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Two New Pyridyl-Substituted Tris(pyrazolyl)borate Ligands and Their Potassium Salts

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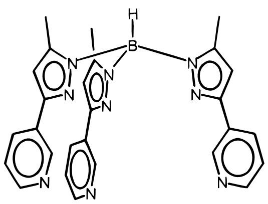
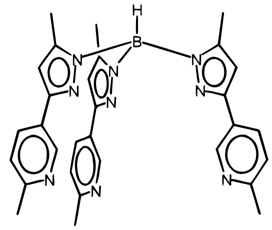
The hydrotris(5-methyl-3-py*-pyrazolyl)borate ligands $Tp^{3Py,Me}$ (py* = 3-pyridyl) and $Tp^{Pic,Me}$ (py* = 5-α-picolyl) were synthesized from the corresponding pyrazoles and KBH_4. They were crystallized as their hydrated potassium salts. In the solid state $KTp^{3Py,Me}\cdot H_2O$ is a coordination polymer in which two of the three pyridine nitrogens of each $Tp^{3Py,Me}$ ligand are used to coordinate neighboring potassium ions. $KTp^{Pic,Me}\cdot 2H_2O$ consists of dimers held together by pairs of K−N(pyridine) interactions. $KTp^{3Py,Me}\cdot H_2O$ crystallizes in the triclinic space group $P\bar{1}$ with $a = 8.893(2)$ Å, $b = 11.733(2)$ Å, $c = 13.272(2)$ Å, $\alpha = 75.48(1)°$, $\beta = 82.93(2)°$, $\gamma = 88.43(2)°$, and $Z = 2$. $KTp^{Pic,Me}\cdot 2H_2O$ crystallizes in the triclinic space group $P\bar{1}$ with $a = 9.481(2)$ Å, $b = 11.613(1)$ Å, $c = 15.516(1)$ Å, $\alpha = 76.68(1)°$, $\beta = 75.13(1)°$, $\gamma = 89.60(1)°$, and $Z = 2$.

It is becoming more and more obvious that Trofimenko's (pyrazolyl)borate (Tp) ligands are a seminal contribution to coordination chemistry. Their value in controlling the reactivity of complexes is only beginning to be exploited since Trofimenko himself[1] and his disciples, including ourselves,[2−6] have begun to design Tp^x ligands for which the superscript x denotes suitable substituents at the pyrazoles' 3- and 5-positions.

One challenge in this respect is the introduction of functional substituents on the pyrazoles, i.e. those that enable solubility in water, the attachment of external centers of reactivity, or the ability to coordinate additional metals. A survey of the literature shows that only two approaches toward this goal could be realized so far. After initial work by Graham,[7] Dias[4] recently began an extensive study of the complex chemistry of fluoroalkyl-substituted Tp^x ligands. Ward[5] prepared Tp^x ligands with 2-pyridyl substituents in the 3-position and used them for transition metal and lanthanide complexes. It could be shown that the fluorines of the fluoroalkyl substituents exhibit donor qualities toward the metal ion coordinated inside the Tp^x ligand as well as toward external metals. The 2-pyridyl substituents, however, were found to be nitrogen donors only for the metals bound to the Tp^x ligand so far.

In the course of our studies of the zinc complex chemistry of Tp^x ligands,[6] we became interested in such ligands that can bind additional external metal ions. We began the search for such ligands with 3-pyridyl-substituted systems. In order to cause the pyridine nitrogens point toward the outside of the Tp^x pocket, we attached the pyridine rings via their 3- or 4-positions to the pyrazole rings. This paper describes the synthesis of two such ligands, $Tp^{3Py,Me}$ and $Tp^{Pic,Me}$, and their structural characterization as potassium salts. The subsequent paper[8] demonstrates their binucleating abilities for zinc complexes. We have already shown[9] how these ligands can assist two Tp^xZn units to encapsulate the unusual $H_3O_2^-$ ligand.


