Ligand-Field Control and Hydrogen Bonding as Design Elements in the Assembly and Crystallization of Poly(azoly1)borate–Metal Complexes: Chelate Complexes versus Coordination Polymers and Symmetrical versus Distorted Grid Sheets

Christoph Janiak,* Tobias G. Scharmann, Wulf Günther, Frank Girgsdies, Holger Hemling, Winfried Hinrichs, and Dieter Lentz

Dedicated to Prof. Dr. Herbert Schumann on the occasion of his 60th birthday

Abstract: The 1- and 2-D coordination polymers [Mn{HB(C\textsubscript{3}H\textsubscript{3}N\textsubscript{3})\textsubscript{3}}\textsubscript{2}(H\textsubscript{2}O)\textsubscript{2}]\textsubscript{4}H\textsubscript{2}O (11) and [Ni{H\textsubscript{2}B(CH\textsubscript{4}N\textsubscript{3})\textsubscript{2}}\textsubscript{2} \textsubscript{(NH\textsubscript{3})\textsubscript{2}} (13), respectively, and the chelate complex [Ni{H\textsubscript{2}B(C\textsubscript{2}H\textsubscript{2}N\textsubscript{3})\textsubscript{2}}\textsubscript{2}(H\textsubscript{2}O)\textsubscript{2}].2H\textsubscript{2}O (12) were synthesized and structurally characterized. The compounds contain ambidentate poly(azoly1)borato ligands (azolyl = triazolyl or tetrazolyl), which can chelate or bridge metal centers. The metal–ligand structures in 11–13 differ from the known coordination modes of the poly(azoly1)borates towards other metal centers. We describe how a change in the metal and/or the conditions of crystallization affects the ligand-field stabilization energy and favors one type of nitrogen donor atom over the other for the poly(triazolyl)borato ligands. The crystal structures of 11 and 12 contain additional water of crystallization; this leads to hydrogen-bonded solvent substructures. In the case of the bis(tetrazolyl)borato ligand the water substructure is shown to function as a "reinforcing bar" that symmetrizes the metal–ligand grid sheet.

Introduction

While the versatile poly(pyrazoly1)borato ligands form exclusively molecular (chelate) complexes as depicted in 1 and 2,[1] the novel hydrotris(1,2,4-triazolyl)- and dihydrobis(1,2,4-triazolyl)borate (3 and 4, respectively) and dihydrobis(tetrazolyl)borate (5)[2] ligands with their multiple bonding centers can, in principle, chelate or bridge metal centers. The latter results in structurally diverse coordination polymers. Furthermore, the nitrogen atoms which are not utilized for metal coordination tend to engage in hydrogen bonding with solvate molecules; this leads to the formation of solvent-stabilized crystal phases with interesting water substructures.[3−6] Tris(triazolyl)borate (3) has been found to function as a tris-chelating ligand by coordination through the endodentate nitrogen

Keywords
chelate ligands · coordination · hydrogen bonds · ligand fields · polymers

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donors to metals such as iron, cobalt, nickel, copper, and zinc to form complexes [6]. In addition, it has been demonstrated that the zinc complex of 3 also exists as a linkage isomer of 6, as a three-dimensional coordination polymer formed by the bridging of three zinc centers by the exodentate nitrogen atoms of the borate (7). The bis(triazolyl)borato ligand (4) has so far been found only to exhibit bridging coordination through transition-metal complexes of 8 and 9. The hydrogen bonds between water of crystallization and the “free” nitrogen atoms have not been included in the formulae 6–10 for clarity.

