are compared. In IV the angles around bismuth range from 94.5 to 103.3°, but in Bi[Mn(CO)$_5$]$_3$, with the bulky Mn(CO)$_5$ groups, they range from 106.9 (1) to 110.3 (1)°.

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Supplementary Material Available: Tables of hydrogen atom positional parameters for I–IV, cation positional parameters for [PPN][I], solvate positional parameters for III·CH$_2$Cl$_2$, and anisotropic thermal parameters and complete bond distances and angles for I–IV (33 pages); tables of observed and calculated structure factors for I–IV (72 pages). Ordering information is given on any current masthead page.

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Hydrotris[3-(2′-thienyl)pyrazol-1-yl]borate: A Ligand of Remarkably Low Steric Requirements

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The new ligand hydrotris[3-(2′-thienyl)pyrazol-1-yl)borate (=L*) was prepared and shown to have the second-lowest steric hindrance among the known poly(pyrazolyl)borates. It forms octahedral L*$_2$M complexes with first-row transition-metal ions but fails to yield stable L*MX species, except with Zn(II). It also reacts with HB(3-Pr^i-4-Br-pz)$_3$CoCl to form octahedral HB(3-Pr^i-4-Br-pz)$_3$CoL*, having C_{3v} symmetry. The structure of L*$_2$Co was determined by X-ray crystallography. Two different crystal forms of the molecule in different conformations are reported. Form A: monoclinic, $C2/c$ (No. 15), $a = 21.577$ (2) Å, $b = 12.464$ (1) Å, $c = 18.298$ (2) Å, $\beta = 113.21$ (1)°, $T = -70$ °C, $V = 4522.6$ Å^3, $Z = 4$. The structure was refined to R, R_w = 0.062, 0.065 by using 3670 diffractometer-collected data. Form B: triclinic, $P\bar{1}$ (No. 2), $a = 10.148$ (2) Å, $b = 11.768$ (2) Å, $c = 12.241$ (3) Å, $\alpha = 61.54$ (1)°, $\beta = 69.06$ (1)°, $\gamma = 67.19$ (1)°, $T = -70$ °C, $V = 1157.5$ Å^3, $Z = 1$. The structure was refined to R, R_w = 0.044, 0.043 by using 4380 diffractometer-collected data. The Mössbauer effect hyperfine parameters for L*$_2$Fe, obtained at 78 and 295 K, are typical of distorted high-spin octahedral iron(II) complexes, but the asymmetric line widths found in the quadrupole doublet indicate the presence of a reduced relaxation rate for the effective paramagnetic hyperfine field.

Introduction

In contrast to cyclopentadienide ligands, with which they have often been compared, the tris(pyrazolyl)borate ligands offer much greater opportunities for modifying their coordinative features.[1] Whereas only one substituent can be placed on C$_5$H$_5$ ($\rightarrow$C$_5$R$_5$) to yield a derivative ligand *with retention of the original ligand symmetry*, there are 15 ways of placing from one to ten identical substituents on the parent HB(pz)$_3$ ligand and still maintain its original C_{3v} symmetry.[2]

As has been shown earlier, effective space management around the coordinated metal in poly(pyrazolyl)borates can be achieved through regiospecific placement of selected substituents in the pyrazolyl 3-position.[3] In the HB(3-Rpz)$_3$ ligands, where R = phenyl, this hinders but does not prevent formation of L$_2$M complexes, and favors formation of tetrahedral LMX species, which can be solvated or complexed with a donor ligand. With R = Bu^t, the metal is quite inaccessible and remains in a tetrahedral or pseudotetrahedral environment for the first-row transition metals. By pseudotetrahedral we are referring to structures such as HB(3-Bu^{t}pz)$_3$Zn(OAc),[4] HB(3-Bu^{t}pz)$_3$Mg(OAc),[5] HB(3-Bu^{t}pz)$_3$Zn(NO$_3$),[6] and HB(3-Bu^t-5-Me-pz)$_3$Co(O$_2$),[7] where some degree of five-coordination could be present.

In the hierarchy of increasing steric hindrance around the metal in 3-substituted tris(pyrazolyl)borates, the currently known series is H < CH$_3$ < C$_6$H$_5$ < Pr^i < Bu^t. In terms of forming octahedral L$_2$M complexes, ligands with R = H and CH$_3$ do so readily, those with R = C$_6$H$_5$ do so reluctantly, and those with R = Pr^i do not form L$_2$M complexes.[8] The ligands with R = Pr^i will form octahedral complexes only with rearrangement of each L to HB(3-Pr^{i}pz)$_2$(5-Pr^{i}pz); they will also form mixed octahedral LML complexes, provided L is a relatively unhindered tris(pyrazolyl)borate ligand.[9] Finally, ligands with R = Bu^t do not form octahedral complexes at all with first-row transition metals.[10]

Conversely, in terms of formation of LMX (X = halide or pseudohalide) species, ligands with R = Bu^t form these stable complexes with ease; with R = Pr^i, LMX complexes are also readily formed, but they possess reactivity for solvation or for displacement of X with anionic nucleophiles; ligands with R = phenyl form LMX species, which are even more reactive toward solvation or substitution of X. When R = methyl, and even more so when R = H, the LMX species become progressively less stable and undergo transformation to the octahedral L$_2$M complexes.

To investigate the effect of reducing the ring size of the 3-substituent (as compared with a phenyl group), we prepared the HB[3-(2′-thienyl)pyrazol-1-yl]$_3$ ligand shown in I and studied its coordinative behavior to see where it fits in the series of tris(pyrazolyl)borates with different 3-substituents.

A priori, tris(pyrazolyl)borates with the 3-(2′-thienyl) substituent were expected to fit between those with 3-phenyl and those

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(2) Considering that the 3-, 4-, and 5-positions of the pyrazolyl group, as well as the boron atom, can be substituted, we have the possibilities of four mono-, six bis-, four tris-, and one tetrakis-substituted HB(pz)$_3$ ligands, all maintaining the original ligand symmetry. The number of possibilities is greatly increased, if substituents are nonidentical.

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(10) They may, however, form octahedral species with second-row metals as, for instance, in HB(3-Bu^{t}pz)$_3$Mo(CO)$_2$NO.[3]

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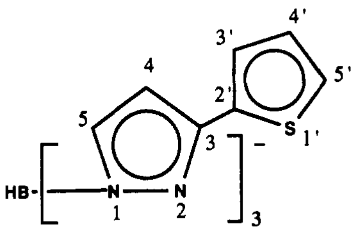

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with 3-methyl substituents in terms of steric hindrance. They also were not expected to show oxidative C–H addition to the metal, as has been observed for the 3-phenyl system.[11]

Experimental Section

The complex $HB(3\text{-}Pr^{i}\text{-}4\text{-}Br\text{-}pz)_3CoCl$ was prepared by the literature procedure.[8] All the other chemicals were reagent grade and were used as received. Elemental analyses were done by Microanalysis, Inc., Wilmington, DE. Infrared spectra were obtained as Nujol mulls with a Perkin-Elmer 283-B infrared spectrophotometer. Proton NMR spectra were obtained with a Nicolet NT360WB spectrometer. Diamagnetic compounds were studied with typical conditions of 16K data points, a sweep width of 3000–4000 Hz, 90° pulse angles, and a recycle time of 4–5 s. Paramagnetic compounds were studied with 64K data points, a sweep width of 100 kHz, 45° pulse angles, and a recycle time of 1.2 s.

The Mössbauer spectra were obtained on a Harwell constant-acceleration spectrometer that utilized a room-temperature rhodium matrix cobalt-57 source and was calibrated at room temperature with α-iron foil. The observed spectra were fitted by using standard computer least-squares minimization techniques, with one quadrupole doublet, which had symmetric areas and different line widths.