$Tp^{3Py,Me}$


$Tp^{Pic,Me}$

Experimental Section

All experimental techniques and the standard IR and NMR equipment were as described previously.[10] The syntheses of the pyridyl-substituted pyrazoles followed the established literature procedures.[11,12]

Potassium Hydrotris(5-methyl-3-(3-pyridyl)pyrazolyl)borate Hydrate ($KTp^{3Py,Me}\cdot H_2O$). 3-Pyridylbutane-2,4-dione[13] (40.89, 0.25 mol) in ethanol (150 mL) was added dropwise with stirring to a solution of hydrazine hydrate (15.2 g, 0.25 mol) in methanol (150 mL), and the mixture was stirred for 2 h. The solvent was removed and the residue dried in vacuo. The residue was triturated twice with diethyl ether (150 mL) in an ultrasound bath, dried again, and sublimed twice in vacuo. A 23.1 g (58%) yield of colorless, crystalline 5-methyl-3-(3-pyridyl)pyrazole was obtained.

A mixture of 5-methyl-3-(3-pyridyl)pyrazole (15.9 g, 100 mmol) and KBH_4 (1.35 g, 25 mmol) was slowly heated to 200 °C, the temperature being controlled by an immersed thermometer. The resulting melt was kept at 200 °C until it started to turn yellow (ca. 3 h). After cooling to room temperature, the glassy residue was carefully powdered and treated for 30 min with $CHCl_3$ (150 mL) in an ultrasound bath. After filtration, the residue was dried in vacuo and then heated to reflux in undried acetonitrile (200 mL). The mixture was filtered hot and the filtrate kept at −25 °C for crystallization. A 3.42 g (26%) yield of $KTp^{3Py,Me}\cdot H_2O$ was obtained as a colorless powder, mp 263 °C. IR (KBr, cm^{-1}): 3508w (H_2O), 2479m (BH), 1658m, 1595w, 1574m, 1540s (ring vibrations). ^1H-NMR (DMSO-d_6, δ): 2.04 [s, 9H, Me(pz)], 6.38 [s, 3H, H(pz)], 7.30 [dd, J = 8.0 Hz, 4.7 Hz, 3H, py(5)],

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Table 1. Crystallographic Details

	$KTp^{3Py,Me}\cdot H_2O$	$KTp^{Pic,Me}\cdot 2H_2O$
formula	$C_{27}H_{27}BKN_9O_{10}$	$C_{30}H_{35}BKN_9O_{11}$
M_r	543.5	603.6
space group	$P\bar{1}$	$P\bar{1}$
Z	2	2
a (Å)	8.893(2)	9.481(2)
b (Å)	11.733(2)	11.613(1)
c (Å)	13.272(2)	15.516(1)
α (deg)	75.48(1)	76.68(1)
β (deg)	82.93(2)	75.13(1)
γ (deg)	88.43(2)	89.60(1)
V (Å^3)	1330.4(4)	1604.3(4)
d_{calc} (g/cm^3)	1.36	1.35
d_{obs} (g/cm^3)	1.37	1.35
μ (mm^{-1})	0.24	0.21
R_1(obs refl)^a	0.045	0.045
wR_2(all refl)^b	0.135	0.144

^{a} $R_1 = \sum|F_o - F_c|/\sum F_o$. ^{b} $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

7.99 [ddd, $J = 8.0$ Hz, 2.2 Hz, 1.7 Hz, 3H, py(6)], 8.35 [dd, $J = 4.7$ Hz, 1.7 Hz, 3H, py(4)], 8.88 [d, $J = 2.2$ Hz, 3H, py(2)]. ^{13}C-NMR (DMSO-d_6, δ): 12.0 [Me(pz)], 102.1 [py(6)], 123.4 [py(5)], 131.1 [py(3)], 131.5 [py(4)], 144.2 [py(2)], 145.5 [pz(4)], 146.1 [pz(5)], 146.9 [pz(3)].

Anal. Calc for $C_{27}H_{25}BKN_9\cdot H_2O$ ($M_r = 525.5 + 18.0$): C, 46.16; H, 4.33; N, 6.33. Found: C, 46.23; H, 4.18; N, 6.24.

