

Clathrates and Coordination Polymers: New Dimensions in Poly(azolyl)borate Chemistry with Poly-(triazolyl)- and -(tetrazolyl)-borate Ligands

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The X-ray structures of the iron and cobalt bis[hydrotris(triazolyl)borate] complexes show the formation of a 2-D liquid water phase in the crystal lattice and the cobalt, zinc, and cadmium tetrazolylborate complexes are obtained as crystalline coordination polymers.

When Trofimenko introduced the prototypical poly-(pyrazolyl)borate ligands **1** and **2** in coordination chemistry more than 20 years ago, he correctly foresaw an important future for this system.^{1,2} Especially, the tridentate, chelating anion **1** has indeed developed into one of the most versatile auxiliary ligands in (bio-)inorganic coordination chemistry.³

An interesting modification of **1** and **2**, obtained through replacement of the pyrazolyl rings by (1,2,4)-triazolyl or tetrazolyl has only been mentioned briefly, however,^{1,4} or not at all,⁵ although the ambidentate poly-(triazolyl)- and -(tetrazolyl)-borate anions [HB(C₂H₂N₃)₃]⁻, **3**, and [H₂B(CHN₄)₂]⁻, **4**, with their multiple bonding centres let one expect an interesting coordination chemistry. The additional ring nitrogen atoms in **3** and **4** could function as alternative or additional donor atoms, according to an AM1-calculation⁶ (Fig. 1).

To elucidate the coordination chemistry of **3** and **4**, the following complexes were synthesized† and investigated spectroscopically, magneto-chemically as well as through single-crystal X-ray diffraction.‡

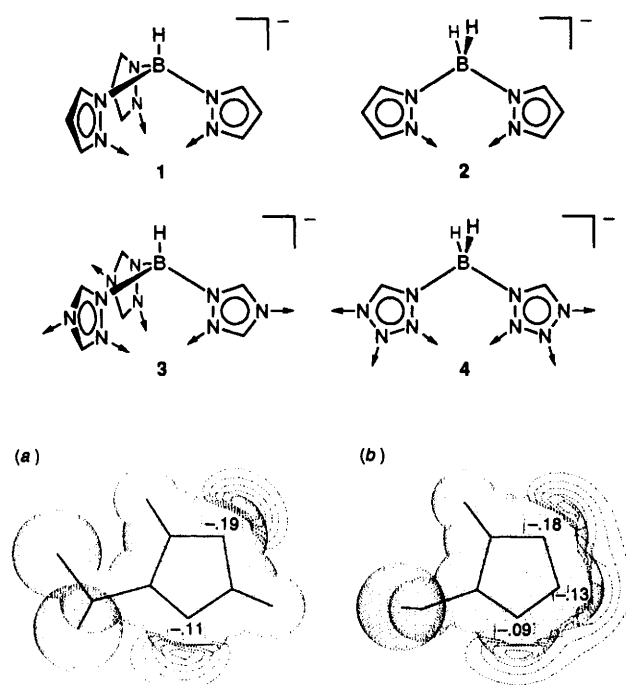
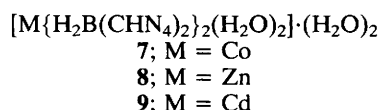
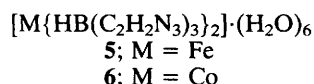


Fig. 1 Charge distribution (for the potential nitrogen donor atoms) and electrostatic potential in a (a) triazolyl- or (b) tetrazolyl-ring of **3** or **4** according to an AM1-calculation.⁶ For clarity only the boron-bonded nitrogens of the other rings are shown. Contour lines: -0.30 (minimum)/ -0.27 / -0.24 / -0.21 / -0.18 (inside-out).

The molecular structure of the isomorphous iron and cobalt complexes from **5** and **6** is shown in Fig. 2. The exocyclic N-atoms in the triazolyl rings of **3** are not utilized for coordination to the metal centre, despite a higher calculated charge density (cf. Fig. 1) and **3** functions as a tris-chelate ligand to give octahedrally coordinated metal complexes analogous to **1**.⁸ However, the exocyclic N-atoms do play a part in the crystal packing. For each molecular unit, six H₂O molecules are embedded in the crystal lattice in **5** and **6**, with two H₂O molecules coordinating to two exocyclic nitrogen atoms through hydrogen bonding. Fig. 3 illustrates the isomorphous crystal structure of **5** and **6**. The solvation forces can compete in **5** and **6** intermolecularly, so that the solvated species transfer together with the complex from the solution to the crystal under formation of a solvate or clathrate. Because of the high number of solvate molecules we have here an unusual example for a stabilization of a crystal phase by host-guest interactions.⁹ The crystal structures of **5** and **6** are alternately built up from 2-D water and metal-complex layers in the form of an intercalate of layer-clathrate.

