

Facial $\pi \cdots \text{Cl} \cdots \pi$ interactions as the directing motif of the supramolecular structures of Mg^{2+} and Ca^{2+} bis[hydrotris(pyrazolyl)borate] chloroform disolvates

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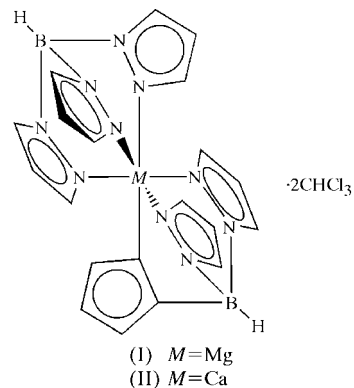
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The isomorphous complexes bis[hydrotris(pyrazolyl)borato]-magnesium(II) chloroform disolvate, $[\text{Mg}(\text{C}_9\text{H}_{10}\text{BN}_6)_2] \cdot 2\text{CHCl}_3$, and bis[hydrotris(pyrazolyl)borato]calcium(II) chloroform disolvate, $[\text{Ca}(\text{C}_9\text{H}_{10}\text{BN}_6)_2] \cdot 2\text{CHCl}_3$, crystallize in the cubic space group $P\bar{a}3$ with $Z = 4$. The metal atoms occupy sites of $\bar{3}$ symmetry, and their coordination is very similar to

that found for the unsolvated $\text{Mg}[\text{HB}(\text{Pz})_3]_2$ and $\text{Ca}[\text{HB}(\text{Pz})_3]_2$ complexes (Pz is pyrazole). The inclusion of chloroform molecules on threefold rotation axes not only leads to high-symmetry crystal structures but also plays an important role in stabilizing the three-dimensional supramolecular architecture through facial $\text{Pz} \cdots \text{Cl} \cdots \text{Pz}$ interactions.

Comment

The coordination chemistry of the tris(pyrazolyl)borate ligand (Tp) has been studied extensively since its introduction in 1966 (Trofimenko, 1966). Tp forms a great variety of complexes with most metals and metalloids in a tridentate fashion. Trofimenko (1999) has termed this ligand and its derivatives 'scorpionates', since the two equatorial pyrazole (Pz) rings look like the claws and the pseudo-axial pyrazole ring looks like the stinger of a scorpion. In this paper, we report the structures of the Mg^{2+} , (I), and Ca^{2+} , (II), bis[hydrotris(pyrazolyl)borate] chloroform disolvates.



The molecular structures of (I) and (II) are shown in Figs. 1(a) and 2(a), and selected bond lengths and angles are

