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Caveats for poly(methimazolyl)borate chemistry: the novel inorganic heterocycles $[H_2C(mt)_2BR_2]Cl$ (mt = methimazolyl; BR_2 = BH_2, BH(mt), 9–BBN)

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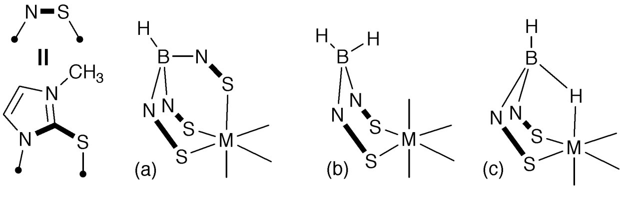
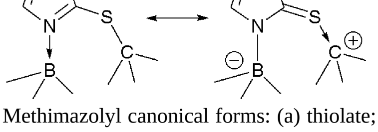
Whilst frequently used for reactions of poly(methimazolyl)borates, dichloromethane is not an innocent solvent, but rather slowly forms heterocyclic salts $[H_2C(mt)_2BR_2]Cl$, three examples of which (BR_2 = BH_2, BH(mt), 9-borabicyclononyl) have been structurally characterised to confirm the unprecedented $B(NCS)_2C$ connectivity.

Trofimenko's poly(pyrazolyl)borates have long captured the imagination of coordination chemists.[1] Their utility arises from their innocence, acting as spectator ligands with enormously variable steric and electronic properties. It is therefore hardly surprising that following Reglinski and Parkin's respective reports of the $HB(mt)_3$ (mt = methimazolyl, Scheme 1)[2] and $H_2B(mt)_2$ ligands[3] these have been quickly embraced.[4–8] These ligands present an anionic set of two or three 'soft' sulfur donors which appear to be particularly electron releasing. Thus it would appear that they have a promising future, guided but not constrained by the perceived analogy with poly(pyrazolyl)borates. Noting the growing interest in these ligands, we wish to report a simple but significant observation—dichloromethane is an inappropriate solvent for the use of $Na[H_xB(mt)_{4-x}]$ salts in slow reactions, and for the new variant $Na[(mt)_2BBN]$ (BBN = 9-borabicyclononyl).

Thiols react with dichloromethane under basic conditions to provide dithioacetals.[9] We find that a similar albeit slow reaction ensues between $Na[H_2B(mt)_2]$ and dichloromethane to provide the sparingly soluble monohydrated salt $[H_2C(mt)_2BH_2]Cl{\cdot}H_2O$ ([**1**]$Cl{\cdot}H_2O$, Scheme 2). We had initially encountered this salt from a variety of intended reactions between $Na[H_2B(mt)_2]$ and metal halide complexes, however the reaction also proceeds in the absence of metal salts. The poor solubility of this salt precluded the acquisition of useful characteristic spectroscopic data, however the compound was unambiguously identified crystallographically (Fig. 1).† The cation $\mathbf{1}^+$ of the salt comprises a novel eight-membered heterocycle the $B(NCS)_2C$ connectivity of which has not previously been reported.‡ The ring adopts a chair conformation preventing any direct interaction between the hydridic $B–H^{\delta-}$ and presumably acidic $C–H^{\delta+}$ groups. The CH_2 group does however approach the lattice water molecule [O···H: 2.31(3) Å, O···H–C1: 134(2)°], which is itself hydrogen bonded to the chloride counter anion [Cl···H: 2.22(3) Å, Cl···H–O 163(2)°].



Scheme 1 Coordination modes for $H_xB(mt)_{4-x}$ ligands: (a) κ^3-*S*,*S*′,*S*″; (b) κ^2-*S*,*S*′; (c) κ^3-*H*,*S*,*S*′.



Scheme 2 Methimazolyl canonical forms: (a) thiolate; (b) thione.