In the transition metal complexes of the dihydrobis(tetrazolyl)borate ligand, **4**, the formation of 2-D coordination polymers has been the sole structural motif observed so far. Bidentate ligands, which do not form chelates but bridges between metal atoms, are interesting with respect to the preparation of unusual coordination polymers. Fig. 4 illustrates the constitution of a layer polymer for the isomorphous

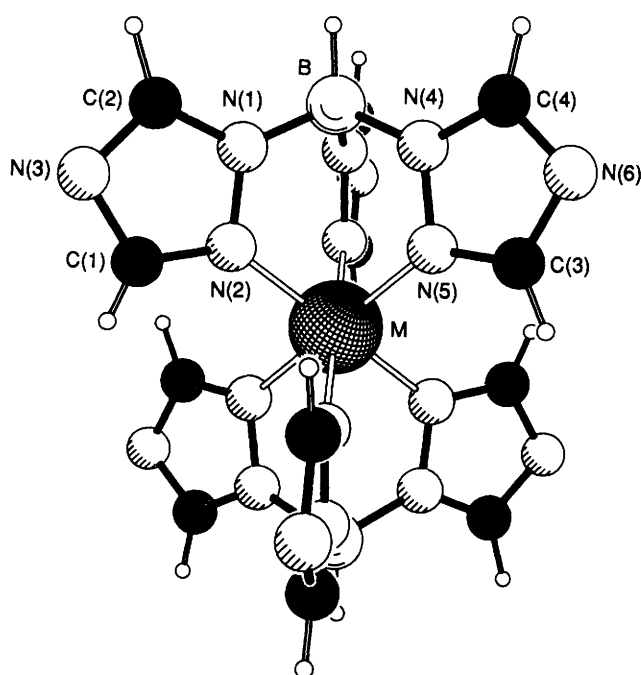


Fig. 2 Isomorphous molecular structure of [M{HB(C₂H₂N₃)₃]₂] in **5** (M = Fe) and **6** (M = Co). (PLUTO¹¹). Selected distances (pm) and angles (°): **5**: Fe–N(2) 199.2(4), Fe–N(5) 199.3(3); *cis* N–Fe–N 87.8(2)–92.2(2), *trans* N–Fe–N 180(1). **6**: Co–N(2) 212.1(5), Co–N(5) 212.7(3), *cis* N–Co–N 84.9(2)–95.1(2), *trans* N–Co–N 180(2).