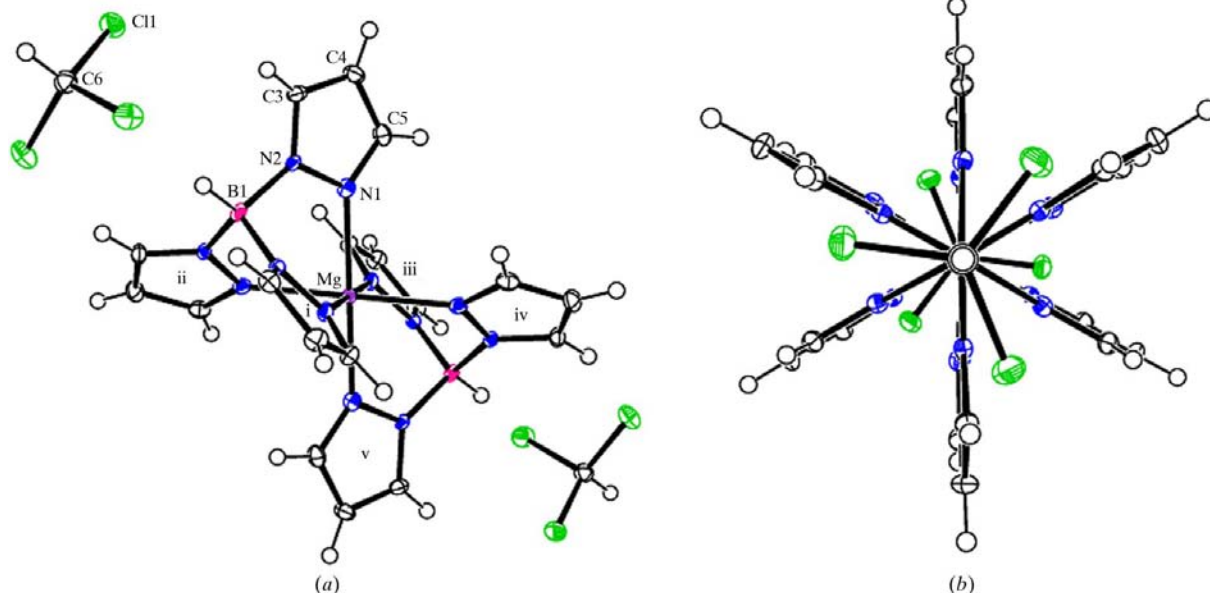


Figure 1

(a) The molecular structure of (I), showing displacement ellipsoids drawn at the 30% probability level [symmetry codes: (i) z, x, y ; (ii) y, z, x ; (iii) $-z + 1, -x + 1, -y + 1$; (iv) $-y + 1, -z + 1, -x + 1$; (v) $-x + 1, -y + 1, -z + 1$] and (b) top view of the structure of (I).

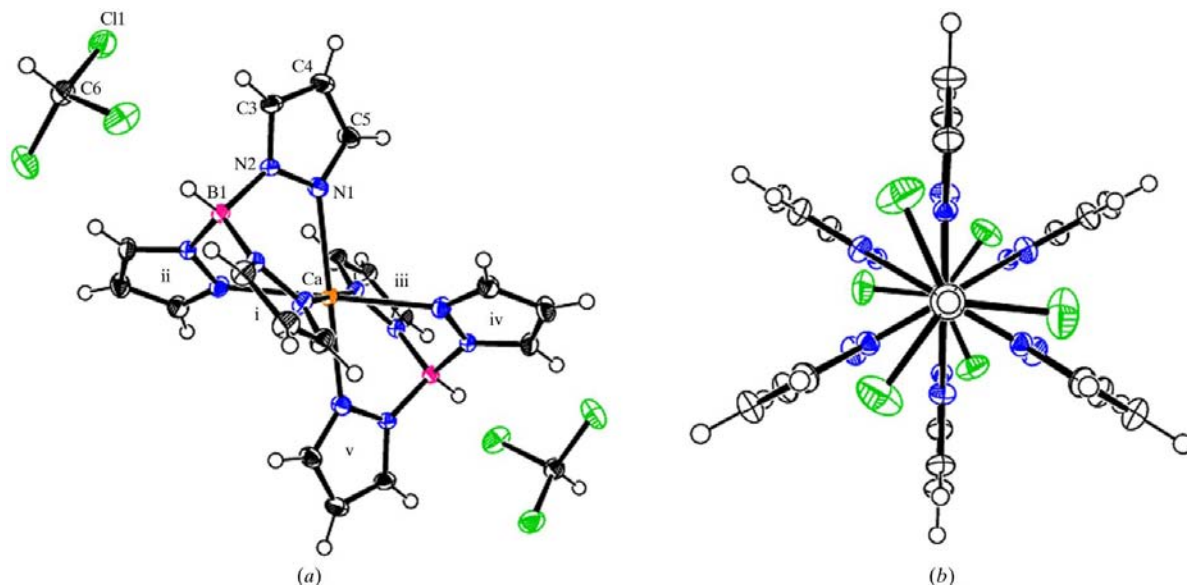


Figure 2

(a) The molecular structure of (II), showing displacement ellipsoids drawn at the 30% probability level [symmetry codes: (i) z, x, y ; (ii) y, z, x ; (iii) $-z + 1, -x + 1, -y + 1$; (iv) $-y + 1, -z + 1, -x + 1$; (v) $-x + 1, -y + 1, -z + 1$] and (b) top view of the structure of (II).

