

3{5}-*tert*-Butylpyrazole is a ditopic receptor for zinc(II) halides†

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The complexes $[\text{ZnX}(\text{Hpz}^{\text{tBu}})_3]\text{X}$ ($\text{X}^- = \text{Cl}^-, \text{Br}^-, \text{I}^-$) contain a non-coordinated X^- anion hydrogen-bonded within a pocket formed by the Hpz^{tBu} *tert*-butyl groups.

There is increasing interest in the development of ditopic ligands that can bind both a metal cation and its charge-balancing anion(s); that is, ligands for metal salts.^{1,2} Such compounds have great potential utility in hydrometallurgical and waste management applications, by allowing the extraction of charged species from crude metal leaches or process streams. While several such receptors have been designed for alkali metal salts,¹ there are still few transition metal ligands that have been adapted to this end.^{3–7} We report here that a simple monodentate pyrazole acts as a ditopic receptor for Zn(II) halide salts in the solid state and in non-polar solvents.

Reaction of ZnX_2 ($\text{X}^- = \text{Cl}^-, \text{Br}^-, \text{I}^-$) with 3 molar equivalents of 3{5}-*tert*-butylpyrazole (Hpz^{tBu})⁸ in MeOH at 290 K rapidly affords colourless solutions, which were evaporated to dryness. Extraction of the solid residues with CH_2Cl_2 , and layering the extracts with pentane at 240 K, affords colourless crystals of $[\text{ZnCl}(\text{Hpz}^{\text{tBu}})_3]\text{Cl} \cdot \frac{1}{2}\text{C}_5\text{H}_{12}$ (**1**), $[\text{ZnBr}(\text{Hpz}^{\text{tBu}})_3]\text{Br} \cdot \frac{1}{2}\text{C}_5\text{H}_{12}$ (**2**) and $[\text{ZnI}(\text{Hpz}^{\text{tBu}})_3]\text{I} \cdot \text{CH}_2\text{Cl}_2$ (**3**), in yields of 62–81%. All the compounds rapidly lose their occluded solvent upon drying.‡ Unusually for salts of halide anions, **1–3** are very soluble in CHCl_3 , CH_2Cl_2 , benzene, toluene, MeCN, MeNO₂, acetone, MeOH, and even sparingly soluble in pentane at room temperature. In the following discussions, 'X' is used to refer collectively to the Cl, Br or I atoms in **1–3**.

The single crystal structures of **1–3** show distorted tetrahedral $[\text{ZnX}(\text{Hpz}^{\text{tBu}})_3]^+$ centres, with the pyrazole ligands coordinated as the 5-substituted tautomer (Fig. 1, Table 1).§ The anion

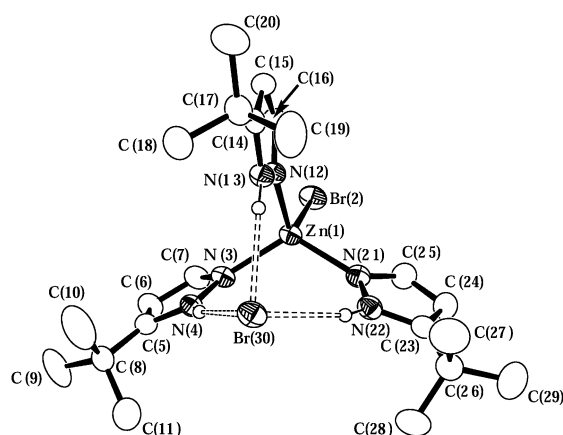


Fig. 1 View of the $[\text{ZnBr}(\text{Hpz}^{\text{tBu}})_3]\text{Br}$ moiety in the crystal of $2 \cdot \frac{1}{2}\text{C}_5\text{H}_{12}$. Thermal ellipsoids are at the 50% probability level. For clarity, all C-bound H atoms have been omitted. The crystal structures of **1** and **3** are visually very similar to that of **2**, apart from differences in the orientations of the *tert*-butyl groups, and use the same atom numbering scheme with Br(2) and Br(30) replaced by Cl or I as appropriate.

