* = 0.140. A *F<sub>o</sub>* Fourier map at this stage showed a number of peaks astride the binary axis at  $x = 0.0$  and  $z = 0.25$ , and two of them were just lying on the axis. Several attempts to show clearly the ethanol molecule, whose presence was suggested by the results of the elemental analysis, were not fully successful. The coexistence of several sets of three atoms at bond distances and angles consistent with the string C–C–O is evident, but it must be assumed that a number of models (at least five), having one or two atoms in common, are present in the crystal. In order to improve the structure refinement, the six highest peaks obtainable both from *F<sub>o</sub>* and from  $\Delta F$  maps were used for subsequent least-squares cycles. All these peaks were treated as carbon atoms and were assigned population parameters of 0.5 in agreement with the results of the elemental analysis. The vanadium and potassium atoms were refined anisotropically and a fixed contribution of hydrogen atoms, calculated as in the previous structure, was used. Anomalous dispersion terms for vanadium and potassium atoms were also introduced. Two cycles, so structured, gave *R* and *R<sub>w</sub>* of 0.07 and 0.075, respectively. A final cycle in which also the nitrogen atoms were treated anisotropically was run, in spite of the low reflections/variables ratio (ca. 4). This gave the final *R* and *R<sub>w</sub>* values of 0.063 and 0.065, respectively, although an evident but not dramatic increase of the standard deviations was also observed. The solvent description as it is at the end of refinement is not a very accurate one. Nevertheless the model can be considered satisfactory enough to derive the desired chemical information. Final atomic parameters for this structure are given in Tables II and III. Observed and calculated structure factors of both structures are available as supplementary material.

## Results and Discussion

**Complexes with the Ligands HB(pz)<sub>3</sub><sup>-</sup> and B(pz)<sub>4</sub><sup>-</sup>.** Chromium(II) and vanadium(II) complexes having the general formula [ML<sub>2</sub>] have been obtained with these ligands; they are moderately air stable. All the complexes are paramagnetic with magnetic moment values close to those expected for high-spin d<sup>4</sup> and d<sup>3</sup> configurations (Table IV). The reflectance spectra of the complexes [Cr(HB(pz)<sub>3</sub>)<sub>2</sub>] and [Cr(B(pz)<sub>4</sub>)<sub>2</sub>] show two well-separated d–d bands in the visible region (Table IV and Figure 1). The absorption at ca. 17 500 cm<sup>-1</sup> is on the low-frequency side of a more intense charge-transfer band in the near-UV region. These reflectance spectra are typical of distorted octahedral chromium(II) complexes.<sup>8</sup> A distortion is expected in six-coordinated chromium(II) complexes with six identical ligands, as a result of the Jahn–Teller effect inherent in the high-spin d<sup>4</sup> configuration. Moreover the steric requirements of the ligands<sup>2</sup> may also lower the *O<sub>h</sub>* symmetry of the crystal field around chromium and cause splitting of the <sup>5</sup>E → <sup>5</sup>T<sub>2</sub> transition.

The octahedral geometry assigned to [Cr(B(pz)<sub>4</sub>)<sub>2</sub>] on the basis of its electronic spectrum implies that the tetrakis(1-

Table II. Atomic<sup>a</sup> Parameters for the Structure of  $K[V(H_2B(pz)_2)_3] \cdot C_2H_5OH$  (All Quantities  $\times 10^3$ )<sup>b</sup>

Atom	x	y	z	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
V1	3253 (1)	2140 (3)	3842 (2)	367 (24)	501 (27)	353 (23)	-2 (25)	135 (19)	-14 (25)
K	2567 (2)	4606 (4)	2316 (3)	672 (39)	585 (42)	738 (41)	-6 (33)	301 (33)	189 (37)
N1	3056 (9)	2514 (11)	2549 (12)	516 (144)	553 (164)	504 (139)	-14 (116)	273 (125)	-16 (109)
N2	2509 (8)	2425 (11)	1776 (13)	478 (142)	734 (159)	447 (142)	-109 (110)	197 (120)	-149 (113)
N3	2374 (7)	1692 (11)	3275 (12)	535 (130)	540 (134)	232 (134)	84 (107)	193 (115)	-20 (109)
N4	1955 (8)	1723 (12)	2393 (13)	530 (146)	360 (153)	586 (148)	35 (120)	284 (125)	-77 (115)
N5	3033 (8)	3543 (13)	4035 (10)	432 (125)	307 (144)	564 (127)	-56 (114)	284 (105)	64 (103)
N6	3382 (7)	4282 (14)	4267 (10)	398 (131)	414 (147)	508 (122)	46 (118)	313 (106)	90 (105)
N7	4147 (8)	2571 (14)	4508 (11)	600 (130)	196 (164)	519 (130)	-95 (112)	264 (104)	-95 (108)
N8	4319 (8)	3474 (15)	4703 (11)	223 (142)	614 (159)	631 (141)	-64 (136)	103 (119)	-31 (132)
N9	3486 (7)	1748 (14)	5149 (11)	582 (119)	182 (151)	543 (130)	-44 (111)	320 (99)	-29 (123)
N10	3639 (7)	871 (15)	5479 (12)	589 (136)	355 (158)	569 (157)	-144 (125)	222 (120)	-269 (136)
N11	3538 (6)	762 (12)	3711 (12)	503 (124)	519 (134)	247 (134)	12 (111)	174 (113)	40 (123)
N12	3726 (7)	81 (13)	4353 (11)	424 (123)	437 (142)	466 (127)	127 (107)	277 (112)	39 (112)

<sup>a</sup> The form of the thermal ellipsoid is  $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + \dots)]$ . <sup>b</sup>  $F$  relative scale factor = 92 250.

