

Binary [Hydrotris(1,2,4-triazolyl)borate]metal Complexes $[M\{\text{HB}(\text{C}_2\text{H}_2\text{N}_3)_3\}_2]$ with $M = \text{Fe}, \text{Co}, \text{Cu}, \text{Zn}$: Synthesis, Characterization, Magnetochemistry, and X-ray Structure of $[\text{Cu}\{\text{HB}(\text{C}_2\text{H}_2\text{N}_3)_3\}_2 \cdot 4\text{CH}_3\text{OH}$ and $\text{K}[\text{HB}(\text{C}_2\text{H}_2\text{N}_3)_3] \cdot 2\text{H}_2\text{O}$

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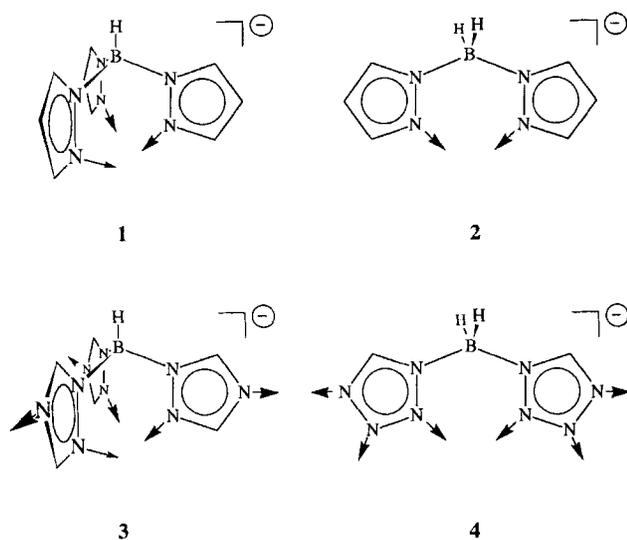
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The bis[hydrotris(1,2,4-triazolyl)borate]metal complexes $[M\{\text{HB}(\text{C}_2\text{H}_2\text{N}_3)_3\}_2]$ with $M = \text{Fe}$ (**5**), Co (**6**), Cu (**7**), Zn (**8**) are obtained from MX_2 and $\text{K}[\text{HB}(\text{C}_2\text{H}_2\text{N}_3)_3]$ (**9**). The complexes are characterized by IR, UV/Vis, and MS. Temperature-variable magnetic measurements show a Curie-Weiss behavior for the paramagnetic complexes **6** and **7** with a temperature-dependent magnetic moment for **6**. The iron complex **5** exhibits a spin crossover from diamagnetic to paramagnetic, starting at around 270 K. Single-crystal X-ray structures of the solvates $\mathbf{7} \cdot 4\text{CH}_3\text{OH}$ and $\mathbf{9} \cdot 2\text{H}_2\text{O}$ have been determined. The

structure of $\mathbf{7} \cdot 4\text{CH}_3\text{OH}$ shows the Jahn-Teller distorted copper complex **7** surrounded by methanol molecules through hydrogen bonding to exocyclic nitrogen atoms of the tris(1,2,4-triazolyl)borate ligand. The crystal system for $\mathbf{7} \cdot 4\text{CH}_3\text{OH}$ is monoclinic, space group $P2_1/n$. Compound $\mathbf{9} \cdot 2\text{H}_2\text{O}$ is a one-dimensional coordination polymer with the potassium atom bridged by the water molecules and the tris(1,2,4-triazolyl)borate ligand and crystallizes in the orthorhombic space group $Ccm2_1$.

The prototypical poly(pyrazolyl)borate ligands **1** and **2**, which were introduced into coordination chemistry by Trofimenko more than 20 years ago^[1,2], have developed into one of the most versatile auxiliary ligands in (bio)inorganic coordination chemistry^[3,4]. Modifications of **1** and **2**, where the pyrazolyl rings are replaced by e.g. 1,2,4-triazolyl or tetrazolyl residues have only been mentioned briefly^[1,5,6], however, although the ambidentate polytriazolyl- and polytetrazolylborate anions, $[\text{HB}(\text{C}_2\text{H}_2\text{N}_3)_3]^-$ (**3**) and $[\text{H}_2\text{B}(\text{CHN}_4)_2]^-$ (**4**), with their multiple bonding centers let one expect an interesting coordination chemistry.



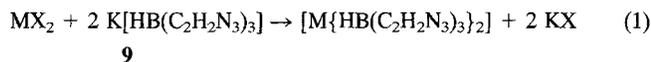
We recently investigated the X-ray structures of metal complexes of **3** and **4**^[7]. The ligand **3** was found to function as a tridentate chelate through the endocyclic nitrogen atoms with the formation of octahedral ML_2 complexes for $M = \text{Fe}$ and Co . The additional exocyclic coordination centers in the tris(triazolyl)borate system **3** extend this molecular coordination chemistry to the dimension of the solid state, however, through hydrogen bonding to water molecules of crystallization, leading to the formation of a two-dimensional water-intercalate or -layer clathrate^[8].

In the following we report on the synthesis of the homoleptic iron, cobalt, copper, and zinc complexes of **3**, their magnetic properties and the result of an X-ray study of the copper and potassium compound of **3**.

