Supplementary Material (ESI) for New Journal of Chemistry

The Effect of Different Ligand Substituents on the Chemistry of a Zinc/Pyrazole Anion Host

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Electronic Supplementary Information

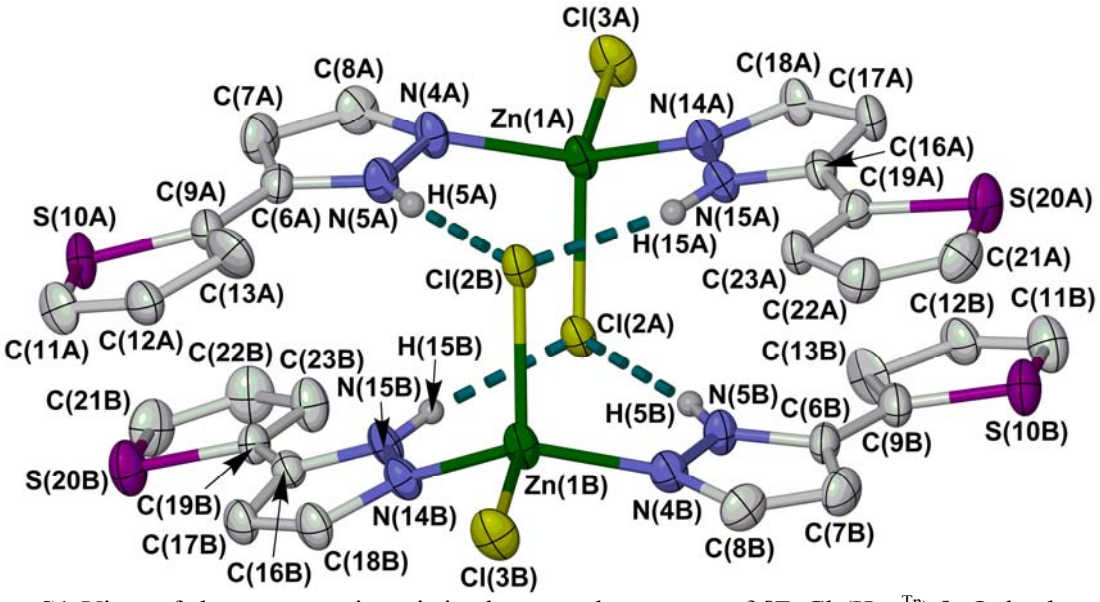

Figure S1 View of the asymmetric unit in the crystal structure of $[ZnCl_2(Hpz^{Tn})_2]$. Only the major orientations of the disordered thienyl groups C(9A)-C(13A) and C(9B)-C(13B) are shown. All H atoms not involved in hydrogen bonding have been omitted for clarity, and displacement ellipsoids are at the 50% probability level. Colour code: C, white; H, grey; Cl, yellow; N, blue; S, purple; Zn, green.

Table S1 Selected bond lengths and angles in the crystal structure of $[ZnCl_2(Hpz^{Tn})_2]$ (Å, °).

Zn(1A)–Cl(2A)	2.3506(11)	Zn(1B)–Cl(2B)	2.3469(11)
Zn(1A)–Cl(3A)	2.2322(11)	Zn(1B)–Cl(3B)	2.2279(12)
Zn(1A)–N(4A)	2.029(3)	Zn(1B)–N(4B)	2.021(4)
Zn(1A)–N(14A)	2.038(3)	Zn(1B)–N(14B)	2.026(3)
Cl(2A)–Zn(1A)–Cl(3A)	117.68(4)	Cl(2B)–Zn(1B)–Cl(3B)	114.26(4)
Cl(2A)–Zn(1A)–N(4A)	99.49(10)	Cl(2B)–Zn(1B)–N(4B)	102.10(10)
Cl(2A)–Zn(1A)–N(14A)	101.19(10)	Cl(2B)–Zn(1B)–N(14B)	105.60(10)
Cl(3A)–Zn(1A)–N(4A)	107.33(10)	Cl(3B)–Zn(1B)–N(4B)	107.41(10)
Cl(3A)–Zn(1A)–N(14A)	105.68(10)	Cl(3B)–Zn(1B)–N(14B)	107.03(10)
N(4A)–Zn(1A)–N(14A)	126.25(13)	N(4B)–Zn(1B)–N(14B)	120.73(14)