Crystallographic data and constants for each compound are summarized in Tables I and II. Interestingly, the asymmetric repeat unit in both cases is half the molecule with the Co lying on an inversion center. In addition, each crystallizes with half a solvent molecule related by inversion (benzene) or 2-fold ($CHCl_3$) symmetry. In a latter, the chloroform was found to be disordered across the 2-fold axis. This was refined by an appropriate combination of multiplicity and thermal parameter treatment. Also, in both molecules there is evidence of 2-fold disorder of the thienyl rings from rotation along the C–C ring junction. In the benzene derivative, this is evident from the lengthening of the C(26)–C(27) ring bond as well as the difficulty refining the hydrogen atom attached to C(27), which was the only hydrogen required to be held fixed (negative thermal parameter). In the chloroform case, elongated carbon thermal ellipsoids (C(17)) undoubtedly result from the same mechanism.

Atomic coordinates and equivalent isotropic thermal parameters are listed in Tables III and IV. Interatomic distances are listed in Tables V and VI, while intramolecular angles are listed in Tables VII and VIII, respectively. Tables of observed and calculated structure factor amplitudes are given in the supplementary material.

Preparation of 3-(2′-Thienyl)pyrazole. To a slurry of 128 g (2.4 mol) of dry sodium methoxide in 1 L of toluene, stirred rapidly in a 4-L beaker at room temperature, was added in one portion a mixture of 300 g (2.38 mol) of 2-acetylthiophene and 500 mL (large exesss) of ethyl formate. Within seconds, the reaction slurry became a semisolid mass. This was stirred manually with a large spatula, having been thinned by the addition of 1 L of ether, and was then filtered. The filter cake was pressed dry and washed with ether. The crude solid was dissolved in 2 L of methanol, and the solution was mixed with an aqueous solution of 2.38 mol of hydrazine hydrochloride. After 1 h of stirring, the product was extracted with methylene chloride. The extracts were filtered through a bed of alumina, stripped, and distilled, collecting the product, bp 152 °C/1.6 Torr, which was obtained in 220 g (61.6%) yield; mp 97–98 °C (lit.[12] 96.5–98 °C). NMR: d 7.62, d 7.33, t 7.06, d 6.52 ppm (1:1:1:1), plus broad NH at 12.8 ppm.

Preparation of Potassium Hydrotris[3-(2′-thienyl)pyrazol-1-yl]borate (=KL*). A mixture of 75 g (0.4 mol) of 3-(2′-thienyl)pyrazole and 5.4 g (0.1 mol) of KBH_4 was heated with stirring, the emanating gases being measured by a wet test meter. Hydrogen evolution commenced around 145 °C and continued, as the temperature rose to 190 °C, until 7.5 L of hydrogen was evolved. The clear melt was allowed to cool somewhat and was poured into 300 mL of stirred toluene; the mixture was boiled briefly and allowed to cool. The slurry was diluted with some hexane and was filtered to yield, after washing with hexane and drying, 40 g (80%) of white solid with BH at 2410 cm^{-1}. The solid was dissolved in THF to yield a 0.2 M solution, which was used to make complexes of the title ligand.

Table I. Summary of X-ray Diffraction Data for $[Co(HB(3\text{-}(2'\text{-}thienyl)pz)_3)_2](CHCl_3)$

formula	$CoCl_3S_6N_{12}C_{43}B_2H_{33}$	vol, Å^3	4522.6
space group	$C2/c$ (No. 15)	Z	4
a, Å	21.577 (2)	fw	1097.11
b, Å	12.464 (0)	calc dens, g/cm^3	1.611
c, Å	18.298 (2)	μ(Mo), cm^{-1}	8.72
α, deg	90	radiation λ, Å	0.710690
β, deg	113.21 (1)	transm factor	0.66–1.05
γ, deg	90	R, R_w	0.062, 0.065
temp, °C	–70		

Table II. Summary of X-ray Diffraction Data for $[Co(HB(3\text{-}(2'\text{-}thienyl)pz)_3)_2](C_6H_6)$

formula	$CoS_6N_{12}C_{48}B_2H_{38}$	vol, Å^3	1157.5
space group	$P\bar{1}$ (No. 2)	Z	1
a, Å	10.148 (2)	fw	1055.85
b, Å	11.768 (2)	calc dens, g/cm^3	1.515
c, Å	12.241 (3)	μ(Mo), cm^{-1}	6.79
α, deg	61.54 (1)	radiation λ, Å	0.710690
β, deg	69.06 (1)	transm factor	0.75–1.19
γ, deg	67.19 (1)	R, R_w	0.044, 0.043
temp, °C	–70		

Table III. Atomic Coordinates and Equivalent Isotropic Thermal Parameters for $[Co(HB(3\text{-}(2'\text{-}thienyl)pz)_3)_2](CHCl_3)$

atom	x	x	z	B_{iso}
Co(1)	2500	2500	0	1.2 (1)
Cl(1)	0	1193 (2)	2500	10.0 (2)
Cl(2)	654 (1)	3153 (2)	2497 (2)	9.8 (1)
S(1)	4322 (1)	–765 (1)	141 (1)	3.2 (1)
S(2)	4974 (1)	3531 (1)	–141 (1)	3.2 (1)
S(3)	1709 (1)	–1797 (1)	–141 (1)	3.2 (1)
N(11)	3566 (2)	1845 (3)	1529 (2)	1.5 (1)
N(12)	3389 (2)	1628 (2)	737 (2)	1.4 (1)
N(21)	2596 (2)	3004 (3)	–1530 (2)	1.4 (1)
N(22)	3013 (2)	3030 (2)	–734 (2)	1.4 (1)
N(31)	1937 (2)	1340 (3)	–1532 (2)	1.5 (1)
N(32)	2142 (2)	1096 (3)	–736 (2)	1.4 (1)
C(13)	3866 (2)	947 (3)	709 (2)	1.6 (1)
C(14)	4337 (2)	736 (4)	1475 (2)	2.2 (1)
C(15)	4127 (2)	1314 (3)	1972 (2)	2.0 (1)
C(16)	3874 (2)	420 (3)	–9 (2)	1.7 (1)
C(17)	3579 (2)	751 (3)	–858 (2)	2.0 (1)
C(18)	2767 (2)	–101 (4)	–1268 (3)	2.4 (1)
C(19)	4151 (2)	–887 (4)	–839 (3)	2.7 (1)
C(23)	3607 (2)	3418 (3)	–705 (2)	1.6 (1)
C(24)	3563 (2)	3639 (3)	–1477 (2)	2.2 (1)
C(25)	2919 (2)	3363 (3)	–1975 (2)	2.0 (1)
C(26)	4230 (2)	3521 (3)	7 (2)	1.7 (1)
C(27)	4344 (2)	2671 (3)	857 (2)	2.0 (1)
C(28)	5075 (2)	3748 (4)	1283 (3)	2.5 (1)
C(29)	5437 (2)	3702 (4)	837 (3)	2.6 (1)
C(33)	2052 (2)	29 (3)	–708 (2)	1.6 (1)
C(34)	1800 (2)	–401 (3)	–1476 (2)	2.2 (1)
C(35)	1734 (2)	455 (3)	–1973 (2)	2.0 (1)
C(36)	2152 (2)	–604 (3)	9 (2)	1.7 (1)
C(37)	2592 (2)	–421 (3)	855 (2)	2.0 (1)
C(38)	2478 (2)	–1346 (4)	1286 (3)	2.4 (1)
C(39)	2051 (2)	–2093 (4)	834 (3)	2.6 (1)
C(41)	105 (6)	2494 (10)	2825 (6)	4.2 (3)
B(1)	1891 (2)	2499 (4)	–1824 (2)	1.6 (1)

Preparation of L*Tl. This derivative was prepared by stirring the KL* solution with excess aqueous $TlNO_3$, extraction of the product with methylene chloride, filtration through alumina, evaporation, and recrystallization from toluene; mp 218–220 °C. IR: 2450 cm^{-1}. Anal. Calc for $C_{21}H_{16}BN_6S_3Tl$: C, 38.0; H, 2.56; N, 12.7. Found: C, 38.1; H, 2.48; N, 12.6.