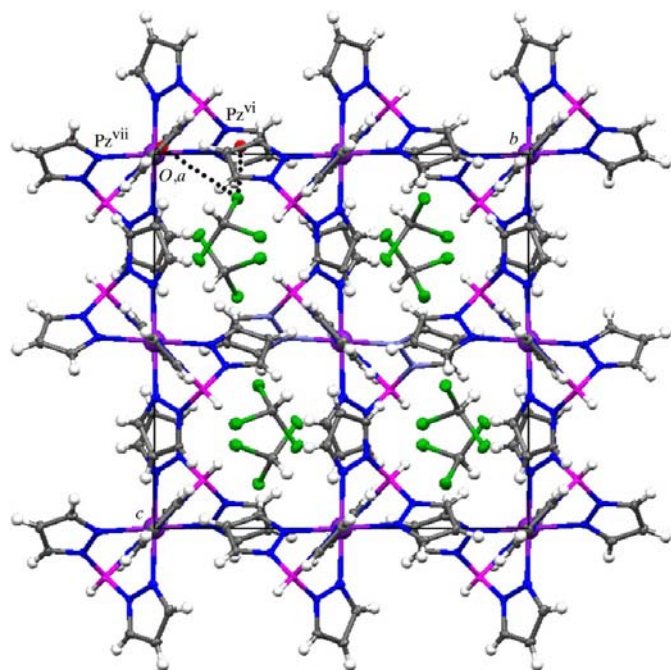


Figure 3

The three-dimensional network structure of (I), built up through $\pi \cdots \text{Cl} \cdots \pi$ interactions. [Symmetry codes: (vi) $z, -x + \frac{1}{2}, y - \frac{1}{2}$; (vii) $-z + \frac{1}{2}, x - \frac{1}{2}$.] Compounds (I) and (II) are isomorphous.

listed in Tables 1 and 2, respectively. In each complex, the metal atom occupies a site of $\bar{3}$ symmetry and both Tp ligands are symmetrically tridentate; the geometry about the metal atom is trigonally distorted octahedral, with an $M-N$ bond length of 2.173 (3) Å in (I) and 2.4241 (18) Å in (II). The corresponding intraligand $N-M-N$ bond angles are 84.94 (10) and 79.45 (6)°. The $N \cdots N$ distances, which correlate with the bite angles of the ligand, are 2.934 (2) and

3.098 (2) Å for (I) and (II), respectively, and are governed by the relative ionic radii of the Mg^{2+} (0.65 Å) and Ca^{2+} (0.99 Å) ions (Huheey *et al.*, 1993).

The coordination geometry in (I) and (II) is very similar to that seen in the corresponding unsolvated $\text{Mg}[\text{HB}(\text{Pz})_3]_2$ and $\text{Ca}[\text{HB}(\text{Pz})_3]_2$ complexes (Sohrin *et al.*, 1994). The former crystallizes in the triclinic space group $P\bar{1}$, with two crystallographically independent molecules lying across different inversion centres, whereas the latter crystallizes in the monoclinic space group $C2/c$, with two crystallographically independent molecules on twofold rotation axes. In contrast, the chloroform solvates (I) and (II) exhibit high symmetry and crystallize in the cubic space group $Pa\bar{3}$, with the metal atoms on sites of $\bar{3}$ symmetry and the chloroform solvent molecules on threefold rotation axes. The influence of chloroform on the regulation of crystal structure has been documented by comparing the structures of the chloroform (monoclinic, space group $P2_1/c$; Nielson *et al.*, 2003) and toluene (triclinic, space group $P\bar{1}$; Davidson *et al.*, 2003) solvates of the zwitterion bis[tris(3,5-dimethyl-2-oxidobenzyl- κO)ammonium]zirconium(IV), and those of *trans*-bis(2,2-diphenylethylamine- κN)bis(5,5-diphenylhydantoinato- κN^3)copper(II) and its chloroform solvate (triclinic, space group $P\bar{1}$, and orthorhombic, space group $Pbca$, respectively; Akitsu & Binaga, 2005). In both cases, chloroform influences crystallization to give structures that are more symmetric than those observed for unsolvated complexes or those solvated by other solvents.