Syntheses and Properties of $[M\{\text{HB}(\text{C}_2\text{H}_2\text{N}_3)_3\}_2]$ with $M = \text{Fe}$ (**5**), Co (**6**), Cu (**7**), and Zn (**8**)

The hydrotris(triazolyl)borate anion **3** in the form of its potassium salt **9** reacts with iron(II) sulfate, cobalt(II) chloride, and zinc(II) chloride in water with the formation of bis[hydrotris(triazolyl)borate]iron(II) **5**, -cobalt(II) **6**, and -zinc(II) **8** [Eq. (1)]. The analogous copper complex **7** is obtained from anhydrous copper(II) chloride and **9** in methanol. Upon slow diffusion of solutions of the reactants the complexes together with solvent of crystallization are obtained as magenta (**5**), yellow (**6**), dark-blue (**7**), and colorless (**8**) crystals directly from the reaction mix-

ture in 40–60% crystal yield. A 1:1 molar ratio of MX_2 and **9** also gives the bis(ligand)metal complexes.



| | M | X |
|----------|----|------------------------------|
| 5 | Fe | (SO_4) $_{1/2}$ |
| 6 | Co | Cl |
| 7 | Cu | Cl |
| 8 | Zn | Cl, O_2CCH_3 |

X-ray structural investigations show that the crystals of **5** and **6** contain six molecules of water per formula unit^[7], while **7** crystallizes with four molecules of methanol (see below). The crystals of **5–7** quickly eliminate the incorporated solvent when taken out of the water or methanol phase. Complexes **5–8** are only sparingly soluble in polar solvents such as water, methanol, dichloromethane or chloroform and insoluble in nonpolar organic solvents like toluene or hexane. They are thermally very stable and decompose at 305–310°C (**7** and **8**) or above 350°C (undetermined; **5** and **6**); the latter two compounds can be sublimed. Complex **5** shows a reversible color lightening upon heating and eventually becomes white at ca. 115°C due to the low-spin/high-spin crossover (see below). The infrared spectra of the complexes are similar in the range $\tilde{\nu} = 400\text{--}4000 \text{ cm}^{-1}$ and feature the ligand moiety (see Table 5). Small differences in the spectra of **7** versus **5**, **6** and **8** indicate the lower symmetry in the copper complex.

X-ray Structure of **7** and **9**

The molecular structure of **7** is shown in Figure 1. Figure 2 provides a stereo view of the crystal structure. The copper atom in **7** is octahedrally coordinated by the tris(chelate) ligand **3**, and complex **7** exhibits the expected Jahn-Teller distortion for the d^9 ion with four short and two long Cu–N distances. The two independent short Cu–N bonds around 200 pm are unremarkable in comparison with other Cu–N contacts^[9]. As in the structures of **5** and **6**^[7] the exocyclic nitrogen atoms are again not utilized for a coordination to the metal center due to the chelate effect of the endocyclic nitrogens atoms. The atom N-3 plays, however, a role in the crystal packing. For each molecular unit four methanol molecules are embedded in the crystal lattice of **7**, two of which coordinate to the exocyclic N-3 nitrogen atoms through hydrogen bonding. The other two CH_3OH molecules then form a hydrogen bond to these “ligand-fixed” methanol molecules. As a result the complex molecule of **7** appears to be surrounded by solvent molecules (Figure 2). The facile loss of the CH_3OH molecules when the crystal is removed from solution indicates, however, rather weak solvent-solute interactions in this solvate.

At the outset of investigations of the structural chemistry of **3** it was hoped for that the exocyclic N atom could also take part in a metal coordination, thereby allowing the complexation of several, different metal ions to a polynuclear system. An indication of a possible exocyclic N–M coordination could, so far, be only obtained from the structure of the potassium salt **9**, which is shown in Figure 3a.

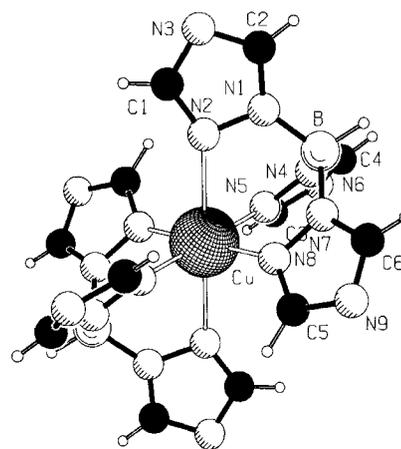


Figure 1. PLUTON plot^[26] of the molecular structure of $[\text{Cu}\{\text{HB}(\text{C}_2\text{H}_2\text{N}_3)_3\}_2]$ in $7 \cdot 4 \text{ CH}_3\text{OH}$; selected distances [pm] and angles [$^\circ$]: Cu–N2 243.9(3), Cu–N5 199.0(3), Cu–N8 201.1(3); *cis*-N–Cu–N 83.8(1)–96.2(1), *trans*-N–Cu–N 180.0(4)

There, the tris(triazolyl)borate ligand **3** exhibits a chelate coordination by two endocyclic N atoms and participates in the formation of the one-dimensional coordination polymer with the exocyclic N donor atom. The potassium coordination sphere is concluded by four oxygen centers from solvating water molecules which bridge the potassium atoms to give an extended kinked chain array along the z axis.