Table III. Atomic Parameters for the Structure of  $K[V(H_2B(pz)_2)_3] \cdot C_2H_5OH$  (All Quantities  $\times 10^3$ )

Atom	x	y	z	$U_2, \text{\AA}^2$
B1	1963 (14)	2403 (20)	1755 (20)	756 (103)
B2	3907 (13)	4315 (21)	4208 (18)	667 (92)
B3	3492 (12)	17 (21)	4953 (19)	589 (87)
C1	3434 (11)	2693 (18)	2347 (18)	849 (90)
C2	3122 (13)	2737 (21)	1421 (20)	1155 (103)
C3	2579 (13)	2619 (19)	1109 (18)	994 (99)
C4	2154 (10)	1218 (16)	3639 (14)	595 (76)
C5	1596 (9)	905 (15)	3005 (15)	583 (68)
C6	1502 (10)	1238 (16)	2267 (15)	602 (77)
C7	2564 (10)	3828 (17)	4031 (13)	601 (76)
C8	2617 (10)	4746 (18)	4269 (14)	669 (74)
C9	3143 (10)	5003 (17)	4433 (14)	520 (73)
C10	4620 (10)	2005 (16)	5005 (13)	462 (63)
C11	5086 (9)	2605 (15)	5574 (13)	558 (72)
C12	4896 (11)	3502 (17)	5359 (15)	593 (73)
C13	3667 (9)	2347 (15)	5828 (16)	529 (71)
C14	3952 (9)	1850 (17)	6589 (15)	759 (78)
C15	3931 (10)	928 (17)	6374 (17)	729 (76)
C16	3766 (9)	542 (16)	3237 (13)	539 (69)
C17	4127 (9)	-238 (17)	3569 (15)	668 (74)
C18	4063 (10)	-501 (16)	4254 (14)	533 (73)
C19 <sup>a</sup>	5000	1403 (47)	2500	2216 (262)
C20 <sup>a</sup>	5000	5360 (48)	2500	2646 (280)
C21 <sup>a</sup>	4851 (23)	1934 (44)	1604 (36)	1308 (223)
C22 <sup>a</sup>	4881 (41)	2678 (84)	1693 (58)	2099 (377)
C23 <sup>a</sup>	4792 (30)	4599 (60)	1822 (50)	1702 (298)
C24 <sup>a</sup>	4636 (36)	3550 (83)	1399 (54)	1974 (379)

<sup>a</sup> Atom belonging to solvent.

pyrazolyl)borate behaves as a tridentate ligand, one pyrazole ring being uncoordinated.

The chromium(II) complexes are soluble in acetone and 1,2-dichloroethane and are not conductors in these solvents.

Table IV. Some Physical Data for the Complexes

Compd	Color	$\mu_{\text{eff}}$ (293 K)	Absorp max <sup>a</sup> ( $\bar{\nu}$ , $\text{cm}^{-1} \times 10^3$ ) of electronic spectra, with extinction coeff ( $\epsilon_{\text{molar}}$ , $\text{M}^{-1} \text{cm}^{-1}$ ) in parentheses
$[Cr(H_2B(pz)_2)_2]$	Orange red	4.80	a: 11 br, 20.5
$[Cr(HB(pz)_3)_2]$	Light green	4.75	a: 10.7, 17.7 sh b: 10.5 br, 18.1 (24)
$[Cr(B(pz)_4)_2]$	Yellow	4.90	a: 11.0, 17.5 sh b: 12.0 sh, 18.5 (33)
$K[V(H_2B(pz)_2)_3] \cdot C_2H_5OH$	Green	3.83	a: 16.4, 22.2 sh b: 15.8 (172), 22.2 (234)
$[V(HB(pz)_3)_2]$	Brown	3.83	a: 18.5, 24.0 sh c: 18.5 (100), 23.7 sh, 26.0 (5450), 28.5 sh, 37.0 sh, 40.0 (7150)
$[V(B(pz)_4)_2]$	Reddish brown	3.81	a: 18.8 sh, 23.8 sh c: 18.5 (180), 23.8 sh, 25.6 (5100)

<sup>a</sup> Key: a, solid at room temperature; b, acetone solution; c, dichloroethane solution; br, broad; sh, shoulder.