Potassium Hydrotris(5-methyl-3-(5-α-picolyl)pyrazolyl)borate Dihydrate ($KTp^{Pic,Me}\cdot 2H_2O$). 5-Methyl-3-(5-α-picolyl)pyrazole was prepared as above from 5-methyl-3-(5-α-picolyl)butane-2,4-dione[14] (37.0 g, 209 mmol) and hydrazine hydrate (13.1 g, 209 mmol). The yellow raw product was first crystallized from toluene at −25 °C and then sublimed in vacuo. The yield of the pyrazole was 20.3 g (56%).

As above, the pyrazole (12.0 g, 69.3 mmol) and KBH_4 (934 mg, 17.3 mmol) were converted to the raw (pyrazolyl)borate. This was carefully powdered and heated to reflux in toluene (250 mL), and the mixture was cooled to 40 °C and filtered. The residue was dried in vacuo and then heated to reflux in undried acetonitrile (200 mL), the solution was filtered hot, and the filtrate was kept at −25 °C for crystallization. A 3.63 g (37%) yield of $KTp^{Pic,Me}\cdot 2H_2O$ was obtained as a colorless powder, mp 198 °C. IR (KBr, cm^{-1}): 3359w (H_2O), 2450m (BH), 1609m, 1568m, 1540m (ring vibrations). ^{1}H-NMR (DMSO-d_6, δ): 2.03 [s, 9H, Me(py)], 2.43 [s, 9H, Me(pz)], 6.33 [s, 3H, H(pz)], 7.16 [d, $J = 8.0$ Hz, 3H, py(5)], 7.88 [dd, $J = 8.0$ Hz, 1.7 Hz, 3H, py(6)], 8.74 [d, $J = 1.7$ Hz, 3H, py(2)]. ^{13}C-NMR (DMSO-d_6, δ): 12.0 [Me(pz)], 23.6 [Me(py)], 101.8 [py(6)], 122.6 [py(5)], 128.3 [py(3)], 131.9 [py(4)], 144.0 [py(2)], 145.3 [pz(4)], 145.6 [pz(5)], 154.9 [pz(3)].

Anal. Calc for $C_{30}H_{31}BKN_9\cdot 2H_2O$ ($M_r = 567.6 + 36.0$): C, 59.70; H, 5.84; N, 20.89. Found: C, 59.56; H, 5.82; N, 20.91.

Structure Determinations. Both crystals were obtained by cooling saturated solutions in undried acetonitrile to 0 °C. They were sealed in capillaries together with a drop of solvent. Diffraction data were recorded at room temperature with the $\omega/2\theta$ technique on a Nonius CAD4 diffractometer fitted with a molybdenum tube (Kα, $\lambda = 0.7107$ Å) and a graphite monochromator. The structures were solved without an absportion correction by direct methods and refined anisotropically with the SHELX program suite.[15] Hydrogen atoms were included with fixed distances and isotropic temperature factors 1.2 times those of their attached atoms. Drawings were produced with SCHAKAL.[16] Table 1 lists the crystallographic data.

Results and Discussion

The motivation for this work was the intended use of the pyridyl substituents on the tris(pyrazolyl)borates as nitrogen donors for additional metal ions, as nitrogen acceptors of hydrogen bonds, and as a means of creating a more polar ligand pocket around the Tp-bound metal. The steric bulk of $Tp^{3Py,Me}$ should be identical to that of $Tp^{Ph,Me}$, and that of $Tp^{Pic,Me}$ should be identical to that of the corresponding tolyl-substituted tris(pyrazolyl)borate. Thus, they should, with a reasonable degree of certainty, prevent the formation of bis(ligand) complexes and ensure the accessibility of $Tp^xM{-}X$ species with tetrahedrally coordinated transition metals M.

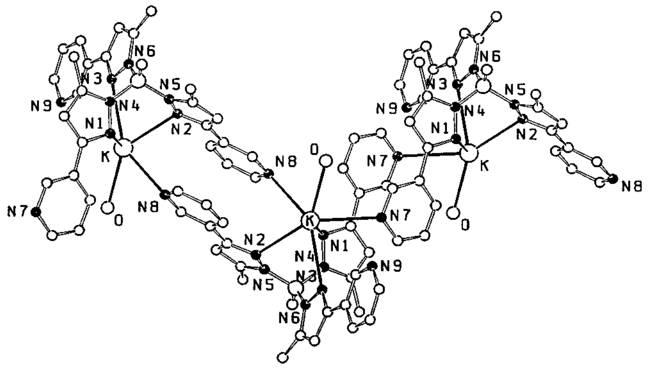

Figure 1. Solid state arrangement of $KTp^{3Py,Me}\cdot H_2O$.