The severe disorder of the anion **3** in the structure of **9**, which is evident from Figure 3a, is detailed again in Figure 3b. The anion lies in a mirror plane passing through the H–B–N4 atoms. Thus, the triazolyl ring defined by the atoms N4–N5a–C3a–N6a–C4a which is not coplanar with this mirror plane is subject to a crystallographically induced disorder as the symmetry operation requires a second position of the ring. Independently, the other unique triazolyl ring shows also a disorder problem which can be described by a ring tilt around the N1–C2 bond. Two positions each could be found for the other ring atoms N2, C1, and N3. The two ring planes form an angle of ca. 28°. The disorder could be fully resolved by assuming equally occupied split positions.

Optical Spectra

The positions of absorption maxima and the extinction coefficients for the complexes **5–7** are given in Table 1 together with the assignments. The optical spectra of the complexes studied are all very similar to each other in as much as they feature a weak d-d transition and strong metal-to-ligand charge-transfer bands. The spectra are also closely related to those of the analogous bis[hydrotris(pyrazolyl)borate]metal complexes^[10–12] whose electronic spectral assignments were used for those of **5–7** in Table 1.

Mass Spectra

The mass-spectrometric data for the bis[hydrotris(triazolyl)borate]metal complexes are compiled in Table 2. The peak of the molecular ion is detected as the highest mass fragment. For **5** and **6** the molecular ion is also the base

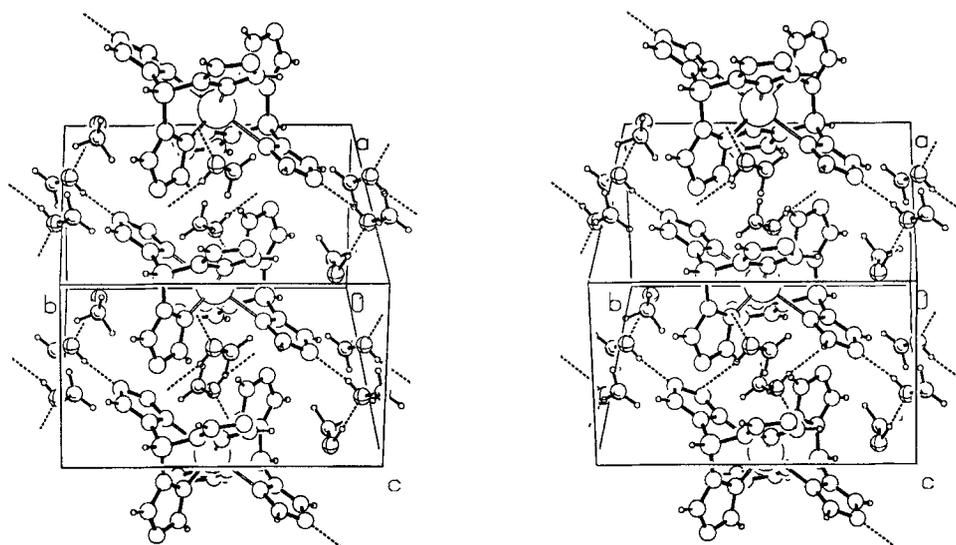


Figure 2. Stereo view of the crystal structure of $7 \cdot 4 \text{CH}_3\text{OH}$; the atoms of the complex molecules are shown as void circles, while the oxygen and carbon atoms of the methanol molecules are given as crossed and segmented circles; hydrogen bonds to the exocyclic N-3 nitrogen atoms and between the methanol molecules are indicated

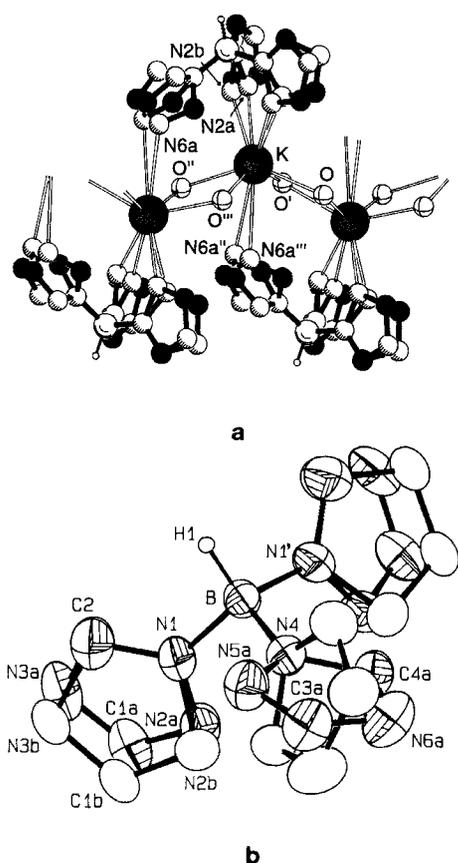


Figure 3. (a) PLUTON plot^[26] of the crystal structure of $9 \cdot 2 \text{H}_2\text{O}$; bridging H_2O molecules between the potassium ions; selected distances [pm] and angles [°]: K–N2a 291.6(5), K–N2b 289.3(6), K–N6a' 326.5(5), K–O 276.5(3), K–O'' 281.2(3), N2a–K–N2a'' 62.4(2), N2b–K–N2b' 75.7(2), N2a–K–N6a'' 136.9(2), O–K–O' 82.27(7), O–K–O'' 141.32(8), O–K–O''' 85.95(8); (' = $-x, y, z$; '' = $-x, -y, 0.5 + z$; ''' = $x, -y, 0.5 + z$); for a better illustration of the disorder in the $[\text{HB}(\text{C}_2\text{H}_2\text{N}_3)_3]^-$ anion **3** see its molecular structure in (b) (ORTEP^[27], 50% probability ellipsoids); one set of disordered (a/b) atoms is drawn as void ellipsoids; H atoms on C and O atoms are omitted in a and b for clarity