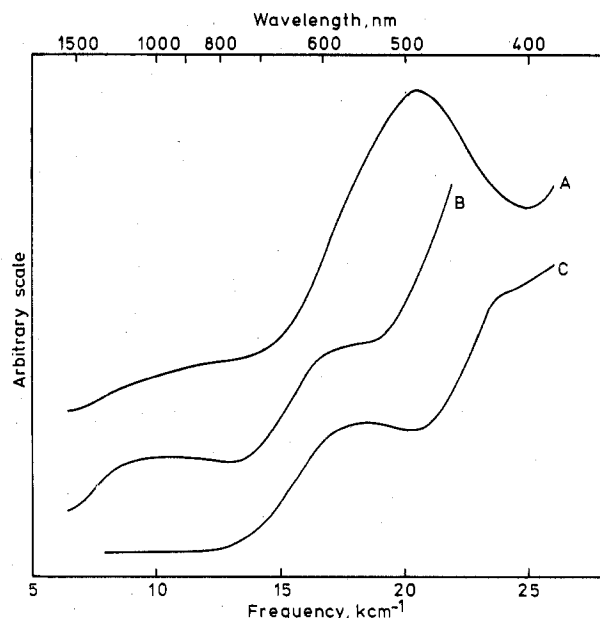
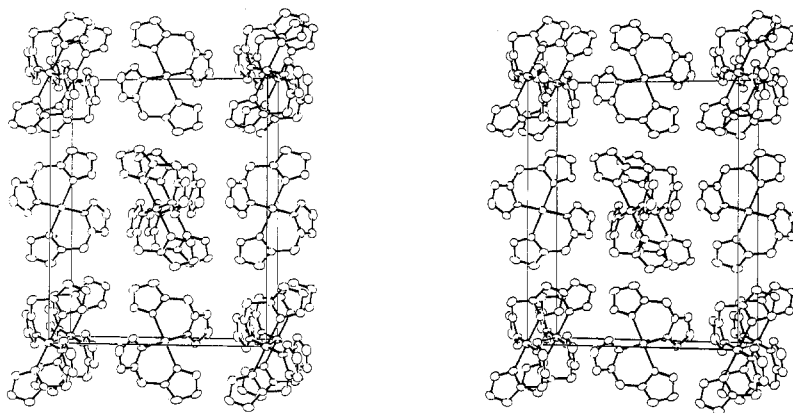


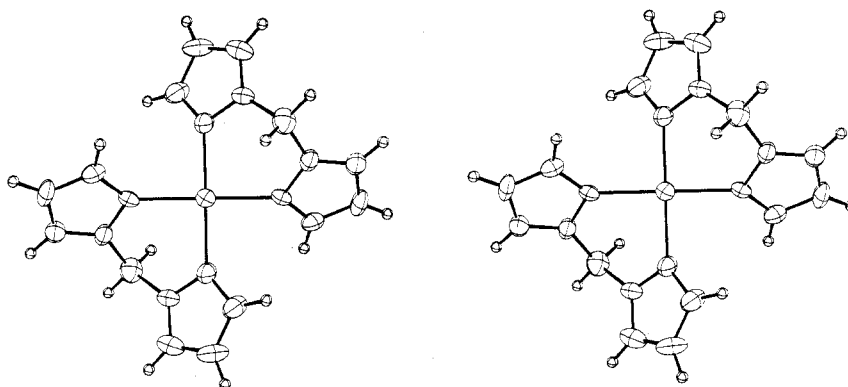
Figure 1. Reflectance spectra of:  $[Cr(H_2B(pz)_2)_2]$ , curve A;  $[Cr(HB(pz)_3)_2]$ , curve B;  $[V(HB(pz)_3)_2]$ , curve C.

Solid reflectance spectra and absorption spectra of the complexes dissolved in acetone are all substantially similar (Table IV), thus indicating that the same coordination geometry is retained in solution.

The ligand-field spectra of the solid  $[V(HB(pz)_3)_2]$  and  $[V(B(pz)_4)_2]$  derivatives in the 5000–25 000- $\text{cm}^{-1}$  region are quite similar and exhibit a band at ca. 18 500  $\text{cm}^{-1}$  and a poorly resolved shoulder at ca. 24 000  $\text{cm}^{-1}$  (Table IV and Figure 1).



**Figure 2.** Stereoscopic view of the structure of  $[\text{Cr}(\text{H}_2\text{B}(\text{pz})_2)_2]$  showing the crystal packing. The  $a$  axis is vertical, the  $b$  axis is horizontal, and the  $c$  axis points into the paper.



**Figure 3.** Stereoscopic view of the  $[\text{Cr}(\text{H}_2\text{B}(\text{pz})_2)_2]$  molecule.

The latter band is partially masked by the more intense charge-transfer absorption at higher energy. Three spin-allowed transitions are expected for the octahedral  $d^3$  configuration,<sup>12</sup> and the bands at 18 500 and 24 000  $\text{cm}^{-1}$  correspond to the first two transitions  ${}^4\text{A}_2 \rightarrow {}^4\text{T}_2$  and  ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1$ . The third  ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1(\text{P})$  transition is calculated to occur at ca. 36 000  $\text{cm}^{-1}$ <sup>13</sup> and therefore is out of the spectral range investigated. This assignment is in agreement with that previously proposed for other vanadium(II) octahedral complexes with six imidazole ligands.<sup>14</sup>

Again, in the  $[\text{V}(\text{B}(\text{pz})_4)_2]$  derivative, the  $\text{B}(\text{pz})_4^-$  ion behaves as a tridentate ligand.