† Electronic supplementary information (ESI) available: tabulated and plotted NMR data for **1–3** in the presence and absence of added NBu_4X ($\text{X}^- = \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{BF}_4^-$). See <http://www.rsc.org/suppdata/cc/b2/b200551b/>

$\text{X}(30)$ is hydrogen-bonded to all three Hpz^{tBu} N–H groups, and lies within a bowl-shaped pocket formed by the pyrazole *tert*-butyl substituents. Apart from the $\text{Zn}(1)\text{–X}(2)$ bond lengths, there are two notable differences between the metric parameters at Zn in **1–3**. First, the $\text{Zn}(1)\text{–N}$ bond lengths in **3** are slightly longer than for **1** and **2**, which may reflect the greater size of the $\text{I}(30)$ guest ion. Second, the near- C_3 symmetry at $\text{Zn}(1)$ in **1** and **2** is broken by the angle $\text{N}(3)\text{–Zn}(1)\text{–N}(21)$, which is greater than the other two $\text{N}\text{–Zn}(1)\text{–N}$ angles by an average of $9.08(13)^\circ$ for **1**, and $8.28(14)^\circ$ for **2**. The $\text{N}\text{–Zn}(1)\text{–N}$ angles in **3** are more regular. The $\text{Zn}(1)\cdots\text{X}(30)$ distances are $3.8118(6)$ (**1**), $4.0402(3)$ (**2**) and $4.3364(4)$ Å (**3**). These structures contrast with the literature complex $[\text{Zn}(\text{OCIO}_3)_3\text{L}_3]\text{ClO}_4$ ($\text{L} = 3\text{-tert-butyl-2,4,5,6-tetrahydrocyclopentapyrazole}$), whose pyrazole ligands do not form a C_3 -symmetric cavity and take part in intermolecular hydrogen bonds to both coordinated and non-coordinated perchlorate anions.⁹

The ^{13}C NMR spectra of **1–3** in C_6D_6 , CDCl_3 and CD_2Cl_2 are sharp, and show the number of peaks expected for one Hpz^{tBu} environment (see ESI†). However, in $\{\text{CD}_3\}_2\text{CO}$ the spectra show broadened and/or unobservable resonances for the pyrazole C^3 and C^5 atoms. The latter behaviour is shown by free Hpz^{tBu} in all four solvents, and indicates fluxional tautomerism of the pyrazole ring in solution.¹⁰ This suggests that **1–3** have static structures on the NMR timescale in C_6D_6 , CDCl_3 and CD_2Cl_2 , but that in $\{\text{CD}_3\}_2\text{CO}$ the Hpz^{tBu} ligands are in rapid chemical exchange. The chemical shift of the N–H ^1H NMR resonance (δ_{NH}) for the complexes in a given solvent follows the sequence **1** > **2** >> **3**. This is consistent with the anions' relative polarising powers of $\text{Cl}^- > \text{Br}^- > \text{I}^-$, and implies that N–H $\cdots\text{X}$ hydrogen bonding is an important feature of the solution structures of these compounds. The solvent dependence of δ_{NH} for **1–3** is $\text{C}_6\text{D}_6 > \text{CDCl}_3 > \text{CD}_2\text{Cl}_2 \geq \{\text{CD}_3\}_2\text{CO}$, suggesting that the degree of N–H $\cdots\text{X}$ association may decrease along this series of solvents. Consistent with this, the above ordering is exactly the reverse of the relative polarities of these solvents,¹¹ since more polar solvents should favour dissociation or exchange of the halide guests. The magnitude of this solvent dependence follows the trend **3** > **2** \approx **1**, showing that anion dissociation in solution is more important for **3** than for **1** and **2**.