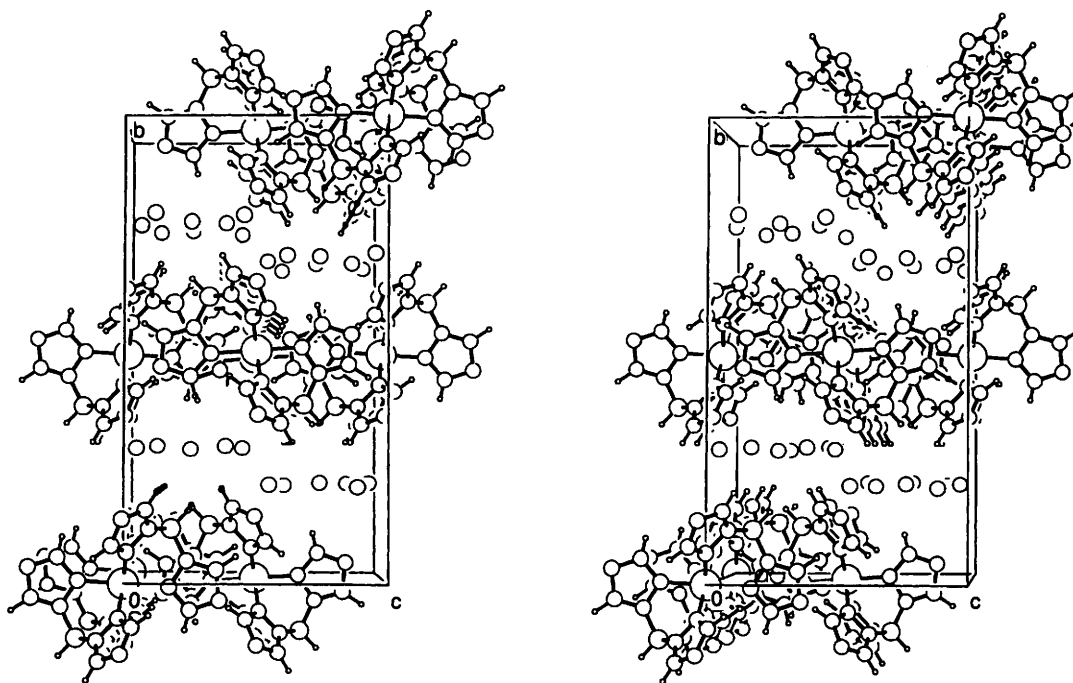


Fig. 3 Stereoview of the isomorphous crystal structure of 5 and 6 illustrating the intercalation of a 2-D water layer between metal-complex layers

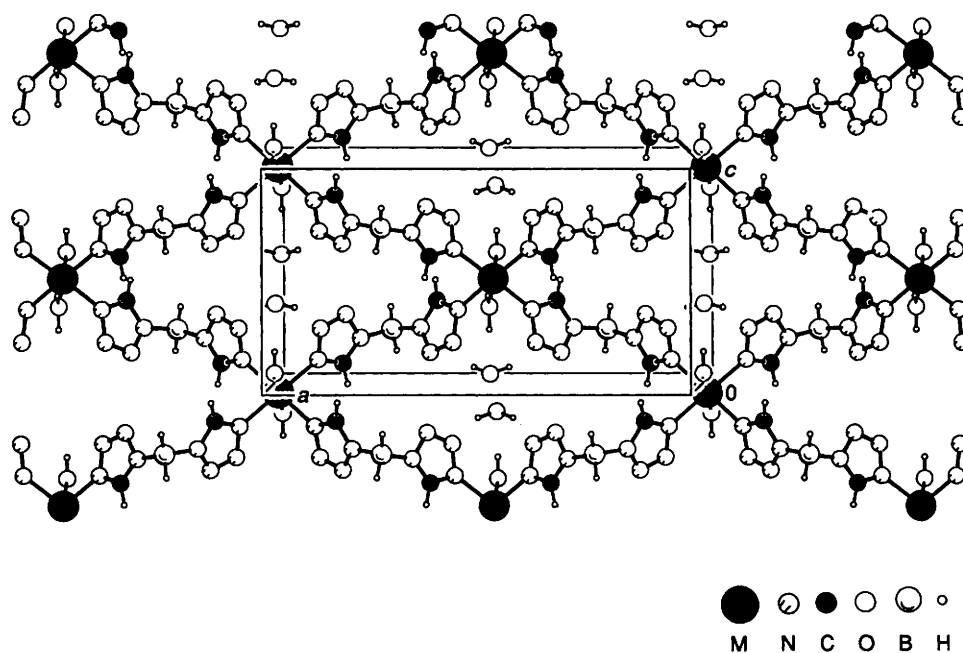


Fig. 4 PLUTO-plot of a layer in the isomorphous crystal structures of $[M\{H_2B(CHN_4)_2\}_2(H_2O)_2] \cdot (H_2O)_2$ 7 ($M = Co$), 8 ($M = Zn$) and 9 ($M = Cd$). Selected distances (pm) and angles ($^\circ$): 7: Co–N 216.4(2)/218.5(2), Co–O 208.0(2)/206.2(2); O–Co–O 178.86(6), *trans* N–Co–N 179.12(7), O–Co–N and *cis* N–Co–N 89.09(6) to 91.77(5). 8: Zn–N 224.6(4)/214.0(6), Zn–O 209.3(4)/208.9(4), O–Zn–O 177.3(1), *trans* N–Zn–N 178.1(1), O–Zn–N and *cis* N–Zn–N 88.5(2) to 92.8(2). 9: Cd–N 235.5(4)/236.2(3), Cd–O 229.0(3)/229.2(3), O–Cd–O 177.2(1), *trans* N–Cd–N 177.3(1), O–Cd–N and *cis* N–Cd–N 87.1(1) to 91.1(1).