These vanadium(II) complexes are sparingly soluble in polar solvents such as alcohols but are soluble in the common nonpolar organic solvents, particularly in dichloromethane, in which they do not conduct. Absorption spectra of  $[\text{V}(\text{HB}(\text{pz})_3)_2]$  dissolved in dichloromethane have been recorded in the range 15 000–40 000  $\text{cm}^{-1}$  (Table IV). These spectra show two extra bands, with respect to the solid-state spectrum, at 26 100  $\text{cm}^{-1}$  ( $\epsilon$  5450) and 40 000  $\text{cm}^{-1}$  ( $\epsilon$  7150) which, due to their high intensity, are attributable to charge-transfer transitions. The weak band at ca. 37 000  $\text{cm}^{-1}$  is thus assigned to the third d-d transition  ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1(\text{P})$  of the vanadium(II) ion. A weak absorption which appears at ca. 28 000  $\text{cm}^{-1}$  is due to a small amount of vanadium(III) species in solution. Indeed, on deliberate oxidation of the solution, the intensity of this band increases, whereas the other bands disappear.

**Complexes with the Ligand  $\text{H}_2\text{B}(\text{pz})_2^-$ .** The complexes having the formulas  $[\text{Cr}(\text{H}_2\text{B}(\text{pz})_2)_2]$  (I) and  $\text{K}[\text{V}(\text{H}_2\text{B}(\text{pz})_2)_3] \cdot \text{C}_2\text{H}_5\text{OH}$  (II) have been obtained with this ligand.

The orange-red complex I undergoes almost immediately surface oxidation which preserves the inner core of the crystals from further oxidation. The complex is sparingly soluble in the organic solvents which do not induce its decomposition, so that physical measurements in solution are practically

precluded. Complex I is high spin with a magnetic moment value, 4.90  $\mu_{\text{B}}$ , which does not vary with temperature. The electronic spectrum of this compound shows a well-defined absorption at ca. 20 500  $\text{cm}^{-1}$  (Table IV and Figure 1). A very weak and ill-defined absorption is also present between 10 000 and 12 000  $\text{cm}^{-1}$ . This spectrum is markedly different from those of the previously discussed octahedral chromium(II) complexes. The stoichiometry of the complex, by itself, suggests, but does not prove, that chromium(II) is tetracoordinated.

The green complex II is moderately air stable and dissolves in polar organic solvents such as  $\text{C}_2\text{H}_5\text{OH}$  and acetone in which it behaves as a 1:1 electrolyte. The complex has a magnetic moment value, 3.85  $\mu_{\text{B}}$ , as expected for a  $d^3$  configuration. Its reflectance spectrum is similar to those of the previously discussed vanadium(II) complexes, except for a red shift of the absorption frequencies (Table IV). To our knowledge complex II is the only polypyrazolylborate complex with a metal to ligand ratio 1:3. All the metal complexes from manganese(II) to zinc(II) with the ligand  $\text{H}_2\text{B}(\text{pz})_2^-$  are neutral species with formula  $\text{ML}_2$  and planar or tetrahedral geometry.<sup>2</sup>

The crystal structures of complexes I and II have been determined by single-crystal x-ray analyses.

The crystal structure of compound I consists of discrete centrosymmetric molecules. A view of the parallel packed molecules within the unit cell is shown in Figure 2. The shortest intermolecular contacts are between  $\text{C}_1$  and  $\text{N}_1$  (3.46 Å) and  $\text{Cr}-\text{C}_2$  (3.51 Å). A stereoscopic view of a single molecule is shown in Figure 3. Selected intramolecular bond distances and angles are reported in Table V. The chromium(II) atom is surrounded by four nitrogen atoms of two different ligand molecules. The coordination of these atoms is strictly square planar as imposed by the presence of a center of inversion at the chromium site, the N-Cr-N angles de-

Table V. Selected Bond Distances (Å) and Angles (deg) within the  $[\text{Cr}(\text{H}_2\text{B}(\text{pz})_2)_2]$  Molecule

Cr-N(1)	2.055 (4)	B-N(2)	1.539 (8)
Cr-N(3)	2.069 (4)	B-N(4)	1.555 (7)
N(1)-Cr-N(3)	90.26 (17)	B-N(4)-N(3)	119.53 (42)
N(2)-B-N(4)	106.64 (45)	B-N(2)-C(3)	130.22 (47)
B-N(2)-N(1)	120.07 (45)	B-N(4)-C(6)	130.62 (47)
Ring 1			
N(1)-N(2)	1.369 (6)	C(2)-C(3)	1.370 (9)
N(1)-C(1)	1.338 (7)	C(3)-N(2)	1.323 (8)
C(1)-C(2)	1.380 (8)		
N(2)-N(1)-C(1)	105.48 (43)	C(1)-C(2)-C(3)	104.37 (51)
N(1)-N(2)-C(3)	109.71 (44)	C(2)-C(3)-N(2)	109.41 (50)
N(1)-C(1)-C(2)	111.02 (48)		
Ring 2			
N(3)-N(4)	1.351 (6)	C(5)-C(6)	1.372 (9)
N(3)-C(4)	1.342 (7)	C(6)-N(4)	1.337 (7)
C(4)-C(5)	1.373 (9)		
N(4)-N(3)-C(4)	106.17 (43)	C(4)-C(5)-C(6)	105.08 (52)
N(3)-N(4)-C(6)	109.85 (43)	C(5)-C(6)-N(4)	108.41 (50)
N(3)-C(4)-C(5)	110.46 (49)		

viating from 90° by less than two calculated standard deviations. The two independent Cr-N distances are very similar to each other (2.055 (4) and 2.069 (4) Å) as are the other structural details in the two crystallographically independent arms of the ligand.