Addition of ca. 1.5 mol equivalents of the relevant NBu_4X ($\text{X}^- = \text{Cl}^-, \text{Br}^-, \text{I}^-$) salt to **1–3** in all four solvents greatly

Table 1 Selected bond lengths (Å) and angles ($^\circ$) for **1–3**

	1 (X = Cl)	2 (X = Br)	3 (X = I)
Zn(1)–X(2)	2.2208(6)	2.3557(3)	2.5674(4)
Zn(1)–N(3)	2.0036(18)	2.0034(19)	2.020(3)
Zn(1)–N(12)	2.0022(18)	2.0013(18)	2.030(2)
Zn(1)–N(21)	2.0005(19)	2.0087(19)	2.012(3)
X(2)–Zn(1)–N(3)	106.17(6)	106.32(5)	107.35(7)
X(2)–Zn(1)–N(12)	109.13(5)	108.52(5)	106.23(7)
X(2)–Zn(1)–N(21)	104.32(6)	104.79(5)	106.34(7)
N(3)–Zn(1)–N(12)	108.00(7)	108.66(9)	110.45(10)
N(3)–Zn(1)–N(21)	118.32(8)	117.77(8)	112.74(11)
N(12)–Zn(1)–N(21)	110.48(8)	110.32(8)	113.26(11)

broadens the pyrazole C³ and C⁵ resonances. This shows that the excess halide promotes Hpz^{tBu} exchange, presumably by acting as a nucleophile to Zn. Unfortunately, this makes it impossible to accurately determine association constants of halide ions for the [ZnX(Hpz^{tBu})₃]⁺ centre by NMR titrations. In contrast, addition of a similar amount of NBuⁿ₄BF₄ to **1–3** has little effect on the linewidths of their ¹³C spectra. This is consistent with the above interpretation, since BF₄[–] should be too poor a nucleophile to coordinate to the Zn centres. In the presence of NBuⁿ₄BF₄, δ_{NH} is lowered by 0.2–0.7 ppm for **1** and **2** and by 1.2–1.5 ppm for **3**, depending on solvent (see ESI[†]), implying that BF₄[–] competes with halides for the complex anion-binding site. This unusual behaviour may reflect complementarity between the C₃-symmetric host and BF₄[–] guest, which will also show threefold symmetry if bound with one B–F bond parallel to the C₃-axis of the [ZnX(Hpz^{tBu})₃]⁺ host.

These NMR results show that a single species is present in C₆D₆, CDCl₃ and CD₂Cl₂ solutions of **1–3**, which must therefore have a 1:3 Zn:Hpz^{tBu} stoichiometry; and, that N–H...X hydrogen bonding is important to their structures in these solvents. This leaves two likely solution structures for these compounds: [ZnX(Hpz^{tBu})₃]X, as observed in the crystal (Fig. 1); or, a dimeric structure [(Zn(μ-X)(Hpz^{tBu})₃)₂]X₂. The latter has been observed previously for some [(M(μ-F)(L')₃)₂][BF₄]₂ (M = Co, Cu; L' = a C-substituted pyrazole) derivatives, although these crystal structures do not show a well-defined binding site for exogenous anions.¹² A third possibility, of a neutral species [ZnX₂(Hpz^{tBu})₃] with intramolecular N–H...X interactions, can be ruled out since BF₄[–] competes for the pyrazole hydrogen bond donors without attacking the Zn ion. Hence, whether mononuclear or dinuclear in solution, it is clear that the basic motif of a [(ZnX(Hpz^{tBu})₃)_n]ⁿ⁺ (n = 1 or 2) receptor accommodating nX[–] guest anions is retained in non-polar solvents. This being the case, the static structures of **1–3** in these solvents are interesting, since Zn(II) complexes of monodentate ligands are often very labile. Either the N–H...X hydrogen bonding templates the structure of the cations' anion-binding cavity; and/or, the stronger host–guest binding in non-polar solvents means that there is insufficient free X[–] nucleophile to promote fluxionality at the Zn centres. To quantify these effects, we are presently studying in more detail the affinity of [ZnX(Hpz^{tBu})₃]⁺ for BF₄[–] and other weakly nucleophilic anions in solution and the solid state.