peak, underscoring the high stability of these symmetrical complex cations. The distorted Cu complex **7** gives a significantly lower molecular ion intensity. The most likely fragmentation is the loss of a hydrotris(triazolyl)borate radical to give the mono(ligand)metal cation as the second most abundant peak for **5** and **6**. Furthermore, fragmentation of the $\text{ML}_2^{+(\cdot)}$ and $\text{ML}^{+(\cdot)}$ ions is rather similar for the different metal complexes with the loss of one or two triazolyl rings together with H, H_2 , and/or HCN. The triazole radical cation forms the base peak in the mass spectra of **7** and **8**.

Magnetochemistry

The magnetic data for **5**–**7** is listed in Table 3. A temperature-variable magnetic measurement of **6** and **7** reveals that the susceptibility obeys a Curie-Weiss law over the temperature range measured. Yet, for **6** the magnetic moment depends on temperature. This situation is illustrated in Figure 4 and is due to the fact that the ground term is degenerate, and degenerate excited states are thermally accessible^[13]. The magnetic moment of **6** is considerably higher than the spin-only value for a high-spin d^7 configuration. Thus, a strong contribution from the orbital angular momentum, i.e. spin-orbit coupling, must be taken into account, as is often the case with cobalt complexes^[13,14].

Complex **5** represents an interesting case of a spin equilibrium between high- and low-spin forms^[15]. From the data in Table 3 and the plot of molar susceptibility and effective magnetic moment against temperature in Figure 5 it can be seen that the iron complex is fully diamagnetic below 270 K and then becomes increasingly paramagnetic with rising temperature. A d^6 metal ion in an octahedral field may have either an $^1\text{A}_{1g}$ (strong-field, low-spin, diamagnetic) or a $^5\text{T}_{2g}$ (weak-field, high-spin, paramagnetic) ground state^[16]. In **5** the critical value of the ligand-field strength is such that a simple variation in temperature can tip the balance in favor of one or the other ground state, so

Table 1. UV/Vis data of 5–7^[a]

| | λ [nm] | $\tilde{\nu}$ [cm ⁻¹] | ϵ | Assignment |
|-------------------------|----------------|-----------------------------------|------------|--|
| 5 in H ₂ O | 526 | 19 000 | 33 | } $1A_{1g} \rightarrow 1T_{1g}$ metal-to-ligand charge transfer |
| | 325 | 30 800 | 1200 | |
| | 290 | 34 500 | 1250 | |
| | 240 | 41 700 | 1400 | |
| 6 in H ₂ O | 509 | 19 600 | 2.5 | } $4T_{1g} \rightarrow 4A_{2g}$ $4T_{1g} \rightarrow 4T_{1g}$ metal-to-ligand charge transfer |
| | 450 | 22 200 | 9 | |
| | 270 | 37 000 | 480 | |
| | 230 | 43 500 | 2600 | |
| 7 in CH ₃ OH | 630 | 15 900 | 17 | } $2B_{1g} \rightarrow 2B_{2g}, 2E_g$ metal-to-ligand charge transfer |
| | 248 | 40 300 | 1300 | |
| | 215 (sh) | 46 500 | 920 | |

^[a] Concentrations: **5**: $3 \cdot 10^{-3}$ mol · l⁻¹, **6**: $1.5 \cdot 10^{-3}$ mol · l⁻¹, **7**: $2.6 \cdot 10^{-3}$ mol · l⁻¹; spectral range $\lambda = 190$ to 1100 nm; additional d-d transitions are possible in this range (e.g. $4T_{1g} \rightarrow 4T_{2g}$ for Co²⁺) but are apparently too weak to be detected with certainty with the instrument used (cf. ref.^[11]).

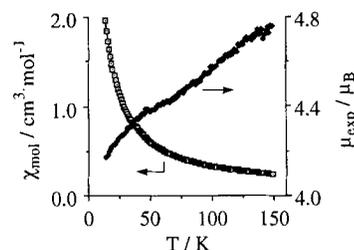
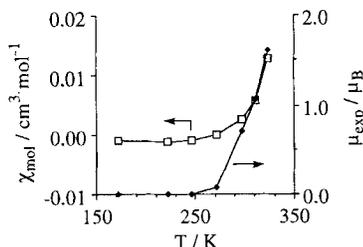
that a spin equilibrium between low- and high-spin forms is observed in a temperature interval^[15].