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Table IV. Atomic Coordinates and Equivalent Isotropic Thermal Parameters for [Co(HB(3-(2′-thienyl)pz)$_3$)$_2$](C$_6$H$_6$)

atom	*x*	*y*	*z*	B_{iso}
Co(1)	5000	5000	5000	1.1 (1)
S(1)	2572 (1)	6956 (1)	8933 (1)	2.5 (1)
S(2)	4518 (1)	−236 (1)	6682 (1)	2.7 (1)
S(3)	4510 (1)	2145 (1)	8647 (1)	3.1 (1)
N(11)	6762 (2)	4471 (2)	6750 (2)	1.5 (1)
N(12)	5374 (2)	5165 (2)	6560 (2)	1.4 (1)
N(21)	7329 (2)	2586 (2)	6086 (2)	1.5 (1)
N(22)	6019 (2)	2843 (2)	5814 (2)	1.4 (1)
N(31)	1826 (2)	5356 (2)	5470 (2)	1.4 (1)
N(32)	2909 (2)	4693 (2)	6138 (2)	1.4 (1)
C(13)	4733 (3)	5722 (2)	7426 (2)	1.6 (1)
C(14)	5710 (3)	5377 (3)	8171 (3)	2.1 (1)
C(15)	6972 (3)	4586 (3)	7708 (2)	2.0 (1)
C(16)	3219 (3)	6539 (2)	7622 (2)	1.7 (1)
C(17)	2127 (3)	7046 (2)	6970 (3)	1.7 (1)
C(18)	785 (3)	7736 (3)	7552 (3)	2.1 (1)
C(19)	871 (3)	7764 (3)	8616 (3)	2.6 (1)
C(23)	5894 (3)	1640 (2)	6045 (2)	1.6 (1)
C(24)	7131 (3)	627 (2)	6454 (3)	2.2 (1)
C(25)	7997 (3)	1259 (2)	6471 (3)	2.1 (1)
C(26)	4626 (3)	1400 (2)	5962 (2)	1.7 (1)
C(27)	3400 (3)	2305 (2)	5360 (2)	1.7 (1)
C(28)	2492 (3)	1515 (3)	5562 (3)	2.3 (1)
C(29)	2960 (3)	183 (3)	6234 (3)	2.4 (1)
C(33)	2253 (3)	4128 (2)	7371 (2)	1.6 (1)
C(34)	745 (3)	4439 (3)	7477 (3)	2.2 (1)
C(35)	518 (3)	5219 (3)	6258 (2)	1.9 (1)
C(36)	2924 (3)	3411 (2)	8477 (2)	1.7 (1)
C(37)	2267 (3)	3622 (3)	9596 (3)	2.4 (1)
C(38)	3083 (4)	2764 (3)	10548 (3)	3.0 (1)
C(39)	4305 (4)	1913 (3)	10164 (3)	3.3 (1)
C(91)	1312 (4)	307 (4)	−623 (3)	3.5 (1)
C(92)	1200 (4)	−742 (3)	542 (3)	3.4 (1)
C(93)	−116 (4)	−1041 (3)	1165 (3)	3.4 (1)
B(1)	7890 (3)	3694 (3)	5944 (3)	1.5 (1)

Table V. Interatomic Distances (Å) for [Co(HB(3-(2′-thienyl)pz)$_3$)$_2$](CHCl$_3$)

Co(1)–N(12)	2.154 (3)	N(21)–B(1)	1.533 (5)
Co(1)–N(22)	2.154 (3)	N(31)–B(1)	1.531 (6)
Co(1)–N(32)	2.157 (3)	C(13)–C(14)	1.394 (5)
Cl(1)–C(41)	1.712 (13)	C(13)–C(16)	1.475 (5)
Cl(2)–C(41)[b]	1.715 (12)	C(14)–C(15)	1.370 (6)
Cl(2)–C(41)	1.733 (11)	C(16)–C(17)	1.485 (6)
S(1)–C(16)	1.729 (4)	C(17)–C(18)	1.470 (5)
S(1)–C(19)	1.690 (5)	C(18)–C(19)	1.334 (7)
S(2)–C(26)	1.730 (4)	C(23)–C(24)	1.404 (5)
S(2)–C(29)	1.685 (5)	C(23)–C(26)	1.462 (5)
S(3)–C(36)	1.730 (4)	C(24)–C(25)	1.373 (6)
S(3)–C(39)	1.681 (5)	C(26)–C(27)	1.488 (6)
N(11)–N(12)	1.373 (4)	C(27)–C(28)	1.462 (5)
N(21)–N(22)	1.377 (4)	C(28)–C(29)	1.334 (6)
N(31)–N(32)	1.379 (4)	C(33)–C(34)	1.399 (5)
N(11)–C(15)	1.337 (5)	C(33)–C(36)	1.473 (5)
N(12)–C(13)	1.350 (5)	C(34)–C(35)	1.372 (6)
N(21)–C(25)	1.340 (5)	C(36)–C(37)	1.480 (6)
N(22)–C(23)	1.351 (5)	C(37)–C(38)	1.471 (5)
N(31)–C(35)	1.335 (5)	C(38)–C(39)	1.340 (7)
N(32)–C(33)	1.348 (5)	C(41)–C(41)[b]	1.095 (20)
N(11)–B(1)[a]	1.533 (5)		

[a] Symmetry operation: $^1/_2 - x$, $^1/_2 - y$, $-z$. [b] Symmetry operation: $-x$, y, $^1/_2 - z$.

Preparation of L$^*_2$M Complexes (M = Fe, Co, Ni). These complexes were prepared by mixing aqueous solutions of the appropriate metal nitrate or perchlorate with 2 equiv of the above ligand solution, dilution with water, extraction of the product with methylene chloride, followed by evaporation of the organic extract, and recrystallization of the complexes from toluene. The products were obtained in 75–85% yields.

L$^*_2$Co: yellow crystals; mp 233–235 °C. IR: broad peak at 2470 cm^{-1} with shoulder at 2490 and 2430 cm^{-1} NMR: 83.3 (1 H, BH), 65.4 (3 H, pz 5-H), 47.5 (3 H, pz 4-H), 0.16 (3 H, thienyl 4-H), −0.74 (3 H, thienyl 5-H), −25.1 ppm (3 H, thienyl 3-H). Anal. Calc for $C_{42}H_{32}B_2N_{12}S_3$: C, 51.6; H, 3.28; N, 17.2. Found: C, 51.6; H, 3.43; N, 17.0.

Table VI. Interatomic Distances (Å) for [Co(HB(3-(2′-thienyl)pz)$_3$)$_2$](C$_6$H$_6$)

Co(1)–N(12)	2.182 (2)	C(13)–C(14)	1.399 (3)
Co(1)–N(22)	2.190 (2)	C(13)–C(16)	1.468 (3)
Co(1)–N(32)	2.139 (2)	C(14)–C(15)	1.374 (4)
S(1)–C(16)	1.731 (3)	C(16)–C(17)	1.373 (4)
S(1)–C(19)	1.700 (3)	C(17)–C(18)	1.422 (4)
S(2)–C(26)	1.724 (2)	C(18)–C(19)	1.352 (4)
S(2)–C(29)	1.673 (3)	C(23)–C(24)	1.403 (3)
S(3)–C(36)	1.714 (3)	C(23)–C(26)	1.465 (3)
S(3)–C(39)	1.689 (3)	C(24)–C(25)	1.364 (4)
N(11)–N(12)	1.366 (3)	C(26)–C(27)	1.451 (3)
N(21)–N(22)	1.371 (3)	C(27)–C(28)	1.435 (3)
N(31)–N(32)	1.362 (3)	C(28)–C(29)	1.353 (4)
N(11)–C(15)	1.338 (3)	C(33)–C(34)	1.400 (3)
N(12)–C(13)	1.347 (3)	C(33)–C(36)	1.461 (3)
N(21)–C(25)	1.351 (3)	C(34)–C(35)	1.378 (4)
N(22)–C(23)	1.353 (3)	C(36)–C(37)	1.387 (4)
N(31)–C(35)	1.350 (3)	C(37)–C(38)	1.408 (4)
N(32)–C(33)	1.353 (3)	C(38)–C(39)	1.352 (5)
N(11)–B(1)	1.537 (3)	C(91)–C(92)	1.374 (5)
N(21)–B(1)	1.531 (3)	C(91)–C(93)[b]	1.369 (5)
N(31)–B(1)[a]	1.541 (3)	C(92)–C(93)	1.367 (5)

[a] Symmetry operation: $1 - x$, $1 - y$, $1 - z$. [b] Symmetry operation: $-x$, $-y$, $-z$.