It has been shown that the bis(1-pyrazolyl)borate or -gallate ligands form square-planar nickel(II) and copper(II) complexes.<sup>15</sup> Some of their structural features are fully comparable with those found in the chromium(II) derivative. All these compounds have in common a square-planar structure where each six-membered chelate ring, X-(NN)<sub>2</sub>-M (X = B, Ga; M = Cr, Ni, Cu) is in a boat conformation, whereas the whole molecule has a pseudochair conformation. The only available square-planar Cr(II)-N bonds to compare with our values are those found in the crystal structure of  $\{\text{Cr}[\text{N}(\text{Si}(\text{CH}_3)_3)_2]_2(\text{THF})_2\}$  (2.098 (10) Å, average).<sup>16</sup> The small difference, if of any significance, may be related to the presence of two bulky Si(CH<sub>3</sub>)<sub>3</sub> groups in the latter compound.

The structure of complex II is comprised of discrete potassium cations and tris[dihydrobis(1-pyrazolyl)borato]vanadium(II) anions, disordered ethanol molecules also being present in the cell. Selected intramolecular bond distances and angles within the complex anion are reported in Table VI.

Three short contacts of about 3.05 Å between the potassium cation and nitrogen atoms of the ligands are observed.

A stereoscopic view of the  $[\text{V}(\text{H}_2\text{B}(\text{pz})_2)_3]^-$  anion is shown in Figure 4 as viewed down the coordination pseudotrifold axis. The donor nitrogen atoms of the three H<sub>2</sub>B(pz)<sub>2</sub> ligands form a slightly distorted octahedron around the vanadium. The metal-nitrogen distances fall in the range 2.15 (2)-2.19 (2) Å and compare well with the V-N distances (2.189 (2) Å) found in the crystal structure of tetrapyridinodichlorovanadate(II), the only coordination compound of vanadium(II) for which an x-ray structure is available.<sup>17</sup>

The bis(1-pyrazolyl)borate ligand has been compared to β-diketonate ligands,<sup>2b</sup> both because they are anionic and because they both form six-membered chelate rings in coordinating metal atoms. Although the β-diketonate ions have been known to give rise to a variety of complexes with stoichiometry  $[\text{M}(\text{diketo})_3]^{0,1-}$ ,<sup>18</sup> to date no metal ion has been found to coordinate to three H<sub>2</sub>B(pz)<sub>2</sub> molecules. The lack of this type of coordination has been attributed to the steric hindrance exerted by the ligand molecules with respect to each other.<sup>19</sup> This hindrance is partially released in the present complex through a rearrangement of the ligand conformation toward planarity. Moreover the bulky vanadium(II) coor-

Table VI. Selected Bond Distances (Å) and Angles (deg) within the  $[\text{V}(\text{H}_2\text{B}(\text{pz})_2)_3]^-$  Anion