(1) MnCl₂ + 2K[H₂B(C₆H₃N₃)₂] → 
\[
\frac{1}{2}[\text{Mn}[\text{H₂B(C₆H₃N₃)₂]₂(H₂O)₂}] + 2\text{H₂O} + 2\text{KCl}
\]

(hydrated) nickel(II) chloride and ligands 4 and 5 furnished amorphous blue-violet powders. These nickel compounds were soluble in aqueous ammonia (presumably with formation of nickel–ammine complexes) from which pink-violet crystals of 12 (needle-shaped) [Eq. (2)] and 13 [Eq. (3)] could be grown upon slow solvent evaporation. In line with the crystallization from ammonia, complex 13 could be obtained in a crystalline form directly from the reaction mixture when the diffusion method was used with water or methanol as a solvent and hexaamminenickel(II) chloride as a starting material [Eq. (4)].

X-ray structural investigations show that crystals of 11 and 12 contain four and two water molecules of crystallization per formula unit, respectively. Crystals of 11 do not lose this incorporated solvent when removed from the aqueous phase, or only eliminate it very slowly, while crystals of 12 quickly lose water of crystallization. Except for the solubility of 12 and 13 in aqueous ammonia, the complexes (11–13) are insoluble in aqueous or organic solvents once they have formed. For 11 this is especially noteworthy as the analogous molecular iron, cobalt, nickel, and zinc complexes are at least sparingly soluble in water. Aside from the loss of water of crystallization, the compounds are thermally stable to over 500 °C (11), 260 °C (12), and 250 °C (13). The infrared spectra reflect the ligand moieties, yet they exhibit distinct differences from the spectra of the structurally authenticated homologues, 6 and 8–10. In the case of 13 the differences with respect to 10 are illustrated in Figure 1. The obvious splitting of the C–H and B–H stretching frequencies (around 3150 and 2480 cm⁻¹, respectively) indicates a lower site symmetry of the borato ligand in 13 by comparison with the solid-state structure of 10, where both triazolyl rings of the borate are symmetry-related. The lower symmetry in 13 is indeed verified by the crystal structure analysis (see below).
molecules, as has often been observed in metal structures of the novel poly(azoly1)borates
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the incorporation of the four water molecules of crystallization
dentate donor atoms of the triazolyl rings. The third triazolyl
or bis(tetrazo1yl)borato complexes, at least one nitrogen donor
structures. In all other structurally characterized poly(triazoly1)-
a "free" azolyl ring makes this manganese structure unique
base peak at higher temperature. The frag-
mentation pattern corresponds to those of the other binary metal complexes of 3.[15-7]
Attempts to study the bis(azoly1)borato sys-
tems by other methods (FAB, CI) have so far failed.
Temperature-variable magnetic measurements of 11-13 show normal paramagnetic
Curie-Weiss behavior in the temperature range measured (14-300 K). In the poly-
meric complexes 11 and 13 there is no mag-
netic coupling transmitted through the
ligand, nor is there a through-space interac-
sion among the hitherto investigated modified poly(azoly1)borato
complexes. In 11 and 13, only involved in the hydrogen bonding network. The feature of
contact are

Fig. 1. Infrared spectra (KBr pellets, % transmission) of the nickel complex 13 (top) and the zinc complex 6 (bottom) of the bis(tetrazolyl)borato ligand 5.

X-ray crystal structure of 11: Compound 11 is a one-dimen-
sional coordination polymer with a linear chain structure. Here
and in the structures of 12 and 13 the metal centers are octahe-
drally coordinated, with a coordination polyhedron formed from four nitrogen atoms of the (azoly1)borato ligands and two trans-coordinated solvent ligands (Fig. 2). In 11 the manganese ions are bridged by two borato ligands, each through the exo-
dentate donor atoms of the triazolyl rings. The third triazolyl
ring of the borate is not utilized for the metal coordination and
only involved in the hydrogen bonding network. The feature of
a "free" azolyl ring makes this manganese structure unique
among the hitherto investigated modified poly(azoly1)borato
structures. In all other structurally characterized poly(tetrazolyl)-
or bis(tetrazolyl)borato complexes, at least one nitrogen donor
from each azolyl ring coordinates to the metal.[15-7] sometimes
two do so, as in the structure of the recent silver complex of 3.[12]