In the related bis[poly(pyrazolyl)borate]iron(II) complexes the magnetic moment was found to depend either on changes in the nature of substituents on the pyrazolyl (pz) ring or the boron atom or on temperature. While [Fe{HB(3,5-Me₂pz)₃}₂] and [Fe{HB(Me₃pz)₃}₂] are paramagnetic ($\mu \approx 5.03$ and 5.22 μ_B at room temperature, respectively)^[10,11,17–19], [Fe{B(pz)₄}₂] is a diamagnetic low-spin compound^[20], and [Fe{HB(pz)₃}₂] has an intermediate magnetic moment ($\mu = 2.7 \mu_B$ at room temperature)^[10,21]

Table 2. MS data for the bis[hydrotris(triazolyl)borate]metal complexes 5–8

| 5 (M = Fe) (230 °C) | <i>m/z</i> (%) ^[a] | | | Assignment ^[c] |
|------------------------|-------------------------------|------------------------|---------------------------------------|---|
| | 6 (M = Co) (240 °C) | 7 (M = Cu) (260 °C) | 8 (M = Zn) ^[b] (220 °C) | |
| 488 (100) | 491 (100) | 495 (10) | 496 (80) | C^+ (5 , 8); C^+ (6 , 7) ^[c] [C–C ₂ H ₂ N ₃] ⁺ (⁺ for 6 , 7) ^[c] |
| | | 427 (17) | 428 (54) | |
| | | 426 (23) | | [C–C ₂ H ₂ N ₃ , –H ₂] ⁺ |
| 418 (7) | 421 (7) | 425 (14) | 426 (22) | [C–2C ₂ H ₂ N ₃ , –H] ⁺ |
| 351 (9) | 354 (43) | 358 (37) | 359 (95) | [C–2C ₂ H ₂ N ₃ , –H ₂] ⁺ |
| 350 (10) | 353 (41) | 357 (17) | 358 (43) | [C–2C ₂ H ₂ N ₃ , –H ₂] ⁺ (⁺ for 6 , 7) ^[c] |
| 340 (32) | | | | [C–HB(C ₂ H ₂ N ₃) ₂] ⁺ (⁺ for 6 , 7) etc. |
| | | | 332 (13) | [C–2C ₂ H ₂ N ₃ , –H, –HCN] ⁺ |
| 323 (7) | 326 (12) | 330 (8) | | [C–2C ₂ H ₂ N ₃ , –H ₂ , –HCN] ⁺ |
| 296 (7) | | | | [C–2C ₂ H ₂ N ₃ , –H ₂ , –2HCN] ⁺ |
| 272 (84) | 275 (71) | 279 (4) | 280 (64) | [C–HB(C ₂ H ₂ N ₃) ₃] ⁺ |
| | | | | = [M{HB(C ₂ H ₂ N ₃) ₃ }] ⁺ |
| 218 (7) | 220 (21) | | | [M{HB(C ₂ H ₂ N ₃) ₃ } – 2HCN] ⁺ |
| | | 211 (35) | | [M{HB(C ₂ H ₂ N ₃) ₃ } – 2HCN, –H] ⁺ |
| | | 210 (9) | 211 (52) | [M{HB(C ₂ H ₂ N ₃) ₃ } – C ₂ H ₂ N ₃] ⁺ |
| 203 (17) | 206 (34) | 184 (11) | | [M{HB(C ₂ H ₂ N ₃) ₃ } – C ₂ H ₂ N ₃ , –H] ⁺ |
| | | | | [M{HB(C ₂ H ₂ N ₃) ₃ } – C ₂ H ₂ N ₃ , –HCN] ⁺ |
| 176 (22) | 179 (11) | | 184 (31) | [M{HB(C ₂ H ₂ N ₃) ₃ } – C ₂ H ₂ N ₃ , –H, –HCN] ⁺ |
| 149 (16) | | | 157 (13) | [M{HB(C ₂ H ₂ N ₃) ₃ } – C ₂ H ₂ N ₃ , –H, –2HCN] ⁺ |
| 69 (36) | 69 (11) | 69 (100) | 69 (100) | [C ₂ H ₃ N ₃] ⁺ |
| | | 42 (45) | | [C ₂ H ₃ N ₃ – HCN] ⁺ |

^[a] Peaks listed refer to the most abundant isotope combination: ⁵⁶Fe, ⁵⁹Co, ⁶³Cu, ⁶⁴Zn, ¹¹B. – ^[b] Molecular complex, see “Note (April 26, 1994)”. – ^[c] C = complex; M = metal; for the odd-electron cobalt and copper complexes, **6** and **7**, the radical notation for the fragments has to be reversed, as indicated.

Figure 4. Temperature variations of the molar susceptibility and the magnetic moment of **6**Figure 5. Temperature variations of the molar susceptibility and the magnetic moment of **5**

which is strongly dependent on temperature, due to the spin equilibrium. In this context, **5** is an example where the spin-crossover phenomenon starts at room temperature.

The instrumental setup did not allow a temperature increase above 323 K so that the transition temperature, where the complex becomes fully paramagnetic, could not be reached. However, from the conclusion of the color change from magenta to almost white upon heating the complex to ca. 115 °C, we estimate the transition temperature to be

Table 3. Magnetochemical data for 5–7

| | T [K] | χ_{mol} [$\text{cm}^3 \cdot \text{mol}^{-1}$] [a,b] | $\mu_{\text{exp}}/\mu_{\text{B}}$ [a,c] |
|---|---------|---|---|
| 5 | 323.0 | $12.65 \cdot 10^{-3}$ | 1.61 |
| | 310.8 | $5.687 \cdot 10^{-3}$ | 1.06 |
| | 297.3 | $2.592 \cdot 10^{-3}$ | 0.70 |
| | 271.9 | $0.041 \cdot 10^{-3}$ | 0.08 |
| | 246.5 | $-0.985 \cdot 10^{-3}$ | |
| 6 | 322.9 | 0.105 | 4.64 |
| | 271.7 | 0.127 | 4.69 |
| | 196.2 | 0.178 | 4.71 |
| | 147.2 | 0.235 | 4.69 |
| | 99.5 | 0.344 | 4.66 |
| | 55.2 | 0.551 | 4.40 |
| | 14.0 | 1.961 | 4.17 |
| 7 | 323.2 | 0.0135 | 1.67 |
| | 272.0 | 0.0165 | 1.69 |
| | 196.4 | 0.0236 | 1.72 |
| | 147.4 | 0.0318 | 1.73 |
| | 99.7 | 0.0476 | 1.74 |