V-N(1)	2.172 (22)	B(1)-N(2)	1.487 (50)
V-N(3)	2.148 (18)	B(1)-N(4)	1.526 (44)
V-N(5)	2.184 (21)	B(2)-N(6)	1.513 (47)
V-N(7)	2.157 (19)	B(2)-N(8)	1.560 (34)
V-N(9)	2.168 (20)	B(3)-N(10)	1.466 (38)
V-N(11)	2.188 (19)	B(3)-N(12)	1.547 (49)
N(1)-V-N(3)	90.54 (83)	N(2)-B(1)-N(4)	115.6 (2.0)
N(1)-V-N(5)	91.24 (71)	N(6)-B(2)-N(8)	111.0 (2.5)
N(1)-V-N(7)	93.74 (81)	N(10)-B(3)-N(12)	109.8 (2.5)
N(1)-V-N(9)	177.50 (79)	B(1)-N(2)-N(1)	123.4 (2.5)
N(1)-V-N(11)	89.68 (77)	B(1)-N(4)-N(3)	123.8 (1.9)
N(3)-V-N(5)	90.67 (73)	B(2)-N(6)-N(5)	123.8 (2.2)
N(3)-V-N(7)	175.70 (80)	B(2)-N(8)-N(7)	123.1 (1.6)
N(3)-V-N(9)	91.46 (78)	B(3)-N(10)-N(9)	125.3 (1.9)
N(3)-V-N(11)	93.27 (67)	B(3)-N(12)-N(11)	122.0 (2.0)
N(5)-V-N(7)	88.87 (76)	B(1)-N(2)-C(3)	128.4 (2.0)
N(5)-V-N(9)	90.22 (76)	B(1)-N(4)-C(6)	127.3 (1.8)
N(5)-V-N(11)	175.94 (79)	B(2)-N(6)-C(9)	126.7 (2.2)
N(7)-V-N(9)	84.27 (73)	B(2)-N(8)-C(12)	127.6 (2.1)
N(7)-V-N(11)	87.12 (70)	B(3)-N(10)-C(15)	126.8 (2.2)
N(9)-V-N(11)	88.72 (79)	B(3)-N(12)-C(18)	130.7 (2.1)
Ring 1			
N(1)-N(2)	1.393 (22)	C(2)-C(3)	1.290 (49)
N(1)-C(1)	1.311 (46)	C(3)-N(2)	1.360 (49)
C(1)-C(2)	1.410 (41)		
N(2)-N(1)-C(1)	108.9 (2.2)	C(1)-C(2)-C(3)	108.6 (3.1)
N(1)-N(2)-C(3)	105.9 (2.3)	C(2)-C(3)-N(2)	111.9 (1.9)
N(1)-C(1)-C(2)	106.6 (2.4)		
Ring 2			
N(3)-N(4)	1.369 (24)	C(5)-C(6)	1.310 (40)
N(3)-C(4)	1.309 (39)	C(6)-N(4)	1.338 (37)
C(4)-C(5)	1.397 (28)		
N(4)-N(3)-C(4)	106.4 (1.7)	C(4)-C(5)-C(6)	103.7 (2.5)
N(3)-N(4)-C(6)	107.0 (2.2)	C(5)-C(6)-N(4)	111.9 (1.9)
N(3)-C(4)-C(5)	110.9 (2.1)		
Ring 3			
N(5)-N(6)	1.334 (27)	C(8)-C(9)	1.363 (39)
N(5)-C(7)	1.353 (39)	C(9)-N(6)	1.345 (35)
C(7)-C(8)	1.368 (35)		
N(6)-N(5)-C(7)	106.5 (2.0)	C(7)-C(8)-C(9)	104.2 (2.6)
N(5)-N(6)-C(9)	108.9 (2.1)	C(8)-C(9)-N(6)	109.7 (2.1)
N(5)-C(7)-C(8)	110.6 (2.4)		
Ring 4			
N(7)-N(8)	1.356 (29)	C(11)-C(12)	1.363 (32)
N(7)-C(10)	1.372 (27)	C(12)-N(8)	1.369 (27)
C(10)-C(11)	1.415 (28)		
N(8)-N(7)-C(10)	108.8 (1.6)	C(10)-C(11)-C(12)	108.1 (1.7)
N(7)-N(8)-C(12)	109.2 (1.8)	C(11)-C(12)-N(8)	107.6 (2.0)
N(7)-C(10)-C(11)	106.1 (1.9)		
Ring 5			
N(9)-N(10)	1.357 (29)	C(14)-C(15)	1.370 (36)
N(9)-C(13)	1.355 (31)	C(15)-N(10)	1.366 (33)
C(13)-C(14)	1.359 (33)		
N(10)-N(9)-C(13)	108.4 (1.8)	C(13)-C(14)-C(15)	107.7 (2.2)
N(9)-N(10)-C(15)	107.9 (1.9)	C(14)-C(15)-N(10)	107.7 (2.1)
N(9)-C(13)-C(14)	108.3 (2.0)		
Ring 6			
N(11)-N(12)	1.385 (26)	C(17)-C(18)	1.402 (43)
N(11)-C(16)	1.355 (38)	C(18)-N(12)	1.336 (36)
C(16)-C(17)	1.396 (32)		
N(12)-N(11)-C(16)	106.5 (1.8)	C(16)-C(17)-C(18)	101.0 (2.5)
N(11)-N(12)-C(18)	106.9 (2.2)	C(17)-C(18)-N(12)	113.0 (2.0)
N(11)-C(16)-C(17)	112.5 (2.2)		

dination environment does not require short metal-donor linkages and allows the ligand molecules to stay apart.

It has been previously shown<sup>5,20</sup> that polypyrazolylborate ligands attain a degree of flexibility through rotation of the

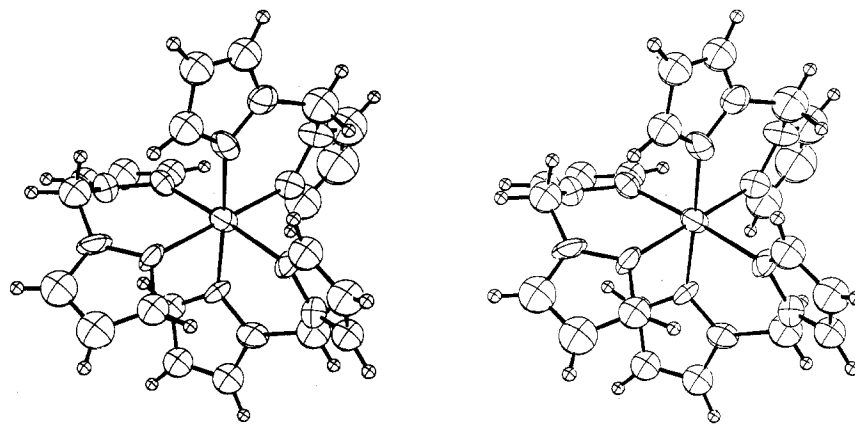


Figure 4. Stereoscopic view of the  $[V(H_2B(pz)_2)_3]^-$  anion.