A further important aspect in the discussion of the crystal
structure of 11 is the stabilization of the crystal phase by solvent
molecules, as has often been observed in metal structures of the
novel poly(azoly1)borates 3-5.[11-7] Figures 3 and 4 illustrate the incorporation of the four water molecules of crystallization
as a tetramer with homodromic hydrogen bonds.[11-3] These wa-
ter clusters are hydrogen-bonded further to the endodentate
nitrogen atoms and to the metal-bound aqua ligands. The sec-
ond hydrogen atom of the aqua ligand bridges the exodentate N
atom of a free triazolyl ring. The util-
ization of all (O)-H atoms in hydro-
gen bonding allows the unproblematic location and refinement of these hydrogen atoms in the room
temperature structure and explains the slow loss of the water of crystal-
llization upon drying. We note also that C-H-O hydrogen bonds are
formed between two of the man-
ganese-coordinated triazolyl rings and the coplanar aqua ligands
(Table 1 lists the lengths and angles of the hydrogen bonds). The
aspect of C-H-O bonding and its importance for molecular
alignment[14] in the crystal structures of the poly(azoly1)borates is,
however, still under investigation, and a comparative account
will be published later. The crystal of 11 was taken from a batch
which had been stored under water for several months. In view
of the known slow transformation of the analogous zinc com-
plex from a molecular chelate to a 3-D coordination polymer (6
to 7)[6] and in the light of a mass spectrum typical of a molecular
compound, the possibility of a second (molecular) crystal phase,
or in other words, the representative nature of the single crystal

Fig. 2. Metal coordination and section of the linear chain structure with the atomic numbering scheme in 11 (PLATON-TME [11], 50% probability ellipsoids). The water of crystallization is not shown. Selected distances (Å) and angles (°): Mn-01 2.197(2), Mn-N3 2.255(2), Mn-N6a/d 2.250(2), 01-Mn-Olc 180, 01-Mn-N3 89.47(9), O1-Mn-N3c 90.53(9), O1-Mn-N6a 87.59(9), 01-Mn-N6d 92.41(9), N3-Mn-N6d 90.79(9), N3-Mn-N6d 89.21(9). Symmetry transformations: a = x - 1, i, z; b = x + 1, y, z; c = -x + 1, -y + 1, -z + 1.

Fig. 3. Stereo plot of the crystal structure of 11 (crossed circles = oxygen atoms) (PLUTON [11]).

Fig. 4. Hydrate structure in 11. Distances and angles of the hydrogen-bonding scheme are listed in Table 1.

with respect to the bulk material, had to be investigated. A powder diffraction study (Fig. 5) proved the identity of the single crystal with the bulk material as well as with a freshly prepared sample. Thus, no intermediate molecular chelate complex is formed in the case of 11, unlike that of the zinc complex (6).

X-Ray crystal structure of 12: The structural analysis of 12 shows the formation of a molecular chelate complex (Fig. 6) whose crystal structure is again stabilized by incorporated water (Figs. 7 and 8). The low-temperature water substructure can be described as being made up of H$_2$O dimers, with one of the molecules bridging exodentate nitrogens of different complex molecules with its hydrogen atoms. The aqua ligands also form bridges between N atoms with their hydrogens. No bridge between the aqua ligands and the water of crystallization could be found from the localized hydrogen atoms. At room temperature, however, such a connection may be possible, since one of the water molecules of crystallization (O3) still possesses a free hydrogen. In the “frozen” structure this oxygen is just 3.05 Å away from an aqua ligand (O2). Table 2 contains the lengths and angles of the hydrogen bonds.

Table 2. Hydrogen-bonding scheme in 12 [a] (distances in Å, angles in °).