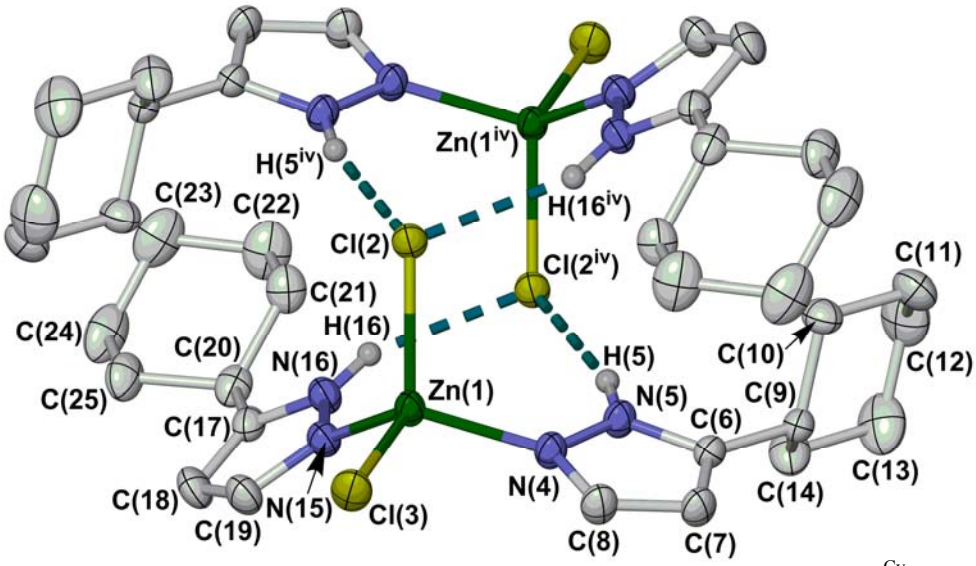

Figure S2 View of the hydrogen-bonded dimer in the crystal structure of $[ZnCl_2(Hpz^{Cy})_2]$. All H atoms not involved in hydrogen bonding have been omitted for clarity, and displacement ellipsoids are at the 50% probability level. Symmetry code: (iv) *–x*, 1*–y*, 1*–z*. Colour code: C, white; H, grey; Cl, yellow; N, blue; Zn, green.

Table S2 Selected bond lengths and angles in the crystal structure of $[ZnCl_2(Hpz^{Cy})_2]$ (Å, °).

Zn(1)–Cl(2)	2.3101(4)
Zn(1)–Cl(3)	2.2469(4)
Zn(1)–N(4)	2.0378(10)
Zn(1)–N(15)	2.0334(10)
Cl(2)–Zn(1)–Cl(3)	116.141(14)
Cl(2)–Zn(1)–N(4)	106.89(3)
Cl(2)–Zn(1)–N(15)	105.64(3)
Cl(3)–Zn(1)–N(4)	104.50(3)
Cl(3)–Zn(1)–N(15)	107.38(3)
N(4)–Zn(1)–N(15)	116.75(4)

Table S3 Metric parameters for hydrogen bonds in the $[ZnCl_2(Hpz^R)_2]$ structures (Å, °). Symmetry codes: (i) 1–*x*, 1–*y*, 1–*z*; (ii) –*x*, –½+*y*, $^3/_2$–*z*; (iii) 1–*x*, ½+*y*, $^3/_2$–*z*; (iv) –*x*, 1–*y*, 1–*z*; (v) –*x*–½, ½+*y*, $^3/_2$–*z*.

	D–H (D = N, C)	H…Cl	D…Cl	D–H…Cl
$[ZnCl_2(Hpz^{Ph})_2]\cdot CHCl_3$				
N(5)–H(5)…Cl(2^i)	0.88	2.42	3.2569(17)	160.2
N(16)–H(16)…Cl(2^i)	0.88	2.48	3.3292(17)	161.1
C(26)–H(26)…Cl(3)	1.00	2.55	3.534(3)	167.8
$[ZnCl_2(Hpz^{Tn})_2]$				
N(5A)–H(5A)…Cl(2B)	0.88	2.34	3.216(3)	170.4
N(15A)–H(15A)…Cl(2B)	0.88	2.37	3.230(4)	167.1
N(5B)–H(5B)…Cl(2A)	0.88	2.38	3.247(3)	169.1
N(15B)–H(15B)…Cl(2A)	0.88	2.37	3.240(3)	168.2
C(7A)–H(7A)…Cl(3B^{ii})	0.95	2.78	3.662(4)	155.1
C(7B)–H(7B)…Cl(3A^{iii})	0.95	2.75	3.684(4)	167.5
$[ZnCl_2(Hpz^{Cy})_2]$				
N(5)–H(5)…Cl(2^{iv})	0.88	2.32	3.1811(10)	164.5
N(16)–H(16)…Cl(2^{iv})	0.88	2.45	3.2755(11)	156.4
C(7)–H(7)…Cl(3^v)	0.95	2.80	3.6773(14)	154.4