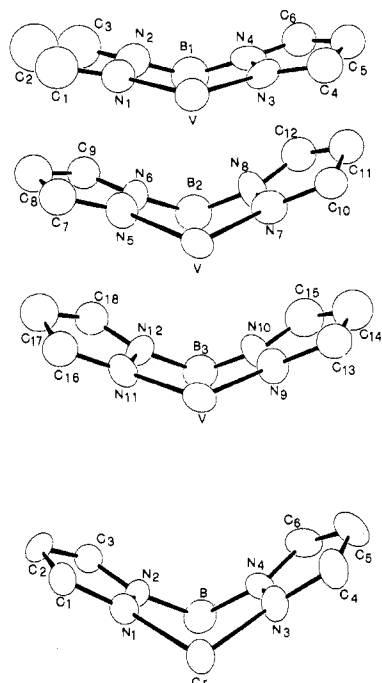


Figure 5. Separated views of the ligand molecules in the complexes  $[V(H_2B(pz)_2)_3]^-$  and  $[Cr(H_2V(pz)_2)_2]$ . All the six-membered rings  $B-(NN)_2-M$  ( $M = V, Cr$ ) are isooriented with the  $N_4$  planes almost perpendicular to the plane of the paper. Dihedral angles between each  $N_4$  plane and any adjacent pyrazole ring plane have values, from left to right and from top to bottom, of 11.2, 10.5, 16.9, 27.5, 26.0, 26.0, 31.4, and 34.5°, respectively.

pyrazole rings about the N–N vector. In the present case such a rotation is accompanied by a more or less pronounced flattening of the boat conformation of the six-membered chelate rings, mainly at the metal side, the boron atom remaining out of the plane containing the four nitrogen atoms. This effect can be seen by observing Figure 5 where the conformations of the ligand molecules in complexes I and II are shown.

It is worth mentioning that almost complete planarity of the whole six-membered chelate rings was previously observed in the structure of bis[*dimethylbis*(3,5-dimethyl-1-pyrazolyl)gallate]copper(II),<sup>15c</sup> where the copper atom is so allowed to adopt a pseudotetrahedral geometry by the removal of steric hindrance effects.

### Conclusions

The  $[Cr(H_2B(pz)_2)_2]$  complex, whose synthesis and molecular structure have been reported above, is one of the rare four-coordinated chromium(II) compounds so far isolated with

Table VII. Stereochemistries<sup>a</sup> of Metal Complexes with the Ligand  $H_2B(pz)_2^-$

V	Cr	Mn	Fe	Co	Ni	Cu	Zn
O	P	T	T	T	P	P	T

<sup>a</sup> Key: O = octahedral, P = planar, T = tetrahedral. All the complexes have the general formula  $ML_2$ , with the exception of the vanadium(II) complex which has the formula  $VL_3^-$ .

a square-planar coordination geometry.<sup>16,21</sup>

In the  $K[V(H_2B(pz)_2)_3] \cdot C_2H_5OH$  complex a new binding mode for the bis(1-pyrazolyl)borate ligands has been described. The ligand has been found in the past to give complexes with a metal to ligand ratio of 1:2, both with bivalent and trivalent 3d metals. Several factors may be of importance in determining the unusual coordination mode of the ligand in the present complex, such as the bulkiness of the vanadium(II) ion, the ascertained flexibility of the ligand, and the crystal field stabilization energy of the  $d^3$  configuration in  $O_h$  symmetry. Perhaps significantly all the vanadium(II) complexes so far known are six-coordinated.

In Table VII the stereochemistries of 3d metal complexes with the ligand  $H_2B(pz)_2^-$  are summarized. This series is one of the most extensive series of chelate complexes of bivalent 3d metals with the same ligand. Interestingly, the same pattern was found in the series of complexes containing the anionic ligand dipivaloylmethane<sup>22</sup> (the vanadium complex is not comprised in this series). It is evident from these data that the electronic requirements of bivalent metal ions play a very important role in fixing the coordination geometries of the complexes.

**Acknowledgment.** We thank Professor L. Sacconi for helpful suggestions and constant encouragement. We are indebted to Mr. G. Scapacci for technical assistance.

**Registry No.** I, 65415-30-7; II, 65442-03-7;  $Cr(HB(pz)_3)_2$ , 58080-10-7;  $Cr(B(pz)_4)_2$ , 58117-47-8;  $V(HB(pz)_3)_2$ , 65415-29-4;  $V(B(pz)_4)_2$ , 65415-28-3.

**Supplementary Material Available:** Listing of structure factor amplitudes for both structures (9 pages). Ordering information is given on any current masthead page.

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## Molecular and Electronic Structure of Tetrakis(dimethylamido)molybdenum(IV)

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Received November 3, 1977

The molecular structure of Mo(NMe<sub>2</sub>)<sub>4</sub> has been determined by x-ray crystallography and used to interpret the available data pertaining to the electronic structure of the molecule. The structure possesses virtual *D*<sub>2d</sub> symmetry with the C–N–C planes perpendicular to the vertical symmetry plane of the *D*<sub>2d</sub> point group. Both a qualitative symmetry analysis and a Hartree–Fock calculation in the Fenske–Hall approximation led to the conclusion that the two molybdenum 4d electrons should occupy the b<sub>1</sub> (*x*<sup>2</sup> – *y*<sup>2</sup>) orbital to give a singlet ground state, as observed, with the ordering of the empty d orbitals being z<sup>2</sup>, (*xz*, *yz*), *xy*. It is then possible to give a satisfactory interpretation of both the electronic absorption spectrum and the photoelectron spectrum. The compound crystallizes in the triclinic system with *a* = 8.442 (2) Å, *b* = 12.142 (2) Å, *c* = 14.196 (2) Å, α = 104.17 (2)°, β = 100.73 (1)°, γ = 84.67 (2)°, *V* = 1384.5 (8) Å<sup>3</sup>, and *Z* = 4. There are two crystallographically independent molecules which have essentially identical dimensions. The average values (over both molecules and assuming *D*<sub>2d</sub> symmetry in each) of some important dimensions are the following: Mo–N, 1.926 (6) Å; N–C, 1.466 (15) Å; N–Mo–N, 109.5 (19)°; Mo–N–C, 124 (1)°, C–N–C, 110 (1)°.