A similar product may be isolated from reactions of $Na[HB(mt)_3]$ in dichloromethane to provide the essentially insoluble salt $[H_2C(mt)_2BH(mt)]Cl{\cdot}H_2O$ [**2**]$Cl{\cdot}H_2O$ (Fig. 2).† Once again, an eight-membered heterocycle is formed which in this case bears a pendant mt heterocycle. As for [**1**]$Cl{\cdot}H_2O$, the methylene group participates in hydrogen bonding, however in this case it is to the chloride [H···Cl: 2.52 Å] which is also hydrogen bonded to two lattice water molecules [Cl···H: 2.381, 2.351 Å] and weakly to three mt C–H groups [H···Cl: 2.61, 2.72, 2.80 Å] forming a network of hydrogen bonding. Such interactions may well account for the low solubilities of both [**1**]$Cl{\cdot}H_2O$ and [**2**]$Cl{\cdot}H_2O$. The ring

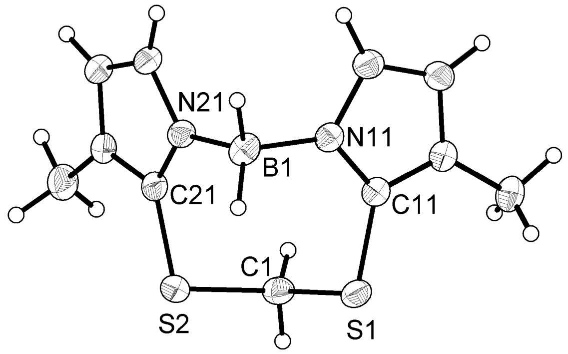


Fig. 1 Structure of the cation $[H_2C(mt)_2BH_2]^+$ in a crystal of [**1**]$Cl{\cdot}H_2O$ (40% probability ellipsoids). Selected bond lengths (Å) and angles (°): S1–C1 1.816(2), S1–C11 1.737(2), S2–C1 1.819(2), S2–C21 1.739(2), N11–C11 1.342(2), N11–B1 1.562(3), N12–C11 1.346(3), N21–C21 1.345(3), C1–S1–C11 101.06(9), C1–S2–C21 102.74(10), C11–N11–B1 128.10(17), C21–N21–B1 127.17(17), S2–C1–S1 117.42(12), S1–C11–N11 127.30(15), S2–C21–N21 127.46(15), N21–B1–N11 107.56(15).

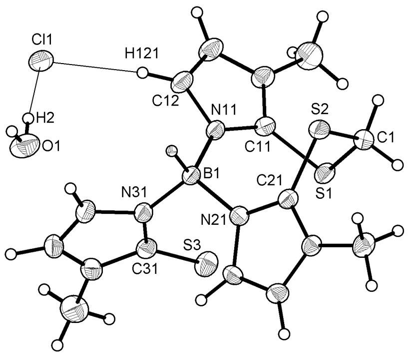


Fig. 2 Structure of $[H_2C(mt)_2BH_2]Cl{\cdot}H_2O$, [**2**]$Cl{\cdot}H_2O$, in the crystal (40% probability ellipsoids). Selected bond lengths (Å) and angles (°): S1–C1 1.813(2), S1–C11 1.740(2), S2–C1 1.826(2), S2–C21 1.746(2), S3–C31 1.697(2), N11–C11 1.341(2), N11–B1 1.570(3), N12–C11 1.349(2), N21–C21 1.346(3), N21–B1 1.569(3), N31–B1 1.538(3), C1–S1–C11 99.0(1), C1–S2–C21 98.1(1), C11–N11–C12 107.57(16), C11–N11–B1 133.86(16), C21–N21–B1 127.17(16), S1–C1–S2 114.05(11), S1–C11-N11 127.02(14), S2–C21–N21 125.74(14), N11–B1–N21 113.79(15), N11–B1–N31 109.69(16), N21–B1–N31 110.06(15).

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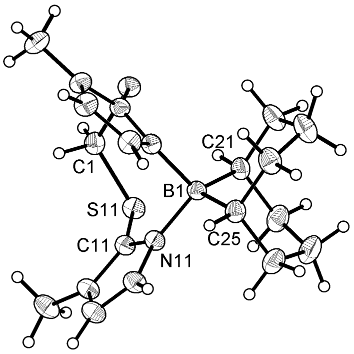

Fig. 3 Structure of the cation $[H_2C(mt)_2BBN]$ in a crystal of [**3**]Cl·THF (40% probability ellipsoids). Selected bond lengths (Å) and angles (°): S11–C11 1.739(2), S11–C1 1.814(2), N11–C11 1.349(3), N11–C14 1.379(3), N11–B1 1.616(3), C11–S11–C1 103.11(13), C11–N11–B1 129.2(2), S11–C1–S11* 118.21(19), C21–B1–C25 106.0(3), C21–B1–N11 114.9 (2), C25–B1–N11 110.46(18), N11–B1–N11* 100.0(2).