<table>
<thead>
<tr>
<th>D-H...A</th>
<th>D-A</th>
<th>D-H</th>
<th>H...A</th>
<th>D-H-A</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1-H1/C1-O2</td>
<td>2.75(3)</td>
<td>0.83(4)</td>
<td>1.94(4)</td>
<td>166(4)</td>
</tr>
<tr>
<td>O1-H11/C1-C9</td>
<td>2.77(4)</td>
<td>0.87(4)</td>
<td>1.91(4)</td>
<td>169(4)</td>
</tr>
<tr>
<td>O2-H22/C1-O3g</td>
<td>2.86(5)</td>
<td>0.89(5)</td>
<td>1.98(5)</td>
<td>177(4)</td>
</tr>
<tr>
<td>O2-H21/C1-N5</td>
<td>2.83(3)</td>
<td>0.88(4)</td>
<td>1.99(4)</td>
<td>170(4)</td>
</tr>
<tr>
<td>O3-H32/C1-O2</td>
<td>2.87(4)</td>
<td>0.87(4)</td>
<td>2.01(4)</td>
<td>173(4)</td>
</tr>
<tr>
<td>O3-H31/C1-N8g</td>
<td>2.98(4)</td>
<td>0.88(4)</td>
<td>2.14(4)</td>
<td>161(4)</td>
</tr>
<tr>
<td>O1-C1-C1-C1</td>
<td>3.32(3)</td>
<td>0.93(4)</td>
<td>2.86(4)</td>
<td>112(4)</td>
</tr>
<tr>
<td>O2-C1-C1-C1</td>
<td>3.33(4)</td>
<td>0.92(4)</td>
<td>2.89(4)</td>
<td>110(4)</td>
</tr>
</tbody>
</table>

[a] The hydrate structure is shown in detail in Figure 4. Symmetry operations for equivalent atoms: $x = -x + 1$, $y = -y + 1$, $z = -z + 1$; $e = -x + 2$, $-y + 2$, $-z + 2$; $f = -x + 1$, $-y + 1$, $-z + 1$; $g = -x + 2$, $-y + 2$, $-z + 2$. All other O...O contacts are longer than 4.0 Å, O...N contacts longer than 3.7 Å. [b] D = donor, A = acceptor.

The bis(triazolyl)borate (4) functions as a bidentate chelate ligand here, with the exodentate nitrogen atoms as donors. Comparison of the Ni-O and Ni-N bond lengths reveals only a small distortion of the pseudooctahedral coordination sphere. The ligand arrangement in the molecular structure (Fig. 6) leads one to expect an inversion symmetry at the nickel center. However, the normalized structure factor amplitudes point to an acentric space group. Of the space groups possible according to the systematic absences only Cmc2$_1$ permitted successful refinement. The heavy atoms in 12 have a pseudo-hexagonal symmetry (Fig. 9), so that the data set was at first (erroneously) recorded in the hexagonal setting. However, no refinement was possible in this crystal system—the arrangement of the ligands demanded an orthorhombic setup. Furthermore, Figure 9 illustrates the presence of channels which extend along c through the lattice and contain the water of crystallization. A diameter of about
5 Å is estimated between the surrounding nitrogen and hydrogen centers, correspondingly less if the covalent or van der Waals radii of these atoms are taken into account. One might be tempted to invoke self-assembly of the complexes here. The intermolecular interaction responsible in part would have to be the formation of a bridge by the hydrogen bonds of an aqua ligand between two exodentate nitrogen atoms of two neighboring complex molecules (Figs. 7 and 8). In addition, we think of the channel formation as caused by the intimate solvent–complex interactions carried over from solution to the solid phase. The channels could result from the formation of a chain along c by hydrogen bonds in the water of crystallization. This water chain is probably of a more continuous, dynamic nature at room temperature and interrupted at low temperature in an ordering process, a phase transition giving the dimeric units (cf. the dynamics and the ordering of the “two-dimensional” water substructure in 6, demonstrated especially in the case of the nickel complex).