[a] No diamagnetic correction employed. – [b] From a plot of $1/\chi$ against T a Curie-Weiss constant Θ of 1.8 K is obtained for **6** and of 11.5 K for **7**. – [c] The experimental magnetic moment can be compared to a calculated effective magnetic moment with spin-orbit coupling ($\mu_{\text{eff}}/\mu_{\text{B}} = [L(L+1) + 4S(S+1)]^{1/2}$) of 5.48 for a ^5D free-ion ground term (Fe^{2+}), 5.20 for ^4F (Co^{2+}), and 3.00 for ^2D (Cu^{2+}), or to a spin only value ($\mu_{\text{eff}}/\mu_{\text{B}} = 2[S(S+1)]^{1/2}$) for ^5D (Fe^{2+}) of 4.90, for ^4F (Co^{2+}) of 3.87, and for ^2D (Cu^{2+}) of 1.73.

around this value. In studies of the spin equilibria in octahedral iron(II) poly(pyrazolyl)borates it has been found that in this case the diamagnetic or partially diamagnetic complexes are deeply colored magenta compounds due to the $^1\text{A}_{1g} \rightarrow ^1\text{T}_{1g}$ transition at $\tilde{\nu} \approx 19000 \text{ cm}^{-1}$ (cf. Table 1) while the fully paramagnetic compounds are almost colorless^[10]. A spin crossover would also be possible in the case of Co(II) complexes, such examples are, however, much less numerous than those concerning iron(II) complexes^[22].

Conclusion

In summary, it can be noted that the introduction of additional coordination centers into the poly(pyrazolyl)borate

ligands **1** and **2**, as exemplified by the tris(1,2,4-triazolyl)borate system **3**, extends the hitherto molecular coordination chemistry of the poly(azolyl)borate ligands to the dimension of the solid state. The added functionality leads to supramolecular two- and three-dimensional arrays. The crystal phase in the bis[hydrotris(1,2,4-triazolyl)borate]-copper complex **7** is stabilized by host-guest interactions^[8] involving hydrogen bonds between exocyclic triazolyl ring nitrogen atoms and methanol molecules. Furthermore, in comparison with the long known tris(pyrazolyl)borate ligands, the additional ring nitrogen atom in the tris(1,2,4-triazolyl)borate systems represents an electronic fine tuning which, for example, was found to drastically affect the beginning of the spin crossover in the bis[hydrotris(triazolyl)borate]iron complex **5**.

Note (April 26, 1994): The bis[hydrotris(triazolyl)borate]zinc complex **8** was found to crystallize in two modifications: cubic shaped platelets as a first, fast crystallizing form and parallel-epipeds upon extremely slow crystallization. X-ray studies which have been carried out in the meantime revealed that in the former a molecular octahedral zinc complex with embedded water layers isomorphous to **5** and **6**^[7] is present, while the latter allotrope represents a linkage isomer with the tris(triazolyl)borate ligand coordinating solely through the exocyclic nitrogen atoms to the zinc centers. In this coordination mode each ligand bridges between three zinc ions thereby creating a three-dimensional lattice. Both modifications show differences in the IR and MS. The data given here in Table 2 and 5 refers to the molecular complex.

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Experimental

Bidistilled or de-ionized water was used as a solvent. – CHN analyses: Perkin-Elmer Series II CHNS/O Analyzer 2400. – IR: Nicolet Magna 750. – UV/Vis: Beckman 750. – MS: Varian MAT

Table 4. Yields, melting points, colors, and elemental analyses for the bis[hydrotris(triazolyl)borate]metal complexes 5–8

| | Formula | Mol. Mass | Yield | Color | m. p. | Analyses | | calcd. found [a] | |
|-------|--|-----------|--------------|-----------|--|----------|------|------------------|-------|
| | | | | | | C | H | N | M |
| 5 | $\text{C}_{12}\text{H}_{14}\text{B}_2\text{FeN}_{18}$ | 487.8 | 0.28 g (43%) | magenta | > 350 °C [b] subl. 305 °C/3·10 ⁻⁵ Torr | 29.55 | 2.89 | 51.68 | 11.45 |
| | | | | | | 29.61 | 2.73 | 51.63 | n. d. |
| 6 | $\text{C}_{12}\text{H}_{14}\text{B}_2\text{CoN}_{18}$ | 490.9 | 0.24 g (37%) | yellow | > 350 °C subl. 300 °C/3·10 ⁻⁵ Torr | 29.36 | 2.87 | 51.36 | 12.00 |
| | | | | | | 29.32 | 2.64 | 51.47 | n. d. |
| 7 | $\text{C}_{12}\text{H}_{14}\text{B}_2\text{CuN}_{18}$ | 495.5 | 0.41 g (62%) | blue | 309 °C (dec.) | 29.09 | 2.85 | 50.88 | 12.83 |
| | | | | | | 28.31 | 2.89 | 48.67 | 12.11 |
| 8 [c] | $\text{C}_{12}\text{H}_{14}\text{B}_2\text{N}_{18}\text{Zn}$ | 497.4 | 0.38 g (60%) | colorless | 310 °C (dec.) | 28.98 | 2.84 | 50.69 | 13.15 |
| | | | | | | 28.86 | 2.59 | 50.62 | n. d. |

[a] n.d. not determined. – [b] Reversible decolorization to white between 90 to 115 °C. – [c] Molecular complex, see "Note (April 26, 1994)".