structures of the cobalt 7, zinc 8 and cadmium 9 complexes of 4. The metal centres in 7–9 are in all cases octahedrally coordinated, with the coordination polyhedron being formed from four nitrogen atoms of the ligands and two solvate (H_2O) molecules. Thereby, only the C–H neighbouring N-atom functions as a donor atom, which is in agreement with the charge distribution from the AM1-calculation (Fig. 1). The two other N-atoms establish in part H-bridges to the embedded water of crystallization. The rhombohedral, water-filled openings in Fig. 4 do not extend through the crystal lattice as open channels, though, but the next kinked layer is shifted half a unit cell along *c*, so that the layers interlock and

caves are formed. Reports on similarly arranged interwoven, 2-D nets have appeared under the aspect of (spontaneous) self-organization of molecular building blocks.¹⁰

In summary it can be noted that the introduction of additional coordination centres in the poly(pyrazolyl)borate ligands 1 and 2, as exemplified in the tris(triazolyl)- and bis(tetrazolyl)-borate system 3 and 4, extends the hitherto molecular shaped coordination chemistry of the poly-(azolyl)borate ligands to the interesting dimension of the solid state. The added functionality leads to supramolecular 2- and 3-D arrays.

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Footnotes

† *Experimental*: 10 ml of an aqueous solution of 1.3 mmol of the metal salt (FeSO₄, CoCl₂, CuCl₂, Zn(O₂CMe)₂, CdCl₂) were overlaid with 20 ml of an aqueous solution of 2.6 mmol 3¹ or 4.⁵ The reaction and process of crystallisation was concluded in a few days to a few weeks (5) (crystal yield 40–70%). Crystal colour: 5 magenta; 6 yellow; 7 orange; 8 and 9 colourless.

‡ *Crystal data*: Syntex P21-four-cycle-diffractometer, ω -scan ($0^\circ \leq 2\theta \leq 55^\circ$), room temp., Mo-K α -radiation ($\lambda = 71.069$ pm, graphite-monochromator), structure solution by direct-methods (SHELXS-86)⁷. Refinement: full-matrix least-squares; non-hydrogen atoms were refined with anisotropic temperature factors (SHELX-76);⁷ except for the disordered O-atoms in 5 and 6.

For 5: orthorhombic, space group *Cmca*, $a = 1094.3(2)$, $b = 2074(1)$, $c = 1152.0(6)$ pm, $Z = 4$. 1352 symmetry independent reflections, 894 observed [$F > 4\sigma(F)$], 120 refined parameters, $R = 4.78$, $R_w = 4.65$.

For 6: orthorhombic, *Cmca*, $a = 1084.8(7)$, $b = 2112(1)$, $c = 1184.3(5)$ pm, $Z = 4$. 1475 independent reflections, 1025 observed [$F > 5\sigma(F)$], 117 parameters, $R = 5.59$, $R_w = 5.56$.

For 7: orthorhombic, *Ccm2*₁ (non-standard setting of *Cmc2*₁), $a = 1768.2(5)$, $b = 1029.9(5)$, $c = 943.5(5)$ pm, $Z = 4$. 1040 independent reflections, 1022 observed [$F > 2\sigma(F)$], 141 parameters, $R = 2.81$, $R_w = 2.68$.

For 8: orthorhombic, *Ccm2*₁, $a = 1777.2(3)$, $b = 1026.1(2)$, $c = 944.4(4)$ pm, $Z = 4$. 1063 independent reflections, 976 observed [$F > 3\sigma(F)$], 133 parameters, $R = 5.33$, $R_w = 5.47$.

For 9: orthorhombic, *Ccm2*₁, $a = 1836.6(5)$, $b = 1020.7(2)$, $c =$

965.0(2) pm, $Z = 4$. 1051 independent reflections, 953 observed [$F > 2\sigma(F)$], 139 parameters, $R = 2.93$, $R_w = 3.14$.

Atomic coordinates, bond lengths and angles, and thermal parameters for 5, 6, 7, 8 and 9 have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue, No. 1.

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