X-Ray crystal structure of 13: The structure of 13 is that of a two-dimensional coordination polymer, with the bis(tetrazolyl)borato ligand bridging the octahedrally coordinated nickel atoms through the C–H neighboring N4 atom (Figs. 10 and 11). Two trans-coordinated ammine ligands conclude the nickel coordination polyhedron. All Ni–N distances are very similar. The crystal structure does not contain any water of crystallization. There are no voids in this structure which are large enough for solvent molecules, as can be envisioned from Figure 11 and by a free-space/solvent-accessible area calculation with the PLATON program.[13]

The appearance of 13 and its synthesis by two different routes again required the authentication of the single-crystal X-ray structure by comparison with the two microcrystalline bulk samples by X-ray powder diffractometry (Fig. 12).

Discussion

Table 3 summarizes the structural features of the various metal complexes of the poly(azolyl)borates 3–5 with respect to their mono- or polymeric character and isostructural relationships. It is evident that the respective ligands show a strong preference for a particular structure, regardless of the metal involved. In view of the often isostructural nature of the metal–ligand compounds, the deviations encountered seem at first even more striking. The hydrotris(triazolyl)borato ligand prefers tridentate chelate coordination through the endodentate nitrogen atoms, thus forming molecular complexes from iron to zinc (6), with, in the case of zinc, the possibility of a second (linkage) isomer in the form of a coordination polymer (7). For manganese a coordination polymer only has been found (11). This change cannot be caused by the difference in size of the metal center, as analogous tris(pyrazolyl)borato manganese[14] and zinc chelate derivatives[15] can easily be prepared. Structural data for the dihydrobis(triazolyl)borato ligand is somewhat more scarce, but the difference in structure between the nickel and copper compounds, the former a molecular chelate complex (12), the
Table 3. Structural features of metal complexes with modified poly(azoly1)borato ligands [a].

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Metal</th>
<th>$\text{M}^{2+}$</th>
<th>$\text{Fe}^{2+}$</th>
<th>$\text{Co}^{2+}$</th>
<th>$\text{Ni}^{2+}$</th>
<th>$\text{Cu}^{2+}$</th>
<th>$\text{Zn}^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H[B(C$_2$H$_4$N$_3$)$_3$]</td>
<td>3</td>
<td>1-D coord. polym. (11)</td>
<td>molecular chelate complex (6)</td>
<td>3-D coord. polym. (7)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$_2$B(C$_2$H$_4$N$_3$)$_2$</td>
<td>4</td>
<td>2-D coord. polym. (8)</td>
<td>molecular chelate complex (12)</td>
<td>1-D coord. polym. (19)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$_2$B(C$_2$H$_4$N$_3$)$_2$</td>
<td>5</td>
<td>2-D coord. polym. (symmetry 10)</td>
<td>3-D coord. polym. (symmetry 10)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

[a] Bold-framed windows refer to the structures presented in this manuscript. For the other structures, see ref [3-7]. The same background shading is meant to underscore the isostructural character. Asterisks indicate that the compound has been crystallized from aqueous ammonia.

Full Paper: The coordination polymer can be explained simply by the Jahn-Teller distortion. Numbers in bold refer to the schematic structure drawings in the introduction.

Later a coordination polymer (9), is not immediately understandable. Finally, in most cases the dihydrobis(tetrazoly1)borate exists solely as a bridging ligand in a highly symmetrical 2-D rhombohedral grid structure (10) except for the nickel and copper compounds (13 and 10'). Before the nickel structure of 5 was known, the lower symmetry of its copper structure (10') was explained simply by the Jahn-Teller distortion of the central metal.[6] In view of the new results the structural distortion must be ascribed to a different cause.

In the following we will show how the metal-ligand coordination depends upon and can be controlled by i) the nitrogen donor properties and the chelate effect, ii) the electron count at the metal, and iii) the crystallization conditions.

The difference between the coordination chemistry of manganese and zinc with the ambidentate ligand 3 and that of the analogous complexes from iron to copper can be traced to the zero ligand-field stabilization energy (LFSE) of the $d^5$ (high-spin) and $d^{10}$ metal. In the case of Mn$^{2+}$ (high-spin) and Zn$^{2+}$, no additional energetic driving force results from the LFSE upon substitution of an aqua ligand by a stronger N donor ligand. This fact has been best investigated for the stepwise formation of ethylenediamine complexes and is quantitatively illustrated by a plot of the stability constants as a function of the metal (Fig. 13). The resulting low degree of stability based on $K_1$ and $K_2$ with a (relative) minimum at manganese and zinc and a maximum at copper is also known as the Irving-Williams series.