Table 5. Infrared spectrometric data for the [hydrotris(triazoly)borate]-metal complexes **5**–**9**^[a]

| 5 (Fe) | 6 (Co) | 7 (Cu) | 8 (Zn) [b] | 9 (K) [c] | Assignment |
|---------|---------|--------|------------|-----------|--------------------------------|
| 3130 w | 3127 w | 3134 w | 3126 w | 3125 w | aromatic C-H stretch |
| 3096 w | 3102 w | 3105 w | 3103 w | 3119 sh | |
| | 3089 w | | 3089 w | 3113 sh | |
| 2524 sh | 2517 sh | 2524 w | 2515 w | 2455 w | B-H |
| 2497 w | 2494 w | 2499 w | 2494 w | 2426 w | |
| | | | 1764 w | | C-N ring stretching |
| 1502 s | 1508 s | 1508 s | 1509 s | 1505 s | |
| 1423 m | 1412 m | 1414 m | 1410 m | 1402 m | |
| 1337 m | 1328 m | 1327 m | 1328 m | 1328 m | |
| 1323 m | 1321 m | | 1321 m | 1316 m | |
| 1293 s | 1289 s | 1294 m | 1287 s | 1272 s | |
| | | 1278 m | | | |
| 1220 w | 1228 w | 1228 w | 1227 w | | |
| 1212 w | 1216 w | 1217 w | 1216 w | | |
| 1199 m | 1199 m | 1202 m | 1193 s | 1188 s | |
| 1191 m | 1194 m | 1186 m | | 1179 m | |
| 1150 s | 1150 s | 1150 s | 1150 s | 1151 s | |
| 1142 s | 1145 s | | | 1148 s | |
| | | | | 1135 m | |
| 1102 w | 1103 w | 1105 w | 1102 w | | |
| 1054 w | | 1058 m | | | |
| 1045 w | 1048 m | 1039 s | 1047 m | 1018 m | |
| 1027 s | 1029 s | 1008 m | 1030 s | 1004 m | |
| 962 s | 969 sh | 966 sh | 968 sh | 969 sh | |
| 958 s | 963 s | 961 s | 961 s | 961 m | |
| 920 w | 926 w | 908 w | 926 w | | |
| | 906 sh | | 906 sh | | |
| 893 w | 896 w | 892 w | 896 w | 897 w | |
| 884 w | | 883 w | | 887 w | |
| 864 w | 873 w | 877 w | 874 w | 878 w | |
| 796 w | 784 w | 783 w | 782 w | 758 w | |
| 728 sh | 729 sh | 736 sh | 730 sh | 743 m | |
| 721 s | 719 s | 722 s | 720 s | 729 m | |
| 678 s | 673 s | 671 s | 673 s | 692 w | C-H out-of-plane bending |
| 658 sh | 664 sh | 662 sh | 664 sh | 680 s | |

^[a] Measured as a CsI pellet, 1.6–2.0-mg sample/300 mg CsI; w = weak, m = medium, s = strong, sh = shoulder. – ^[b] Molecular complex, see “Note (April 26, 1994)”. – ^[c] Unsolvated potassium salt.

311A. – Susceptibility measurements: Faraday magnetic balance and AC susceptometer Lakeshore Model 7000. – NMR: Bruker WP 80SY for **9** and Bruker ARX 200 for **5** and **8**.

$K[HB(C_2H_2N_3)]$ (**9**, potassium salt of **3**) was synthesized from KBH_4 and triazole as described in ref.^[1,23] (yield 89%, m.p. 289–290°C) and used as such for the preparation of the transition-metal complexes. A crystalline sample in the form of a dihydrate complex could be obtained by slow evaporation of a concentrated methanolic solution at room temperature in air: m.p. 293–295°C, after gradual loss of solvent at ca. 70°C. – ¹H NMR (D_2O): δ = 7.98 (s, 3H), 8.12 (s, 3H) (BH signal could not be observed). – ¹³C NMR (D_2O): δ = 148.60, 152.76. – $C_6H_{11}BKN_9O_2$ (291.1): calcd. C 24.75, H 3.81, N 43.30, K 13.43; found C 24.40, H 3.54, N 43.06, K 13.94.