Chloroform molecules play an important role in the development of the supramolecular architectures of (I) and (II); its inclusion is governed by electrophile-nucleophile $\text{C}-\text{Cl} \cdots \pi$ interactions (Csöregi *et al.*, 1996), which form a three-dimensional network. Each Cl atom of the chloroform solvent interacts with two pyrazole rings in the same neighbouring molecule. In (I) (Fig. 3), the relevant parameters are $\text{C6}-$

Cl1...Pz^{vi} = 3.5018 (16) Å, C6—Cl1...Pz^{vi} = 91.14 (14)°, C6—Cl1...Pz^{vii} = 3.4906 (16) Å, C6—Cl1...Pz^{vii} = 165.05 (15)°, Cl...Pz...Cl = 158.4 (2)° and Pz...Cl...Pz = 75.7 (2)° [Pz is the centroid of the pyrazole ring; symmetry codes: (vi) $z, -x + \frac{1}{2}, y - \frac{1}{2}$; (vii) $y, -z + \frac{1}{2}, x - \frac{1}{2}$]. The corresponding values for (II) are 3.5148 (12) Å, 94.06 (8)°, 3.5443 (12) Å, 170.79 (9)°, 163.0 (2)° and 76.8 (2)°. Each chloroform molecule is therefore linked to three molecules of the metal complex, generating the three-dimensional network structure.

Interaction lengths and angles are in the mean range for this electrophile–nucleophile $\pi \cdots X \cdots \pi$ motif (Csöregi *et al.*, 1996), as well as for C—Cl... π database studies carried out on organic crystal structures (Prasanna & Guru Row, 2000) and in proteins (Saraogi *et al.*, 2003). The experimental data are typical of Cl... π -facial interactions (Galan-Mascaros *et al.*, 1996), which have been found in both chloride (Demeshko *et al.*, 2004) and C—Cl (Aravindan *et al.*, 2003) interactions with π -deficient heterocycles.

In summary, chloroform inclusion in Mg[HB(Pz)₃]₂ and Ca[HB(Pz)₃]₂ complexes not only leads to highly symmetric structures, in contrast to the unsolvated complexes, but also plays an important role in stabilizing the supramolecular architecture through Pz...Cl...Pz interactions.

Experimental

For the preparation of (I), an ethanol solution (15 ml) of K[HB(Pz)₃] (0.100 g, 0.396 mmol) was added to an ethanol solution (15 ml) of anhydrous MgCl₂ (0.019 g, 0.198 mmol). The resulting solution was stirred for 30 min. The solution was filtered and the filtrate evaporated to dryness under an N₂ atmosphere to give a white powder (0.091 g, 87% yield). Recrystallization from dry chloroform afforded colourless block-shaped crystals suitable for X-ray analysis. ¹H NMR (CDCl₃): δ 6.06 (*t*, 6H, ³*J* = 2.0 Hz, H-4), 7.15, 7.70 (*d, d*, 6H each, ³*J* = 1.8 Hz, H-3,5). Complex (II) was prepared and recrystallized in a similar manner to (I), using K[HB(Pz)₃] (0.100 g, 0.396 mmol) and anhydrous CaCl₂ (0.022 g, 0.198 mmol), to give a white powder (0.099 g, 92% yield). ¹H NMR (CDCl₃): δ 6.15 (*t*, 6H, ³*J* = 1.9 Hz, H-4), 7.51, 7.75 (*d, d*, 6H each, ³*J* = 1.8 and 2.2 Hz, H-3,5).