Table VII. Intramolecular Angles (deg) for [Co(HB(3-(2′-thienyl)pz)$_3$)$_2$](CHCl$_3$)

N(12)–Co(1)–N(12)[a]	180 (11)	Cl(2)[b]–C(41)–C(41)[b]	72 (1)
N(12)–Co(1)–N(22)[a]	90.3 (1)	S(1)–C(16)–C(13)	116.2 (3)
N(12)–Co(1)–N(22)	89.7 (1)	S(1)–C(16)–C(17)	112.7 (3)
N(12)–Co(1)–N(32)[a]	90.4 (1)	S(1)–C(19)–C(18)	114.1 (3)
N(12)–Co(1)–N(32)	89.6 (1)	S(2)–C(26)–C(23)	116.4 (3)
N(22)–Co(1)–N(22)[a]	180 (8)	S(2)–C(26)–C(27)	112.4 (3)
N(22)–Co(1)–N(32)[a]	89.7 (1)	S(2)–C(29)–C(28)	114.2 (3)
N(22)–Co(1)–N(32)	90.3 (1)	S(3)–C(36)–C(33)	116.2 (3)
N(32)–Co(1)–N(32)[a]	180 (12)	S(3)–C(36)–C(37)	112.7 (3)
C(41)–Cl(1)–C(41)[b]	37.3 (7)	S(3)–C(39)–C(38)	114.2 (3)
C(41)–Cl(2)–C(41)[b]	37.0 (7)	N(12)–C(13)–C(14)	110.2 (3)
C(16)–S(1)–C(19)	91.9 (2)	N(12)–C(13)–C(16)	126.1 (3)
C(26)–S(2)–C(29)	91.9 (2)	N(11)–C(15)–C(14)	108.5 (3)
C(36)–S(3)–C(39)	92.0 (2)	N(22)–C(23)–C(24)	110.1 (3)
Co(1)–N(12)–N(11)	111.6 (2)	N(22)–C(23)–C(26)	126.2 (3)
Co(1)–N(22)–N(21)	111.7 (2)	N(21)–C(25)–C(24)	108.3 (3)
Co(1)–N(32)–N(31)	111.6 (2)	N(32)–C(33)–C(34)	110.1 (3)
Co(1)–N(12)–C(13)	142.9 (2)	N(32)–C(33)–C(36)	126.1 (3)
Co(1)–N(22)–C(23)	142.9 (2)	N(31)–C(35)–C(34)	108.5 (3)
Co(1)–N(32)–C(33)	143.0 (3)	C(14)–C(13)–C(16)	123.5 (3)
N(12)–N(11)–C(15)	110.5 (4)	C(13)–C(14)–C(15)	105.4 (3)
N(11)–N(12)–C(13)	105.4 (3)	C(13)–C(16)–C(17)	131.1 (3)
N(22)–N(21)–C(25)	110.7 (3)	C(16)–C(17)–C(18)	105.2 (4)
N(21)–N(22)–C(23)	105.4 (3)	C(17)–C(18)–C(19)	116.1 (4)
N(32)–N(31)–C(35)	110.4 (3)	C(24)–C(23)–C(26)	123.5 (3)
N(31)–N(32)–C(33)	105.5 (3)	C(23)–C(24)–C(25)	105.5 (3)
N(12)–N(11)–B(1)[a]	121.9 (3)	C(23)–C(26)–C(27)	131.2 (3)
N(22)–N(21)–B(1)	121.7 (3)	C(26)–C(27)–C(28)	105.4 (3)
N(32)–N(31)–B(1)	121.8 (3)	C(27)–C(28)–C(29)	116.1 (4)
C(15)–N(11)–B(1)[a]	127.2 (3)	C(34)–C(33)–C(36)	123.6 (3)
C(25)–N(21)–B(1)	127.2 (3)	C(33)–C(34)–C(35)	105.5 (4)
C(35)–N(31)–B(1)	127.4 (3)	C(33)–C(36)–C(37)	131.1 (3)
Cl(1)–C(41)–Cl(2)	110.0 (6)	C(36)–C(37)–C(38)	105.4 (4)
Cl(1)–C(41)–Cl(2)[b]	110.9 (6)	C(37)–C(38)–C(39)	115.7 (4)
Cl(2)–C(41)–Cl(2)[b]	110.1 (7)	N(11)[a]–B(1)–N(21)	110.1 (3)
Cl(1)–C(41)–C(41)[b]	71.4 (4)	N(11)[a]–B(1)–N(31)	110.0 (3)
Cl(2)–C(41)–C(41)[b]	71 (1)	N(21)–B(1)–N(31)	110.2 (3)

[a] Symmetry operation: $^1/_2 - x$, $^1/_2 - y$, $-z$. [b] Symmetry operation: $-x$, y, $^1/_2 - z$.

L$^*_2$Ni: pale lilac crystals; mp 279–281 °C. IR: sharp peak at 2470 cm^{-1} with shoulder at 2490 and 2430 cm^{-1}. Anal. Calc for $C_{42}H_{32}B_2N_{12}S_3$: C, 51.6; H, 3.28; N, 17.2. Found: C, 51.4; H, 3.13; N, 17.0.

L$^*_2$Fe: pale yellowish green crystals; mp 241–243 °C. IR: sharp peak at 2470 cm^{-1} with shoulder at 2490 and 2430 cm^{-1}. Anal. Calc for $C_{42}H_{32}B_2FeN_{12}S_3$: C, 51.7; H, 3.29; N, 17.3. Found: C, 51.4; H, 3.45; N, 16.9.

Preparation of HB(3,5-Me$_2$pz)$_3$MNCO Complexes (M = Zn, Co). To a solution of 100 mL of 0.5 M zinc nitrate or cobalt nitrate, plus 10 g

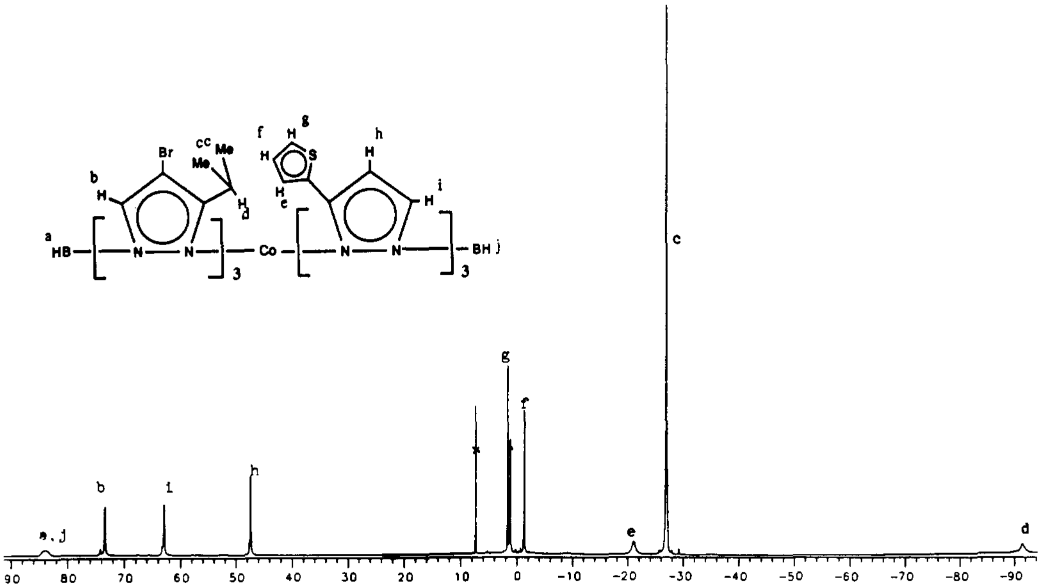

Figure 1. NMR spectrum of HB(3-Pr^i-4-Br-pz)$_3$Co[3-(2'-thienyl)pz]$_3$BH.