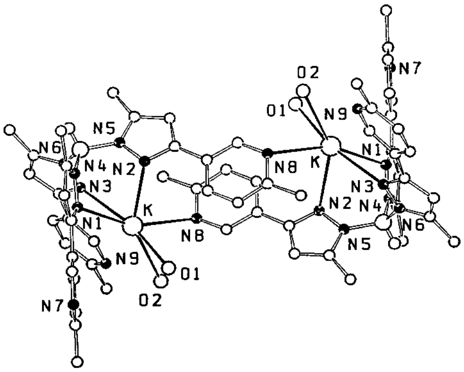

Figure 2. Dimeric units of solid $KTp^{Pic,Me}\cdot 2H_2O$.

In order to achieve this, the pyridyl-substituted pyrazoles and the resulting Tp^x compounds had to be sufficiently inert to survive the harsh synthetic conditions which consist of heating a melt of the pyrazole with KBH_4. After some optimization, this was found to be the case, provided that the pyrazoles are carefully purified before use and that the temperature of the KBH_4/pyrazole reaction mixtures never exceeds 200−210 °C. Still the yields of the KTp^x compounds could not be brought to exceed the 30% range, and our subsequent experience with these compounds has shown that it is not useful to accept lower qualities for having higher yields. Except for this, the synthetic procedure was without problems, and the two new (pyrazolyl)borates were found to be pure and stable.

In both cases, the potassium complexes of the Tp^x ligands could be subjected to a crystal structure analysis, thus providing a primary identification of the ligands. The basis for obtaining good crystals was hydration of potassium brought about by the water content of the crystallization solvent acetonitrile. Figures 1 and 2 display the atomic arrangements in the solid state. $KTp^{3Py,Me}\cdot H_2O$ is a coordination polymer; $KTp^{Pic,Me}\cdot 2H_2O$ is a dimer. In both compounds, potassium is six-coordinate. This implies that, in addition to the three pyrazole nitrogens and the water molecules, the potassium ion in $KTp^{3Py,Me}\cdot H_2O$ has two coordinated pyridine nitrogens and the potassium ion in $KTp^{Pic,Me}\cdot 2H_2O$ has one.

In each case, the coordinating pyridine nitrogens are part of neighboring KTp^x units, and in each case, there are pairwise linkage interactions relating two KTp^x units across a center of

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Table 2. Bond Lengths Involving Potassium (Å)

$KTp^{3Py,Me}\cdot H_2O$		$KTp^{Pic,Me}\cdot 2H_2O$	
K−O	2.806(2)	K−O1	2.619(2)
K−N1	2.798(2)	K−O2	3.378(3)
K−N2	2.814(2)	K−N1	2.791(2)
K−N3	2.990(2)	K−N2	2.811(2)
K−N7	2.996(3)	K−N3	2.932(2)
K−N8	2.898(2)	K−N8	3.058(3)

Table 3. Bond Angles around Potassium (deg)

$KTp^{3Py,Me}\cdot H_2O$		$KTp^{Pic,Me}\cdot 2H_2O$	
N1−K−N2	75.78(6)	N1−K−N2	70.16(7)
N1−K−N3	78.15(6)	N1−K−N3	67.28(6)
N2−K−N3	68.96(6)	N2−K−N3	78.60(6)
O−K−N1	118.28(7)	O1−K−N1	104.62(7)
O−K−N2	139.40(6)	O1−K−N2	108.17(8)
O−K−N3	147.63(6)	O1−K−N3	167.56(8)
O−K−N7	73.29(6)	O1−K−N8	87.83(8)
O−K−N8	68.86(6)	O1−K−O2	77.62(7)
N7−K−N1	82.09(7)	O2−K−N1	145.38(7)
N7−K−N2	146.75(6)	O2−K−N2	142.99(7)
N7−K−N3	82.53(6)	O2−K−N3	103.49(6)
N7−K−N8	126.19(7)	O2−K−N8	53.31(7)
N8−K−N1	83.64(6)	N8−K−N1	158.87(8)
N8−K−N2	75.92(6)	N8−K−N2	89.90(8)
N8−K−N3	143.37(6)	N8−K−N3	102.84(7)