It is also important to realize that the exchange of an aqua for a poly(azoly1)borato ligand will occur stepwise. If the first donor shows the chelate complexes that form for Fe to Zn, these being the major product for Fe to Cu because of the high stability constants (Fig. 13). Coordination polymers of Fe to Cu with 3 were in part obtained as amorphous precipitates upon rapid admixture of the reactants but were not characterized further.

Zinc, however, is a metal which is more stable in a tetrahedral environment than the other first-row transition metals; this explains the rather high stability constants $K_1$ and $K_2$ despite the $d^10$ configuration (Fig. 13). The preferred ammine complex appears to be [Zn(NH$_3$)$_2$]$^{2+}$ rather than [Zn(NH$_3$)$_3$]$^{2+}$, which is only formed at high ammonia concentrations; hence the constant $K_3$ for the octahedral complex is much smaller.[18] This helps to explain the initially observed formation of the octahedral molecular chelate complex of zinc with 3 (6).[44] Its lower stability allows, however, for an opening of the chelate rings by H$_2$O and a new exo N coordination, most likely from a free ligand in solution. In the end a complete transformation to the 3-D coordination polymer as the apparently thermodynamically more stable isomer results. This therefore leads us to conclude that exo N coordination is thermodynamically more stable than the endo N-metal interaction.

In the case of manganese, the effect of LFSE is even more pronounced. Substitution of an aqua ligand results only in a small energy gain so that the nitrogen donor characteristics can determine the position of the exo---endo equilibrium outlined in Scheme 1. With the exodentate nitrogen atom being the better donor, the equilibrium will be shifted to the left, so that coordination polymers are formed.

An additional hint on the importance of the outlined equilibrium in the case of manganese and zinc is obtained from the reaction rates: while admixture of the reactant solution results in immediate precipitation of Fe, Co, Ni, or Cu, the products...
precipitate significantly more slowly for Mn and Zn. Thus in the case of the bis(triazolyl)borato ligand (4) the change from coordination polymer to molecular chelate complex (structure 8 versus 12) from manganese to nickel follows the trend in LFSE and is straightforward. However, the fact that the copper derivative (structure 9) is again a coordination polymer appears to be an anomaly. After all, the LFSE for 1:1 and 1:2 complexes (K, and K') with a bidentate ligand is highest for copper (Fig. 13). This difficulty is resolved when one takes into account the fact that the crystals of 12 and 9 were obtained from ammoniacal solution or a metal–amine complex, respectively. Contrary to the above discussion based on Scheme 1, complex formation then does not proceed from a hexaaqua but from ammine–aqau complexes [Eqs. (5) and (6)]. In the case of nickel, the exchange

\[ [\text{Ni(NH}_3)_4(H_2O)]^{2+} + 4 \rightarrow [\text{Ni(n}_4^4\text{NH}_3)_4]^{2+} + 2H_2O \rightarrow \ldots \]  

(5)

\[ [\text{Cu(NH}_3)_4(H_2O)]^{2+} + 4 \rightarrow [\text{Cu(n}_4^4\text{NH}_3)_4H_2O]^{+} + H_2O \rightarrow \ldots \]  