Compound (I)

Crystal data

[Mg(C ₉ H ₁₀ BN ₆) ₂] ₂ ·2CHCl ₃	Cell parameters from 600 reflections
<i>M_r</i> = 689.13	θ = 20–25°
Cubic, <i>Pa</i> $\bar{3}$	μ = 0.64 mm ^{−1}
<i>a</i> = 14.3475 (12) Å	<i>T</i> = 100 (2) K
<i>V</i> = 2953.4 (4) Å ³	Block, colourless
<i>Z</i> = 4	0.20 × 0.12 × 0.09 mm
<i>D_x</i> = 1.550 Mg m ^{−3}	
Mo <i>K</i> α radiation	

Data collection

Bruker SMART CCD area-detector diffractometer	944 reflections with <i>I</i> > 2σ(<i>I</i>)
φ and ω scans	<i>R</i> _{int} = 0.055
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	θ _{max} = 26.0°
<i>T</i> _{min} = 0.883, <i>T</i> _{max} = 0.945	<i>h</i> = −17 → 14
15868 measured reflections	<i>k</i> = −17 → 17
969 independent reflections	<i>l</i> = −11 → 17

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.0339P)^2 + 10.6109P]$
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.060	where <i>P</i> = (<i>F</i> _o ² + 2 <i>F</i> _c ²)/3
<i>wR</i> (<i>F</i> ²) = 0.124	(Δ/σ) _{max} < 0.001
<i>S</i> = 1.22	Δρ _{max} = 0.39 e Å ^{−3}
969 reflections	Δρ _{min} = −0.36 e Å ^{−3}
63 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters (Å, °) for (I).

Mg—N1	2.173 (3)		
N1—Mg—N1 ⁱ	84.94 (10)	Mg—N1—C5	135.4 (2)
Mg—N1—N2	118.15 (19)		

Symmetry code: (i) *z, x, y*.

Compound (II)

Crystal data

[Ca(C ₉ H ₁₀ BN ₆) ₂] ₂ ·2CHCl ₃	Cell parameters from 600 reflections
<i>M_r</i> = 704.90	θ = 20–25°
Cubic, <i>Pa</i> $\bar{3}$	μ = 0.74 mm ^{−1}
<i>a</i> = 14.6697 (9) Å	<i>T</i> = 100 (2) K
<i>V</i> = 3156.9 (3) Å ³	Block, colourless
<i>Z</i> = 4	0.3 × 0.2 × 0.2 mm
<i>D_x</i> = 1.483 Mg m ^{−3}	
Mo <i>K</i> α radiation	

Data collection

Bruker SMART CCD area-detector diffractometer	1272 reflections with <i>I</i> > 2σ(<i>I</i>)
φ and ω scans	<i>R</i> _{int} = 0.033
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	θ _{max} = 28.3°
<i>T</i> _{min} = 0.808, <i>T</i> _{max} = 0.866	<i>h</i> = −18 → 18
17681 measured reflections	<i>k</i> = −18 → 12
1293 independent reflections	<i>l</i> = −19 → 18

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.0316P)^2 + 4.1829P]$
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.051	where <i>P</i> = (<i>F</i> _o ² + 2 <i>F</i> _c ²)/3
<i>wR</i> (<i>F</i> ²) = 0.109	(Δ/σ) _{max} < 0.001
<i>S</i> = 1.31	Δρ _{max} = 0.44 e Å ^{−3}
1293 reflections	Δρ _{min} = −0.40 e Å ^{−3}
63 parameters	
H-atom parameters constrained	

Table 2

Selected geometric parameters (Å, °) for (II).

Ca—N1	2.4241 (18)		
N1—Ca—N1 ⁱ	79.45 (6)	Ca—N1—C5	135.03 (15)
Ca—N1—N2	118.72 (12)		

Symmetry code: (i) *z, x, y*.

All H atoms were refined as riding on their parent atoms, with B—H distances of 0.98 Å, C—H distances of 0.93 and 0.98 Å, and *U*_{iso}(H) values of 1.5*U*_{eq}(B) and 1.2*U*_{eq}(C).

For both compounds, data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997);

program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *MERCURY* (Version 1.4; Bruno *et al.*, 2002); software used to prepare material for publication: *SHELXL97* and *WinGX-2003* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1623). Services for accessing these data are described at the back of the journal.

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