### Introduction

The purple, extremely volatile compound Mo(NMe<sub>2</sub>)<sub>4</sub> was first isolated a number of years ago by Bradley and Chisholm,<sup>2</sup> who showed it to be a crystalline, diamagnetic compound and proposed a structure of *D*<sub>2d</sub> symmetry on the basis of its diamagnetism and spectroscopic properties. Since then, a great deal of work has been done on the yellow, triply bonded Mo<sub>2</sub>(NMe<sub>2</sub>)<sub>6</sub> and its derivatives, and this has renewed our interest in having a more complete understanding of the mononuclear molecule, Mo(NMe<sub>2</sub>)<sub>4</sub>. One particular objective for characterizing this molecule structurally was to ascertain with certainty whether it could be used to obtain an estimate of the Mo–NMe<sub>2</sub> bond energy that would be required in order to deduce the Mo≡Mo bond energy from the heat of formation of Mo<sub>2</sub>(NMe<sub>2</sub>)<sub>6</sub>. More generally, structure parameters were wanted as a basis for a more thorough study of the electronic structure of the molecule.

### Procedures

The preparation and general properties of Mo(NMe<sub>2</sub>)<sub>4</sub> have been described elsewhere.<sup>2</sup> It is an extremely oxygen- and moisture-sensitive compound and it was always handled in a N<sub>2</sub>-filled glovebox. It is very volatile, subliming slowly at room temperature and 10<sup>-2</sup> Torr, and it melts at ca. 50 °C. Crystals of Mo(NMe<sub>2</sub>)<sub>4</sub> were grown via sublimation in sealed, evacuated 8-mm glass tubes at room temperature. Selected crystals were wedged in thin-walled glass capillaries under N<sub>2</sub> and the capillaries were sealed with a small hand torch.

**X-Ray Crystallography.**<sup>3</sup> An approximately spherical crystal of Mo(NMe<sub>2</sub>)<sub>4</sub> measuring 0.32 mm in diameter was shown to be of good quality by ω scans of several intense reflections which had peak widths at half-height of ca. 0.2°. Cell constants and axial photographs indicated that the crystal belonged to the triclinic system with *a* = 8.442 (2) Å, *b* = 12.142 (2) Å, *c* = 14.196 (2) Å, α = 104.17 (2)°, β = 100.73 (1)°, γ = 84.67 (2)°, and *V* = 1384.5 (8) Å<sup>3</sup>. The observed

volume was consistent with that expected for *Z* = 4. The space group was assumed to be *P* $\bar{1}$ ; this was verified by the structure solution and refinement.

Data were collected at 4 °C on a Syntex *P* $\bar{1}$  autodiffractometer located in a cold room. The diffractometer was equipped with a monochromator and used Cu Kα radiation (λ 1.541 84 Å). The θ–2θ scan technique was used with scans ranging from 1.0° above to 1.0° below the calculated Kα<sub>1</sub>, Kα<sub>2</sub> doublet, variable scan speeds ranging from 6.0 to 24.0°/min and a background to scan time ratio of 0.5. The intensities of three standard reflections were monitored frequently throughout data collection and showed no decrease in intensity. The integrated intensities of 3798 unique reflections having 0° < 2θ(Cu Kα) < 115° were collected.

A spherical absorption correction was applied to the data (μ = 79.0 cm<sup>-1</sup>); the transmission coefficients ranged from 0.213 to 0.278 with an average of 0.250. The data were reduced to a set of relative |*F*<sub>o</sub>|<sup>2</sup> values and the 2861 reflections having |*F*<sub>o</sub>|<sup>2</sup> > 3σ(|*F*<sub>o</sub>|<sup>2</sup>) were used in subsequent structure solution and refinement.

The structure was solved by conventional heavy-atom methods and refined to convergence using anisotropic thermal parameters for the Mo and N atoms and isotropic thermal parameters for the carbon atoms. Final unweighted and weighted residuals were *R*<sub>1</sub> = 0.056 and *R*<sub>2</sub> = 0.086, respectively. A value of 0.07 was used for *p* in the calculation of the weights.<sup>3</sup> The end of an observation of unit weight was 1.993. The largest peaks in a final difference Fourier map were in regions where methyl group hydrogen atoms would be expected, but no attempt was made to include hydrogen atoms in the refined structure.

**Molecular Orbital Calculations.** The approximate but nonparameterized Hartree–Fock–Roothaan type MO Calculation commonly called the Fenske–Hall<sup>4</sup> type was carried out using a program package and molybdenum wave functions kindly provided by Professor M. B. Hall of Texas A&M University. The atomic orbital coefficients and exponents of Richardson and co-workers were used,<sup>5</sup> with double ζ functions for the metal d orbitals. Coefficients of 1.0 and exponents of 2.2 were chosen for the Mo 5s and 5p orbitals and these orbitals