(6)

of H_2O for the stronger bis(triazolyl)borato ligand leads to a gain in LFSE and to the formation of chelating rings. In the tetraamminecopper complex, on the other hand, the four NH3 ligands are bound very strongly to the central metal with short distances in the equatorial plane because of the Jahn–Teller distortion. This is the reason for the maxima of the stability constants K, and K' at copper in the Irving–Williams series (cf. Fig. 13).\[14,19]\] Thus any ammine exchange will have to start at the axial, loosely bound H_2O ligands. Formation of chelating rings from this position through a reorganization of the remaining ligands or through substitution of a cis NH3 ligand might be possible but is energetically highly unfavorable, as is demonstrated by the very small stability constant K, (Fig. 13) in the case of the [Cu(en)]^{2+} complex (log K, = -1.0).\[18]\] More importantly, however, substitution of the weak H_2O ligands in the tetraamminecopper complex by a stronger N donor ligand (even monodentate) is unfavorable to begin with, as can be seen by the stability constant for the pentaaamminecopper complex of log K, = -0.52.\[18]\] Analogously to the equilibria outlined in Scheme 1, a similar exo–endo N equilibrium with a tetraamminecopper ion as intermediate can be formulated, from which crystallization of the thermodynamically more stable exo aduct then occurs (see Scheme 2).

For the bis(tetrazolyl)borato ligand (5), the two-dimensional coordination polymer is the sole structure so far known; the borate functions as a bridging ligand through the C–H neighboring nitrogen donor. Yet it is interesting to note that highly symmetrical two-dimensional rhombic grid sheets (10, or-

thorthombic crystal system, space group Cmca) result when the crystals are grown from water, whereas lower-symmetry distorted 2-D frameworks are obtained when ammonia is involved as a ligand, as has been found in the closely related structures of the nickel and copper derivatives (13 and 10), monoclinic crystal system, space group P2_1/c and P2_1/a.\[6]\] We may not yet have a fully proven explanation for this difference in structure based on the crystallization conditions, but for the packing of the metal–ligand complexes, chains, and layers in the water containing crystal phases (the “secondary structure”, so to speak) we would like to point to the hydrogen bonds as a possibly important design element already well recognized in organic chemistry\[21] and in biological systems\[22] but less so in inorganic chemistry.

The symmetrical structure 10 contains two water molecules of crystallization per formula unit. Hydrogen bonding to the aqua ligands at the metal center gives rise to one-dimensional chains of water molecules that run parallel to the 2-D metal–ligand grid sheets; in ref. [6] it was emphasized that the hydrogen bonds along the water chain are invariant with the change in metal, thereby including metals from manganese to zinc and even cadmium. As regards the water chain, we would like to suggest the metaphor of a reinforcing bar for the metal–ligand framework. With ammine ligands completing the metal coordination spheres in the nickel and copper compounds (13 and 10) no water of crystallization is incorporated, possibly owing to the weaker hydrogen-bond forming capability of NH3. What is observed then is solvent-free crystal packing in the form of a less symmetrical, distorted grid sheet. In view of the increased interest in the controlled synthesis of two- and three-dimensional inorganic materials,\[23,24]\] hydrogen bonding should not be overlooked as a possible design element also in inorganic chemistry.\[24]\]

Conclusions

Using modified, potentially ambidentate poly(triazolyl)borates as examples, we have demonstrated how ligand-field stabilization energy can be used to control metal–ligand assembly during the crystallization process to give either chelate complexes or coordination polymers. The choice of the coordinating solvent ligand is an interesting tuning variable which can not only be a decisive factor for the metal–ligand interaction but can also provide a design element for the (secondary) solid-state structure by transferring solvent–solvent interactions from the solution to the solid phase. The nature of the hydrogen-bonding network built up by incorporated solvent molecules can control the conformation assumed by the metal–ligand framework.

Experimental Procedure

Twice distilled or deionized water was used as a solvent. CHN: Perkin–Elmer Series II CHNS/O Analyzer 2400. IR: Nicolet Magna 750. MS: Varian MAT 311 A.