Table VIII. Intramolecular Angles (deg) for [Co(HB(3-(2′-thienyl)pz)$_3$)$_2$](C$_6$H$_6$)

N(12)–Co(1)–N(12)^a	180 (9)	S(2)–C(29)–C(28)	112.9 (2)
N(12)–Co(1)–N(22)^a	91.56 (7)	S(3)–C(36)–C(33)	126.7 (2)
N(12)–Co(1)–N(22)	88.44 (7)	S(3)–C(36)–C(37)	110.4 (2)
N(12)–Co(1)–N(32)^a	91.38 (7)	S(3)–C(39)–C(38)	112.5 (2)
N(12)–Co(1)–N(32)	88.62 (7)	N(12)–C(13)–C(14)	110.2 (2)
N(22)–Co(1)–N(22)^a	180 (9)	N(12)–C(13)–C(16)	126.4 (2)
N(22)–Co(1)–N(32)^a	89.48 (7)	N(11)–C(15)–C(14)	108.7 (2)
N(22)–Co(1)–N(32)	90.52 (7)	N(22)–C(23)–C(24)	109.9 (2)
N(32)–Co(1)–N(32)^a	180 (9)	N(22)–C(23)–C(26)	125.8 (2)
C(16)–S(1)–C(19)	92.7 (1)	N(21)–C(25)–C(24)	108.6 (2)
C(26)–S(2)–C(29)	92.6 (1)	N(32)–C(33)–C(34)	109.7 (2)
C(36)–S(3)–C(39)	92.2 (1)	N(32)–C(33)–C(36)	127.4 (2)
Co(1)–N(12)–N(11)	111.2 (1)	N(31)–C(35)–C(34)	108.0 (2)
Co(1)–N(22)–N(21)	111.4 (1)	C(14)–C(13)–C(16)	123.3 (2)
Co(1)–N(32)–N(31)	113.4 (1)	C(13)–C(14)–C(15)	104.9 (2)
Co(1)–N(12)–C(13)	143.0 (2)	C(13)–C(16)–C(17)	132.5 (2)
Co(1)–N(22)–C(23)	142.3 (2)	C(16)–C(17)–C(18)	113.0 (2)
Co(1)–N(32)–C(33)	140.0 (2)	C(17)–C(18)–C(19)	112.9 (3)
N(12)–N(11)–C(15)	110.3 (2)	C(24)–C(23)–C(26)	124.2 (2)
N(11)–N(12)–C(13)	105.8 (2)	C(23)–C(24)–C(25)	105.6 (2)
N(22)–N(21)–C(25)	110.0 (2)	C(23)–C(26)–C(27)	131.6 (2)
N(21)–N(22)–C(23)	105.9 (2)	C(26)–C(27)–C(28)	107.5 (2)
N(32)–N(31)–C(35)	110.4 (2)	C(27)–C(28)–C(29)	115.4 (3)
N(31)–N(32)–C(33)	106.3 (2)	C(34)–C(33)–C(36)	122.6 (2)
N(12)–N(11)–B(1)	123.2 (2)	C(33)–C(34)–C(35)	105.6 (2)
N(22)–N(21)–B(1)	122.5 (2)	C(33)–C(36)–C(37)	122.7 (2)
N(32)–N(31)–B(1)^a	121.5 (2)	C(36)–C(37)–C(38)	112.3 (3)
C(15)–N(11)–B(1)	126.5 (2)	C(37)–C(38)–C(39)	112.5 (3)
C(25)–N(21)–B(1)	127.5 (2)	C(92)–C(91)–C(93)^b	120.2 (3)
C(35)–N(31)–B(1)^a	127.2 (2)	C(91)–C(92)–C(93)	119.6 (3)
S(1)–C(16)–C(13)	117.7 (2)	C(91)^b–C(93)–C(92)	120.2 (3)
S(1)–C(16)–C(17)	109.7 (2)	N(11)–B(1)–N(21)	109.9 (2)
S(1)–C(19)–C(18)	111.6 (2)	N(11)–B(1)–N(31)^a	110.5 (2)
S(2)–C(26)–C(23)	116.8 (2)	N(21)–B(1)–N(31)^a	109.2 (2)
S(2)–C(26)–C(27)	111.6 (2)		

[a] Symmetry operation: $1 - x$, $1 - y$, $1 - z$. [b] Symmetry operation: $-x$, $-y$, $-z$.

of KNCO, was added a slurry of 5 g (0.01 mol) of TlHB(3,5-Me$_2$pz)$_3$ in a mixture of 100 mL of DMAC, 50 mL of acetone, and 100 mL of methylene chloride. The slurry was stirred vigorously for 2 h and then added to 1 L of water. The resultant slurry was extracted four times with 800 mL of water. The methylene chloride layer was passed through a short layer of alumina and evaporated under reduced pressure. The residue was boiled with some hexane, and the mixture was cooled and filtered. In each case, there was obtained about 4 g (quantitative) of the appropriate product.

M = Zn: white; mp 314–315 °C. IR: 2540, 2250 cm^{-1}. Anal. Calcd for C$_{16}$H$_{27}$BN$_7$OZn: C, 47.5; H, 5.45; N, 24.3. Found: C, 47.8; H, 5.38; N, 24.1. NMR: s 5.72, s 1.36, s 1.31 ppm (1:3:3).

M = Co: pale purple (but in solution deep blue); sinters and decomposes from 332 °C. IR: 2520, 2225 cm^{-1}. Anal. Calc for C$_{16}$H$_{27}$BCoN$_7$O: C, 48.2; H, 5.53; N, 24.6. Found: C, 48.5; H, 5.38; N, 24.9.

Preparation of L*MNCS (M = Zn, Co). L*ZnNCS was obtained by a method similar to the one described above as a white solid, mp 274–276 °C. IR: 2520, 2110 cm^{-1}. NMR: d 7.95, d 7.78, d 7.40, dd 7.20, d 6.44 ppm (1:1:1:1:1). Anal. Calc: C, 45.4, H, 2.75; N, 16.8. Found: C, 45.3; H, 2.91; N, 16.4.

The initially formed L*CoNCS (as judged by its deep blue color) changed during the course of processing to the yellow L*$_2$Co, identified by IR spectroscopy.

L*Co[HB(3-Pr^i-4-Br-pz)$_3$]. An equimolar mixture of L*Tl and of HB(3-Pr^i-4-Br-pz)$_3$CoCl was stirred at room temperature in methylene chloride. Within 1 min, the deep blue color of the tetrahedral HB(3-Pr^i-4-Br-pz)$_3$CoCl (=LCoCl) changed to the yellow color of the octahedral mixed complex. The mixture was filtered through a bed of Celite and alumina to remove TlCl, and the filtrate was evaporated to dryness. The residue was purified by chromatography on alumina and then by recrystallization from a toluene–heptane mixture. It was obtained as yellow crystals, mp 248–250 °C to a red melt. NMR: 83.7 (2 H, BH, BH′), 73.0 (3 H, 5-H in L), 62.7 (3 H, 5-H in L*), 47.3 (3 H, 4-H in L*), 1.16 (3 H, thienyl 5-H), –1.31 (3 H, thienyl 4-H), –20.9 (3 H, thienyl 3-H), –26.7 (36 H, methyls), –91.0 ppm (3 H, CH in Pr^i). Anal. Calc for C$_{39}$H$_{41}$B$_2$Br$_3$CoN$_{12}$S$_3$: C, 42.8; H, 3.75; N, 15.4. Found: C, 43.0; H, 3.54; N, 15.3.