While we have not measured the ability of Hpz^{tBu} to extract Zn(II) halides in two-phase media, it is unlikely to be a selective extractant because of its ability to form highly soluble, tetragonal [MX₂(Hpz^{tBu})_m] (m = 2 or 4) complexes with Cu(II)¹³ and, potentially, other transition ions. Nonetheless, this work demonstrates that suitably substituted pyrazole rings can be used as a framework for the simultaneous binding of anions and transition metal cations, in solution as well as the solid state. N-Unsubstituted pyrazole groups might thus form useful components of anion or metal salt transport systems, and/or of anion sensors bearing transition metal reporter groups. We are also actively pursuing these possibilities.

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Notes and references

‡ Analytical data: for **1**: found C, 49.8; H, 7.0; N, 16.5. calc. for C₂₁H₃₆Cl₂N₆Zn: C, 49.6; H, 7.1; N, 16.5%. For **2**: found C, 42.2; H, 6.0; N, 14.3. calc. for C₂₁H₃₆Br₂N₆Zn: C, 42.2; H, 6.1; N, 14.1%. For **3**: found C, 36.5; H, 5.3; N, 12.1. calc. for C₂₁H₃₆I₂N₆Zn: C, 36.5; H, 5.2; N, 12.1%.

§ Crystal data for **1**: ½C₅H₁₂:C_{23.5}H₄₂Cl₂N₆Zn, M_r = 544.90, monoclinic, P2₁/c, a = 17.1001(3), b = 10.7850(2), c = 17.9314(3) Å, β = 115.1510(7)°, V = 2993.46(9) Å³, Z = 4, T = 150(2) K, μ(Mo-Kα) = 1.020 mm^{–1}; 54618 measured reflections, 6848 independent, R_{int} = 0.048; R(F) = 0.040, wR(F²) = 0.110.

Crystal data for **2**: ½C₅H₁₂:C_{23.5}H₄₂Br₂N₆Zn, M_r = 633.82, monoclinic, P2₁/c, a = 17.3533(2), b = 10.5568(2), c = 18.4428(2) Å, β = 114.9379(9)°, V = 3060.45(8) Å³, Z = 4, T = 150(2) K, μ(Mo-Kα) = 3.434 mm^{–1}; 38904 measured reflections, 7008 independent, R_{int} = 0.052; R(F) = 0.031, wR(F²) = 0.080.

Crystal data for **3**: CH₂Cl₂:C₂₂H₃₈Cl₂I₂N₆Zn, M_r = 776.65, orthorhombic, Pbc_a, a = 10.4896(1), b = 19.2431(2), c = 30.6652(4) Å, V = 6187.83(12) Å³, Z = 8, T = 150(2) K, μ(Mo-Kα) = 2.983 mm^{–1}; 24559 measured reflections, 6911 independent, R_{int} = 0.068; R(F) = 0.036, wR(F²) = 0.098.

For **1** and **2**, the pentane solvent molecule is disordered over two equally occupied orientations, about a crystallographic inversion centre. For **1** only, the *tert*-butyl group C(8)–C(11) was also disordered over two equally occupied orientations. The disordered C–C bonds in **1** and **2** were restrained to 1.53(2) Å, and disordered 1,3-C...C distances to 2.50(2) Å. All crystallographically ordered non-H atoms were refined anisotropically. For **3**, the CH₂Cl₂ molecule is disordered over three equally occupied orientations, which were modeled using the restraints C–Cl = 1.76(2) Å, and non-bonded Cl...Cl = 2.87(2) Å. All non-H atoms except the disordered solvent C atoms were refined anisotropically.

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See <http://www.rsc.org/suppdata/cc/b2/b200551b/> for crystallographic data in CIF or other electronic format.

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