conformation in $\mathbf{2}^+$ is twisted (chiral) in contrast to that in $\mathbf{1}^+$ which has an approximate (though not crystallographic) plane of symmetry dissecting the molecule and including the B1···C1 vector. Bond lengths within the $\mathbf{2}^+$ heterocycle are statistically equivalent to those for $\mathbf{1}^+$ however for $\mathbf{2}^+$ the presence of a pendant mt group allows for internal comparison. Thus the thione C31=S3 bond length of 1.697(2) Å is noticeably (20σ) shorter than those within the heterocycle (1.740(2), 1.746(2) Å) whilst the BN–C bond lengths are marginally contracted (6σ) within the heterocycle (1.341(2), 1.346(3) Å) relative to the free mt group (1.364(3) Å). Lastly, the B–N bond lengths within the heterocycle are lengthened relative to the unique B1–N13 bond (10σ). These geometric features taken together suggest that both the canonical forms shown (Scheme 2) contribute to the bonding description.

Trofimenko has described the synthesis of $Na[(pz')_2BBN]$ (pz′ = 3,5-dimethylpyrazole, BBN = 9-borabicyclononyl) from $(9\text{-}HBBN)_2$, Na[pz′] and Hpz′.[10] We find that the salt $Na[(mt)_2BBN]$ is accessible *via* a similar strategy. Our interest in the $(mt)_2BBN$ ligand arises from the prevalence of agostic B–H–metal interactions in $H_2B(mt)_2$ complexes which we wish to circumvent. However, relevant to the current discussion we find that this salt also reacts with CH_2Cl_2 to provide a salt of the novel spirotricyclic cation $[H_2C(mt)_2BBN]^+$ ($\mathbf{3}^+$), structurally characterised as a THF solvate [**3**]Cl·THF (Fig. 3).† The heterocycle in $\mathbf{3}^+$ straddles a crystallographic plane of symmetry that includes the boron (B1), and methylene carbon (C1) atoms as well as the BBN bridgehead carbons (C21, C25). The heterocycle adopts a chair-like conformation akin to that found in $\mathbf{1}^+$, however since the crystal is anhydrous, significant hydrogen bonding is limited to an interaction between the chloride counter-anion and the methylene group [C–H···Cl 2.44(4) Å, C–H–Cl 177.9(2)°].

Notes and references

† *Crystal data for* [**1**]Cl·H_2O: $C_9H_{16}BClN_4OS_2$, M_r = 306.65, orthorhombic, $P2_12_12_1$, a = 9.3392(2), b = 11.9326(2), c = 12.7412(3) Å, V = 1419.89(5) Å^3, Z = 4, d_x = 1.434 Mg m^{-3}, μ(Mo–Kα) = 0.556 mm^{-1}, T = 200 K, 3248 independent reflections. F refinement, R = 0.026, wR = 0.027 for 2582 reflections [$I > 3\sigma(I)$; $2\theta_{max}$ = 55°], 212 parameters, CCDC 237690. *Crystal data for* [**2**]Cl·H_2O: $C_{13}H_{20}BClN_6OS_3$, M_r = 418.80, monoclinic, $C2/c$, a = 22.5917(3), b = 8.0650(1), c = 22.6170(4) Å, β = 110.7819(6)°, V = 3852.75(10) Å^3, Z = 8, d_x = 1.444 Mg m^{-3}, μ(Mo–Kα) = 0.538 mm^{-1}, T = 200 K, 4438 independent reflections. F refinement, R = 0.025, wR = 0.027 for 2500 reflections [$I > 3\sigma(I)$; $2\theta_{max}$ = 55°], 237 parameters, CCDC 237691. *Crystal data for* [**3**]Cl·H_2O: $C_{21}H_{34}BClN_4OS_2$, M_r = 468.90, monoclinic, $P2_1/m$, 0.46 × 0.23 × 0.08 mm, a = 6.9060(14), b = 10.705(2), c = 16.144(3) Å, β = 92.29(3)°, V = 1192.5(4) Å^3, Z = 2, d_x = 1.306 Mg m^{-3}, μ(Mo–Kα) = 0.356 mm^{-1}, T = 200 K, 2761 independent reflections. F^2 refinement, R = 0.054, wR(all) = 0.144 for 2761 reflections [$I > 2\sigma(I)$; $2\theta_{max}$ = 54°], 152 parameters, CCDC 237867. See http://www.rsc.org/suppdata/cc/b4/b407733d/ for crystallographic data in .cif or other electronic format.

‡ The $B(NCS)_2C$ connectivity currently appears in neither the CCDC nor SciFinder databases.

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