L*Mo(CO)$_2$(η^3-methallyl). An equimolar mixture of L*Tl and (MeCN)$_2$Mo(CO)$_2$Cl(η^3-methallyl) was stirred in methylene chloride for 2 h. The slurry was filtered through Celite and chromatographed on alumina, collecting the bright yellow band. Evaporation gave the product in 75% yield; mp 228–230 °C after recrystallization from toluene. Anal. Calc for C$_{27}$H$_{23}$BMoN$_6$O$_2$S$_3$: C, 48.7; H, 3.45; N, 12.6. Found: C, 49.0; H, 3.44; N, 12.3. IR: 2520 (BH), 1925, 1836 cm^{-1}. NMR: dd 7.81 (J = 3.7, 1.1 Hz; 1 H, thienyl 3-H), d 7.68 (J = 2.2 Hz; 2 H, pz 5-H), dd 7.55 (J = 5.1, 1.1 Hz; 1 H, thienyl 3-H), d 7.48 (J = 2.1 Hz; 1 H, pz 5-H), dd 7.39 (J = 3.7, 1.1 Hz; 2 H, thienyl 5-H), dd 7.37 (J = 5.1, 1.1 Hz; 2 H, thienyl 3-H), dd 7.26 (J = 5.1, 3.6 Hz; 1 H, thienyl 4-H), dd 7.11 (J = 5.1, 3.6 Hz; 2 H, thienyl 4-H), d 6.37 (J = 2.2 Hz; 1 H, pz 4-H), d 6.31 (J = 2.2 Hz; 2 H, pz 4-H), s 2.37 (2 H, syn H's), s 1.01 (3 H, methyl), s 0.53 ppm (2 H, anti H's) (1:2:1:1:2:2:1:2:1:2:2:3:2).

Results and Discussion

We have studied the coordinative behavior of the new hydrotris[3-(2′-thienyl)pyrazol-1-yl]borate ligand (=L*) and the NMR spectra of some of its complexes, as well as the X-ray crystallographic structures of two differently solvated L*$_2$Co complexes, plus the Mössbauer spectra of L*$_2$Fe. They are presented and discussed in that order.

Synthesis, Coordinative Behavior, and NMR Spectra. The reaction of KBH$_4$ in excess molten 3-(2′-thienyl)pyrazole produced the hydrotris[3-(2′-thienyl)pyrazol-1-yl]borate ligand (=L*) as the potassium salt, which was isolated with only slight contam-

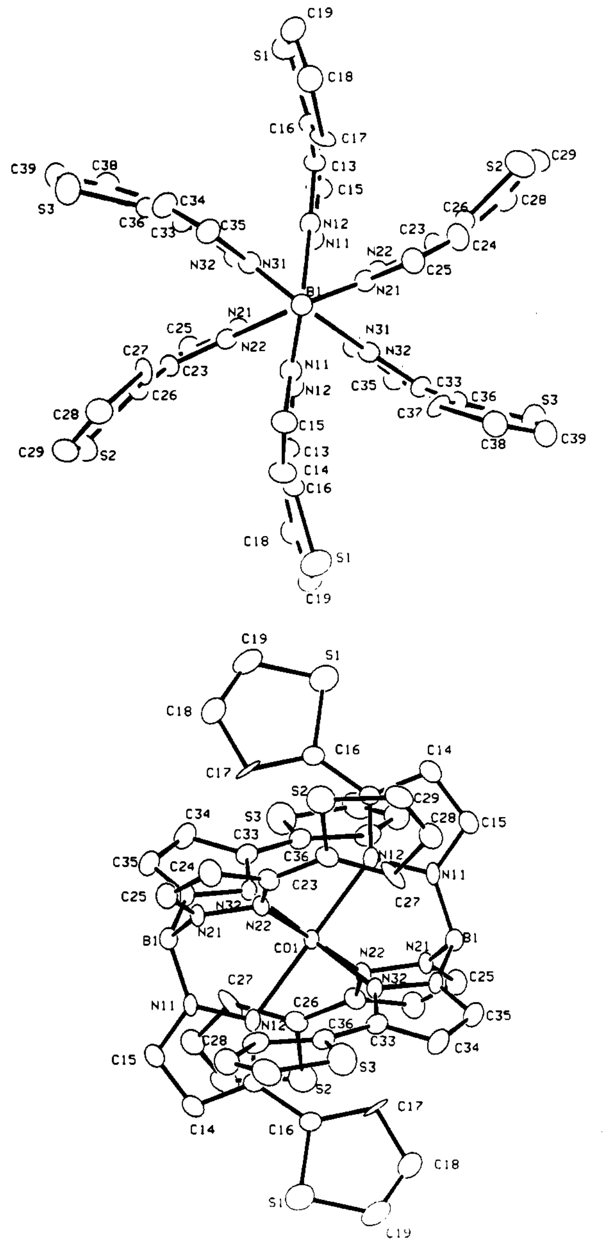

Figure 2. (a, Top) View of [Co(HB(3-(2′-thienyl)pz)$_3$)$_2$](CHCl$_3$) along the B–Co axis and (b, bottom) a side view. The vibrational ellipsoids are drawn at the 50% level in this and the other figures.

ination by the starting pyrazole and which was characterized as the Tl derivative. This ligand reacted rapidly with divalent first-row transition-metal ions (Fe, Co, Ni) to yield high-melting and fairly insoluble L*$_2$M complexes with colors characteristic of octahedral structures. The IR spectra of the Fe, Co, and Ni complexes were superimposable.

The NMR spectrum of the paramagnetic L*$_2$Co complex indicated that all six pyrazolyl groups are identical, and each proton signal could be assigned. The BH, 4-H, and 5-H protons were identified from previous assignments,[3] and 3′-H proton through its large shift, implying proximity to the Co ion, with the 4′- and 5′-protons being progressively less shifted, in line with their increasing distance from Co.

When attempting to prepare L*MX complexes (X = NCS, NCO, N$_3$), it was only possible to isolate them as stable species with Zn(II). With transition-metal ions, the initially formed L*MX complexes (made by slow addition of a KL* solution to a large excess of MX$_2$ in the presence of excess X$^-$ ion) underwent rapid conversion to L*$_2$M.

The ease of formation of L*$_2$M species and the instability of L*MX complexes were in contrast to the behavior of the 3-Ph analogue and in line with expectations. As a further test of the steric requirements of L*, we prepared the mixed octahedral L*CoL complex with HB(3-Pr^i-4-Br-pz)$_3$ (=L) as the other ligand:

$$\mathrm{HB(3\text{-}Pr^i\text{-}4\text{-}Br\text{-}pz)_3CoCl + L^*Tl \rightarrow HB(3\text{-}Pr^i\text{-}4\text{-}Br\text{-}pz)_3Co[3\text{-}(2'\text{-}thienyl)pz]_3BH}$$

The reaction of HB(3-Pr^i-4-Br-pz)$_3$CoCl with other poly(pyrazolyl)borate ligands is a sensitive probe of their steric requirements as a function of the 3-R substituent.[9] While for R = H such mixed octahedral complexes are produced rapidly, and for R = Me rather slowly, when R = phenyl, only two 3-phenylpyrazolyl groups coordinate to Co and the sixth coordination site is occupied by an agostic B–H–Co bond. With L*, the above reaction proceeded readily, and a yellow product was obtained, as expected of an octahedral cobalt(II) tris(pyrazolyl)borate. Further confirmation of the structure was obtained from the paramagnetic NMR spectrum (Figure 1), where each of the ligands was of C_{3v} symmetry (as was the overall symmetry of the molecule), and all the protons were properly accounted for, again in agreement with an octahedral structure. This clearly established L* to be less sterically demanding than its 3-phenyl analogue.