Susceptibility measurements: AC susceptometer Lakeshore Model 7000. X-ray powder diffractograms: INEL, CuKα2 radiation, quartz monochromator, sample in 0.7 mm glass capillaries on rotating probe head. The potassium salts of 3–5 were synthesized from KBF4 and triazole or tetrazole, respectively, according to refs. [2, 5, 25]. The synthesis of 12 was also described in ref. [5].

\[ [\text{[Mn}(\mu_2-\text{HBC}(\text{H}_2\text{N})_3)_8(\text{H}_2\text{O})_2]^{3-}\text{H}_2\text{O}]^{+} \]  

(11): A solution of anhydrous MnCl2 (0.13 g, 1.0 mmol) in degassed H2O (3 mL) in a Schlenk tube under argon was carefully overlayed with a solution of the potassium salt of 3 (0.50 g, 2.0 mmol) in degassed water (8 mL). Within a few days ill-shaped colorless-to-white crystals formed. The reaction could also be carried out in air, but a brown precipitate formed upon prolonged storage of the crystals under water. The crystal yield lay between 0.30 and 0.40 g (50–67%). M.p.:
loss of water of crystallization at 100 -105°C. IR (KBr): v = 3420 brs (OH), 3137 w (CH), 2950 w - m (BH), 1661 s, 1513 s, 1416 s, 1336 w - m, 1283 m, 1217 w, 1191 s, 1139 s, 1107 w, 1078 w, 1061 w, 1031 w, 1008 m, 990 m, 976 w, 989 v, 882 w, 792 sh, 771 sh, 738 m - s, 652 sh cm⁻¹. MS (EI, 70 eV, 320°C, m/z %): 487 (100, [C₃]), 419 (27, [C₃-C₂N₃H₅]⁺), 417 (13, [C₃-C₂N₃H₅-2H⁺], 350 (38, [C₂-C₂N₃H₅-2H⁺]), 349 (19, [C₂-C₂N₃H₅-2H⁺]), 313 (32, [C₂-C₂N₃H₅-H-HCN⁻]), 271 (66, [C₂-C₂N₃H₅-H⁻]⁺), 202 (28, [M₂H(C₂H₃C₅H₅)]⁻, 175 (39, [M₂H(C₂H₃C₅H₅)_2], C₂H₃C₅H₅-H⁻-H⁻), 69 (32, [C₂H₅C₅H₅-]), Magnetic moment: μ = 5.6 μm (295 K). Curie-Weiss constant θ = -1.7 K. C₄H₉Br₂Ni₄N₂ (394.60): calcd. C 12.17, H 3.58, N 6.89; found C 12.53, H 3.55, N 63.52.

**X-Ray structure determinations of 11-13:**

Structure solution was performed by direct methods (SHELXLS-86 [26]). Refinement: Full-matrix least-squares on F² (SHELXLS-93 [26]); all atomic positions including those of the hydrogen atoms found and refined (non-hydrogen atoms with anisotropic temperature factors).

**Crystal data are listed in Table 4 [27].**

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Table 4. Crystal data for compounds 11-13.

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<tr>
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<td>C₄H₉Br₂Ni₄N₂O₆</td>
<td>C₄H₉Br₂Ni₄N₂O₆</td>
<td>C₄H₉Br₂Ni₄N₂</td>
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<td>M (g mol⁻¹)</td>
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<td>592.79</td>
<td>592.79</td>
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<td>0.4 x 0.1 x 0.1</td>
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<td>293(2)</td>
<td>293(2)</td>
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<td>Turbo CAD4 with rotating anode generator</td>
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<td>MoKα 0.71069</td>
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<td>ω, 11-12°</td>
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<td>b (Å)</td>
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<td>c (Å)</td>
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<td>1269; 0.71; 1.133</td>
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</table>

[a] Experimental absorption correction [28]. [b] Largest peak and hole are [c] R₁ = Σ|Fo| - |Fc|/Σ|Fo|, wR₁ = [Σw(|Fo|² - |Fc|²)/Σw|Fo|²]^[1/2]. [d] GOF = [Σw(Fo² - Fc²)^2]/(n-p-1). [e] w = 1/|σ(Fo²) + (a × P) + (b × P)|, where P = (max(Fo²) or 0) + 2 × P²/3. [f] Absolute structure parameter [29].