$[M\{HB(C_2H_2N_3)_2\}_2]$ [M = Fe (**5**), Co (**6**), Zn (**8**)]: A solution of 1.3 mmol of the transition-metal salt [0.36 g $FeSO_4 \cdot 7 H_2O$, 0.31 g $CoCl_2 \cdot 6 H_2O$, 0.18 g $ZnCl_2$ or 0.29 g $Zn(O_2CCH_3)_2 \cdot 2 H_2O$] in 10 ml of water was carefully overlaid in a test tube with a solution of 0.66 g (2.6 mmol) of the potassium salt **9** in 20 ml of water. Some amorphous material precipitated in this process. Slow diffusion of solutions of the starting compounds then led to the formation of **5** · (H_2O)₆, **6** · (H_2O)₆, or **8** · (H_2O)₆, respectively, as analytically pure, well-shaped crystals. The reaction and process of crystallization were concluded within a few days (**6**, **8**) to a few weeks (**5**). Except for the X-ray diffraction studies, the solvate-free

Table 6. Crystal data for compounds **7** · 4 CH_3OH and **9** · 2 H_2O

| | 7·4CH ₃ OH | 9·2H ₂ O |
|--|---------------------------------|--------------------------------|
| Formula | $C_{16}H_{30}B_2CuN_{18}O_4$ | $C_6H_{11}BKN_9O_2$ |
| Mol. mass [g mol ⁻¹] | 623.70 | 291.13 |
| Crystal size [mm] | 0.3·0.3·0.4 | 0.3·0.4·0.5 |
| Temperature [K] | 173 | 293 |
| Crystal system | Monoclinic | Orthorhombic |
| Space group | $P2_1/n$ (No. 14) | $Ccm2_1$ ($Cmc2_1$; No. 36) |
| Cell constants: | | |
| <i>a</i> [pm] | 735.7(2) | 1419.4(5) |
| <i>b</i> [pm] | 1230.1(6) | 1219.3(3) |
| <i>c</i> [pm] | 1536.2(6) | 758.4(3) |
| β [°] | 96.06(4) | 90 |
| <i>V</i> [pm ³] | 1382(1)·10 ⁶ | 1312.6(7)·10 ⁶ |
| <i>Z</i> | 2 | 4 |
| <i>D</i> _{calcd.} [g cm ⁻³] | 1.499 | 1.473 |
| <i>F</i> (000) [electrons] | 646 | 600 |
| μ (Mo- <i>K</i> α) [cm ⁻¹] | 8.5 | 4.1 |
| Absorption correction: | DIFABS | -- |
| max.; min.; av. | 1.060; 0.825; 0.932 | -- |
| Weighting scheme: <i>k</i> ; <i>g</i> | -- (unit weights) | -- |
| No. of reflections: | | |
| measured | 2080 | 885 |
| independent | 1777 | 820 |
| observed | {>5 σ (<i>F</i>)} 1678 | {>4 σ (<i>F</i>)} 710 |
| No. of variables | 232 | 167 |
| <i>R</i> ; <i>R</i> _w [a] | 0.035; 0.036 | 0.031; 0.028 |
| $\Delta\rho$: max.; min [e Å ⁻³] | 0.33; -0.30 | 0.26; -0.20 |

^[a] $R = (\sum \|F_o\| - |F_c|) / \sum \|F_o\|$; $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2}$.

complexes obtained upon air-drying of the crystalline material were analyzed. Yields, colors, melting points as well as the elemental analyses are compiled in Table 4. Mass spectrometrical data are collected in Table 2. The infrared spectral data of the complexes are listed in Table 5. – **5**: ¹H NMR (D_2O , ambient temperature): δ = 6.95 (s), 9.25 (br. s). – **8**: ¹H NMR (D_2O): δ = 7.77 (s), 8.41 (s).

$[Cu\{HB(C_2H_2N_3)_2\}_2]$ (**7**): A solution of 0.18 g (1.33 mmol) of anhydrous $CuCl_2$ in 10 ml of methanol (not dried) was carefully overlaid in a test tube with a solution of 0.66 g (2.66 mmol) of the potassium salt **9** in 20 ml of methanol. Some amorphous white material precipitated in this process. Slow diffusion of solutions of the starting compounds then led to the formation of an upper blue layer from which dark-blue needle-shaped crystals of **7** · (CH_3OH)₄ started growing after 2–3 h. After 10 d, the crystals were collected and manually separated from some white crystalline material of KCl. Except for the X-ray diffraction studies, the solvate-free complex obtained upon air-drying of the crystalline material was analyzed. Yield, color, melting point as well as the elemental analysis are compiled in Table 4. MS data are listed in Table 2 and IR data of the complex in Table 5.

X-ray Structure Determinations of 7 · 4 CH₃OH and 9 · 2 H₂O: CAD4, Enraf-Nonius four-circle diffractometer, ω -2 θ scan ($2^\circ \leq 2\theta \leq 45^\circ$; $0 \leq h \leq 7$, $0 \leq k \leq 13$, $-16 \leq l \leq 16$), $T = 173$ K, crystal size ca. $0.3 \times 0.3 \times 0.4$ mm for **7**; Syntex P2₁ four-circle diffractometer, ω scan ($0^\circ \leq 2\theta \leq 55^\circ$; $0 \leq h \leq 17$, $0 \leq k \leq 20$, $0 \leq l \leq 13$), room temperature, crystal size ca. $0.3 \times 0.4 \times 0.5$ mm for **9**; Mo-*K* α radiation ($\lambda = 71.069$ pm, graphite monochromator). Structure solution was performed by direct methods (SHELXS-

86^[24]). Refinement: Full-matrix least squares; all atomic positions including those of hydrogen atoms found and non-hydrogen atoms refined with anisotropic temperature factors (SHELX-76^[24]). Crystal data are listed in Table 6^[25].

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