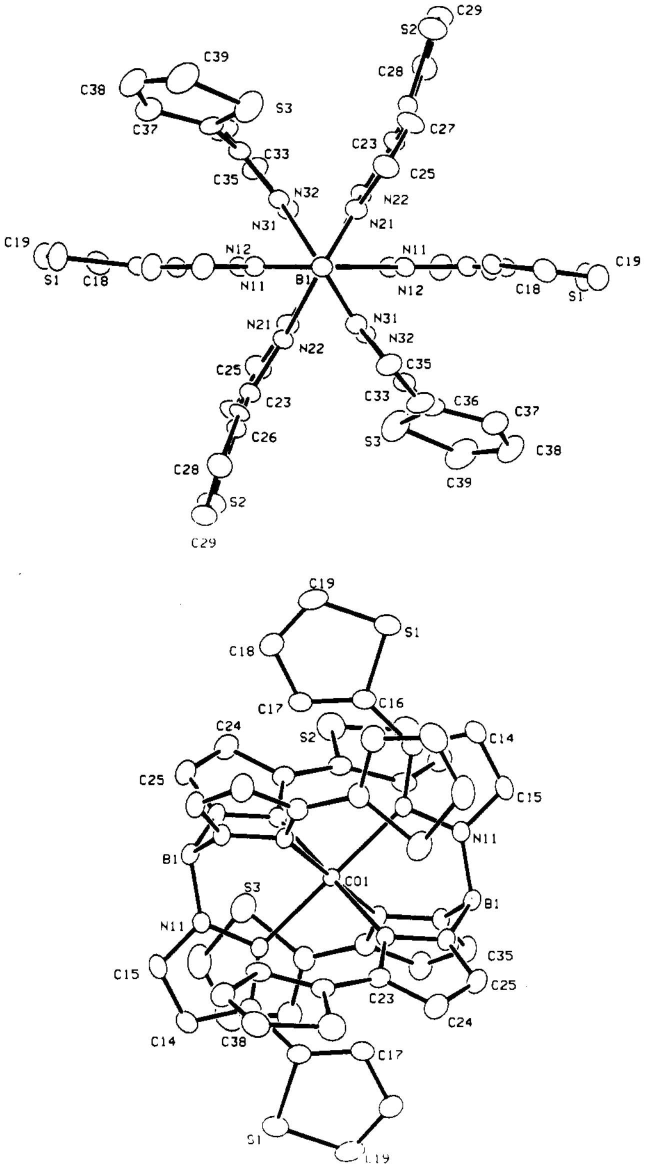

Figure 3. (a, Top) View of [Co(HB(3-(2′-thienyl)pz)$_3$)$_2$](C$_6$H$_6$) along the B–Co axis and (b, bottom) a side view.

X-ray Crystallography of L*$_2$Co. The structure determination of L*$_2$Co was done on two solvated samples containing benzene and chloroform, respectively. Both show Co coordinated in octahedral fashion. However, as is evident from Figures 2 and 3, two different structural conformations exist in the solid state,

Table IX. Mössbauer Effect Hyperfine Parameters

T, K	δ,[a] mm/s	ΔE_Q, mm/s	Γ_1, mm/s	Γ_2, mm/s
295	1.06	3.30	0.42	0.27
78	1.19	3.31	0.50	0.28

[a] Relative to room-temperature natural α-iron foil.

depending on the cocrystallized solvent. In the chloroform solvate the sulfur of all the thienyl group is trans to the Co, while in the benzene solvate two of the 2′-thienyl sulfur atoms are rotated cis to the Co. This is associated with a significant twist of the thienyl ring out of the pyrazolyl plane (43°), while the other 2′-thienyl rings are twisted only slightly (14.5, −7.5°). In the chloroform solvate structure, the dihedral twist angle is remarkably uniform (22.7, 22.8, 22.7°). By comparison, in $Fe(HB(3\text{-}Ph\text{-}pz)_3)_2$ the dihedral phenyl–pz angles range from 23 to 31°.[15] The structural changes associated with different solvations are also manifested in the Co–N bond lengths: the chloroform solvate has these bonds of almost uniform length (average 2.155 (3) Å), while in the benzene solvate two Co–N bonds are longer (2.182 (2), 2.190 (2) Å) and the one with cis sulfur is appreciably shorter (2.139 (2) Å). While these findings underscore the need for caution in assessing the molecular structure from crystals containing various cocrystallizing solvents, they also show a Co–N bond length differing only by 0.025 Å from that in $Co(HB(pz)_3)_2$ (2.155 Å vs 2.130 Å).[13] Although we have no reported structure of $Co(HB(3,5\text{-}Me_2pz)_3)_2$ for comparison purposes, we can compare the M–N bond length differentials between $Fe(HB(pz)_3)_2$ and $Fe(HB(3,5\text{-}Me_2pz)_3)_2$, which is 0.199 Å,[14] and between $Fe(HB(pz)_3)_2$ and $Fe(HB(3\text{-}Ph\text{-}pz)_3)_2$, which is 0.273 Å.[15] Clearly, the M–N bond length in $L^*{}_2Co$ is very close to that of the parent ligand complex $Co(HB(pz)_3)_2$, and this is indicative of a rather similar degree of steric hindrance.

Mössbauer Spectra of $L^*{}_2Fe$. The Mössbauer spectra of $L^*{}_2Fe$, obtained at 78 and 295 K, are illustrated in Figure 4, and the resulting hyperfine parameters are given in Table IX. The isomer shift and quadrupole splitting are typical of distorted high-spin iron(II) complexes,[16] and no evidence for a low-spin state is observed.[17-19] Indeed, the isomer shifts are very similar to those observed in the related $Fe(HB(pz)_3)_2$, $Fe(HB(3,5\text{-}Me_2pz)_3)_2$, and $Fe(HB(3,4,5\text{-}Me_3pz)_3)_2$ complexes when in the high-spin state.[17-19] The quadrupole splitting is however somewhat lower in $L^*{}_2Fe$ than in the high-spin state of any of the related methyl-substituted (or 3-Pr^i- and 3-Pr^i-4-Br-substituted[20]) complexes, indicating a somewhat more symmetric environment at the iron(II) site in $L^*{}_2Fe$. The splitting is, however, similar to that which can be estimated at room temperature in $Fe[HB(pz)_3]_2$ by extrapolation from either high pressure[18] or high temperature.[19] This increased symmetry at the iron site is consistent with the smaller steric demand of the ligands in $L^*{}_2Fe$ and $Fe[HB(pz)_3]_2$. The smaller steric demand permits these ligands to approach more nearly the "ideal" octahedral bond distances and angles in these complexes.

The most striking and unusual aspect of the spectra shown in Figure 4 is the different line widths of the two components of the quadrupole doublet, a difference that increases upon cooling. It is not possible to fit the observed spectra with two doublets with different isomer shifts and quadrupole splittings but with the same, or at least similar, line widths. This is consistent with the single metal site found in the X-ray structure. We are forced to conclude that the asymmetry observed in the line widths is intrinsic to the iron site and is the result of a rate of relaxation that is slightly slower than 10^{-8} s (the relaxation rate on the Mössbauer time scale). This relaxation cannot be associated with spin-state relaxation of the high-spin state with a low-spin state, as was observed in $Fe[HB(pz)_3]_2$,[19] because the hyperfine parameters do not change in a way that would be consistent with the presence of more of the low-spin iron(II), at lower temperatures. It seems more likely that $L^*{}_2Fe$ is showing the presence of a reduced effective paramagnetic hyperfine field relaxation rate, as has been discussed theoretically by several authors.[21-23] A comparison with the results shown by Afanas'ev and Gorobchenko[23] indicates that the relaxation of the hyperfine field is in either the x or the y direction normal to the principal axis of the electric field gradient. Isotropic relaxation in this xy plane may also be consistent with the observed spectra. We plan to study the low-temperature behavior of this compound in more detail in order to determine more precisely the rate and nature of the observed effective paramagnetic hyperfine field relaxation, i.e., whether it is predominantly controlled by a spin–spin or a spin–lattice relaxation mechanism.