symmetry. In $KTp^{3Py,Me}\cdot H_2O$ the N8 nitrogen atoms establish the first pair of linkages and the N7 nitrogens the second pair while the N9 nitrogens remain uncoordinated, thus creating a zigzag-shaped one-dimensional polymer. In dimeric $KTp^{Pic,Me}\cdot 2H_2O$, the linkage is localized in one pair of bridges involving the N8 nitrogen atoms, the N7 nitrogens are uncoordinated, and the N9 nitrogens are within hydrogen-bonding distance (2.90 Å) to one of the water molecules. In addition to the linkage interaction via the pyridine nitrogen atoms, there is in each case a weak stacking interaction between the two parallel pyridine rings across the centers of symmetry.

Tables 2 and 3 list the bonding parameters around potassium. In both complexes, the coordination geometry of the six-coordinate potassium ions cannot be approximated as octahedral. In $KTp^{3Py,Me}\cdot H_2O$, it is roughly similar to a pentagonal pyramid with N1 at the apex, which implies a rather open coordination region opposite N1. In $KTp^{Pic,Me}\cdot 2H_2O$, there is a similar open region above the face defined by O1, O2, N1, and N3. In both cases, these open areas are filled by noncoordinating pyridine rings, i.e. those bearing N7 and N9 in $KTp^{Pic,Me}\cdot 2H_2O$ (see Figure 2) and those of further neighboring ligand units in $KTp^{3Py,Me}\cdot H_2O$ (not depicted in Figure 1).

The K−O and K−N bond distances in $KTp^{3Py,Me}\cdot H_2O$ show a spread of ±0.1 Å about the average value of ca. 2.9 Å, which is normal.[17,18] In $KTp^{Pic,Me}\cdot 2H_2O$, the spread is much wider, with the two distances between potassium and the two water molecules (differing by 0.76 Å) marking the extremes. Although this is still not out of range for the coordination chemistry of potassium, it underlines, together with the bond angles, the very low symmetry of the potassium coordination in $KTp^{Pic,Me}\cdot 2H_2O$.

Although every new (pyrazolyl)borate ligand is synthesized initially as its alkali metal salt, there still exist only a small number of structure determinations for such salts.[4,19−24] They show a high diversity of coordination modes (monomeric, dimeric, polymeric) and bonding types, including π interactions between the metal and aromatic rings. Of the structures determined, five contain potassium, having the coordination numbers 3,[21] 6,[19,20] 8,[22] and 9.[23] None of them bears any resemblance to the type and geometry of the potassium coordination in the two complexes described here. Thus a comparative discussion of alkali metal coordination by (pyrazolyl)borates will have to await the emergence of further structure determinations.

The most important observation in the two structure determinations is the coordination of the potassium ions by pyridine donors belonging to neighboring KTp^x units. This verifies our assumptions that prompted us synthesize the two new ligands. Our pyridine-substituted ligands share this ability with the 3-fluoroalkyl-substituted Tp^x ligands.[4,22−24] But while metal coordination by organic fluorine is of course limited to very hard metals like the alkali metals, the pyridine donors are well suited for transition metals in all oxidation states. Therefore the ligands $Tp^{3Py,Me}$ and $Tp^{Pic,Me}$ should be the first among the (pyrazolyl)borate family allowing the attachment of external metal complex units to an existing complex bearing these ligands.

In summary, we have shown that the new polyfunctional ligands $Tp^{3Py,Me}$ and $Tp^{Pic,Me}$ can be synthesized in a straightforward manner and that the structures of their potassium complexes are proof of their ability to link two metal complex units. We are in the process of exploiting this ability. The following paper[8] describes the first results in zinc complex chemistry.

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Supporting Information Available: Fully labeled ORTEP plots for both structures (2 pages). Two crystallographic files, in CIF format, are available on the Internet only. Ordering and access information is given on any current masthead page.

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