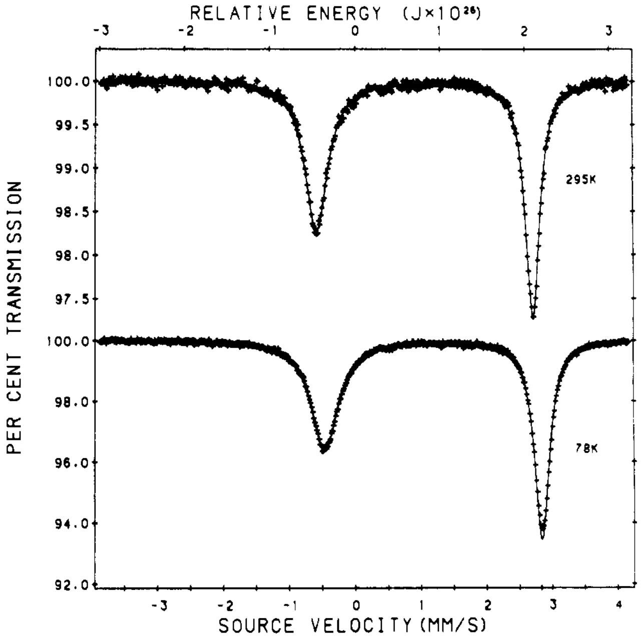

Figure 4. Mössbauer spectra of $L^*{}_2Fe$ obtained at 296 and 78 K and fit with a single quadrupole doublet with symmetric areas.

Conclusions

In the comparison of the L* ligand with a tris(pyrazolyl)borate ligand where 3-R = Me, the following findings provide an indication that L* may be the less sterically demanding of the two:

1. The reaction of L*Tl with $HB(3\text{-}Pr^i\text{-}4\text{-}Br\text{-}pz)_3CoCl$, to form the mixed complex $L^*CoHB(3\text{-}Pr^i\text{-}4\text{-}Br\text{-}pz)_3$, proceeds very rapidly, about as fast as that of the parent $HB(pz)_3$ ligand. By contrast, the reaction of $HB(3,5\text{-}Me_2pz)_3Tl$ is quite slow (many hours, as compared with a few minutes for L*Tl).

2. It is possible to prepare, isolate, recrystallize, and characterize $HB(3,5\text{-}Me_2pz)_3CoNCO$, while under similar conditions the initially formed L*CoNCO is invariably converted to $L^*{}_2Co$.

3. The difference in M–N bond length between $Co(HB(pz)_3)_2$ and $CoL^*{}_2$ is much smaller than that between $Fe(HB(pz)_3)_2$ and $Fe(HB(3,5\text{-}Me_2pz)_3)_2$ (0.025 Å vs 0.199 Å).

While these findings are only suggestive, we are inclined to update the sequence of tris(pyrazolyl)borate 3-R substituents, in order of their increasing steric demand, as follows: H < 2-thienyl < Me < phenyl < Pr^i < Bu^t.[24] The new ligand, HB[3-(2′-

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thienyl)pyrazol-1-yl)]$_3^-$ may thus be of value in fine-tuning systems where $HB(pz)_3^-$ and $HB(3,5\text{-}Me_2pz)_3^-$ have been used until now. That the effect is steric, and unrelated to the pK_a of the respective pyrazoles, can be deduced from the reactivity of the 3-H-, 3-Me-, and 3-Ph-substituted tris(pyrazolyl)borates, which is H > Me > Ph, while their pK_a values are 2.48, 3.27, and 2.09, respectively.[25] The pK_a value for 3-thienylpyrazole is unknown.

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Supplementary Material Available: Full summaries of X-ray diffraction data (Tables I-S and II-S) and listings of thermal parameters (Tables X and XI), hydrogen atom positions (Tables XII and XIII), and complete bond distances and angles (Tables XIV and XV) (13 pages); listings of observed and calculated structure factors (Tables XVI and XVII) (22 pages). Ordering information is given on any current masthead page.

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(24) One of the reviewers suggested determining the cone angles for L*. We have determined the cone angle of the excluded space around Co during rotation of L* around the B–Co axis, with the thienyl group positioned so that its 3-H was in the closest proximity to Co. The "cone angle" thus obtained was 246°, while the "cone angle" for $HB(3\text{-}Ph\text{-}pz)_3$, determined in the same fashion, was 235°. Noting that the cone angle for the extremely hindered $HB(3\text{-}Bu^tpz)_3$ is 244°, one sees there is clearly no correlation between the calculated cone angles and the accessibility of the metal to nucleophilic reagents. Thus, the "cone angles" calculated for tris(pyrazolyl)borate ligands with planar 3-substituents are not meaningful. What is meaningful is the size of the open wedgelike spaces between the pz rings, as defined by the size and orientation of the 3-substituents, through which a nucleophile ligand can approach the metal center. Due to the variety of equilibrium geometries for the planar 3-substituents, calculation of these "wedge angles" is difficult. For 3-substituents such as H, Me, and Bu^t these wedge angles are 120, 91, and 67°, respectively, reflecting in a qualitative way the ease of access to the metal.

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Strong Ferromagnetism between Copper(II) Ions Separated by 6.7 Å in a New Phthalato-Bridged Copper(II) Binuclear Complex

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The crystal structure of $[(dien)(ClO_4)Cu(1)(\mu\text{-}Phth)Cu(2)(dien)](ClO_4)$, where $Phth^{2-}$ is the dianion of phthalic acid and dien is diethylenetriamine, has been determined by direct X-ray methods. The complex crystallizes in the monoclinic space group $P2_1$ with two formula units in a unit cell of dimensions $a = 12.101$ (6) Å, $b = 7.805$ (4) Å, $c = 15.415$ (7) Å, $\beta = 109.82$ (4)°, and $\rho_{calcd} = 1.690$ g/cm^3. The structure was refined to conventional discrepancy factors of $R = 0.054$ and $R_w = 0.060$ for 2173 observed reflections. The acentric monoclinic cell contains binuclear cations $[(dien)(ClO_4)Cu(1)(\mu\text{-}Phth)Cu(2)(dien)]^+$ and isolated perchlorate anions. The Cu centers are bridged by Phth dianions coordinated in both uni- and bidentate fashions to Cu(1) and Cu(2), respectively, through their carboxylic oxygen donor atoms. The two copper environments are dissimilar and irregular. The structure around Cu(1) is close to a square-based pyramid with one of the oxygen atoms of the perchlorate anions in the apical position. The Cu(2) environment is close to a severely distorted octahedron. An oxygen atom of a carboxylato group bridges two Cu(2) atoms of two different binuclear units, rather loosely [Cu(2)–O(22) = 2.318 (8) Å], to infinite chains of binuclear units around a screw axis 2_1. Least-squares fitting of the variable-temperature (4.2–295 K) magnetic susceptibility experimental data to Bleaney–Bowers equation with a molecular field approximation led to a singlet–triplet energy gap of 80 ± 10 cm^{-1}, $g = 2.10$, and $zJ' = -1.81$ cm^{-1}. The EPR spectrum does not exhibit any evidence of triplet state. From an orbital interpretation of the coupling stems a new situation leading to ferromagnetic interaction between magnetic centers separated by multiatom-bridging units.

Introduction

Copper(II) binuclear complexes exhibiting a spin–triplet ground state are very few[2] as compared to those with a spin–singlet ground state. To our knowledge, in all three known cases of ferromagnetically coupled molecular magnetic systems the two magnetic centers are bridged by a single-atom bridging ligand. The ferromagnetic properties of these compounds have been attributed[2,3] either to the accidental or to strict orthogonality of their magnetic orbitals and/or to spin-polarization effects. With this in mind we thought it would be advisable to explore further the fascinating field of molecular ferromagnets. As a consequence, we focused our efforts on the investigation of novel ferromagnetically coupled Cu(II) magnetic systems involving magnetic centers far separated from each other via multiatom–bridging units. Phthalate dianions, due to both their versatile bonding mode with the Cu(II) ions[4] and their peculiar structure—involving carboxylate groups that are noncoplanar with themselves and with the benzene ring—could be good candidates in supporting long-distance ferromagnetic exchange interactions. Within this framework and following our continuing experience on the magnetostructural correlations in multiatom-bridged exchange-coupled systems,[5–7] we came across

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