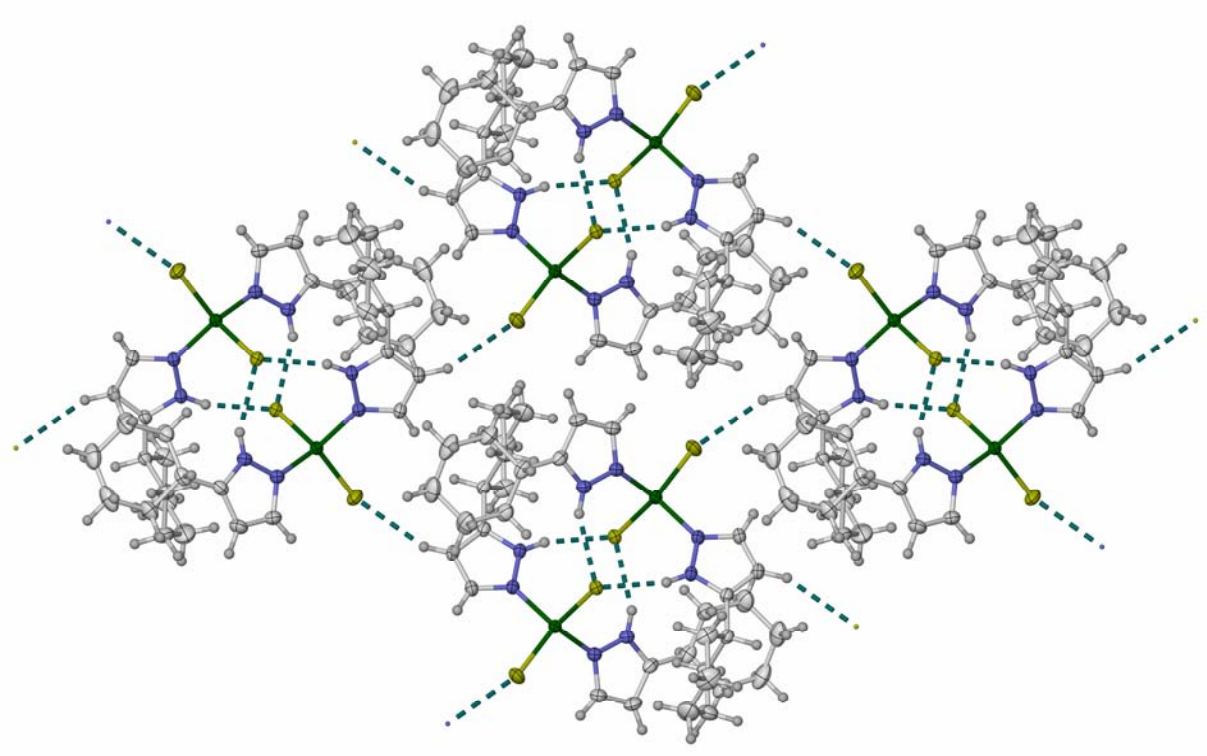

Figure S3 Partial packing diagram of $[ZnCl_2(Hpz^{Cy})_2]$, showing the association of the dimers in the crystal through the C(7)–H(7)…Cl(3^v) interaction (Table S3). The view is along the crystallographic (101) plane with *b* vertical, and displacement ellipsoids are at the 50% probability level. Colour code: C, white; H, grey; Cl, yellow; N, blue; Zn, green.

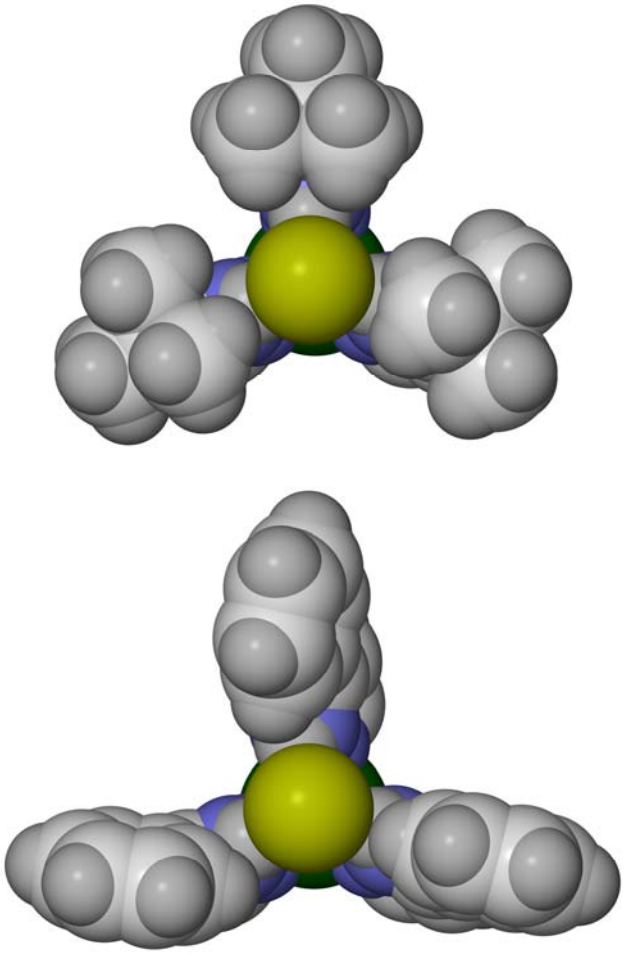

Figure S4 Comparative space-filling views of the guest-binding cavities in [ZnCl(Hpz$^{t\mathrm{Bu}}$)$_3$]Cl (top) and [ZnCl(Hpz$^{\mathrm{Ph}}$)$_3$]Cl (bottom). The view in both cases is parallel to the Zn–Cl bond. Colour code: C, white; H, grey; Cl, yellow; N, blue; Zn, green.

Data for [ZnCl(Hpz$^{t\mathrm{Bu}}$)$_3$]Cl are taken from ref. 15 of the main paper.

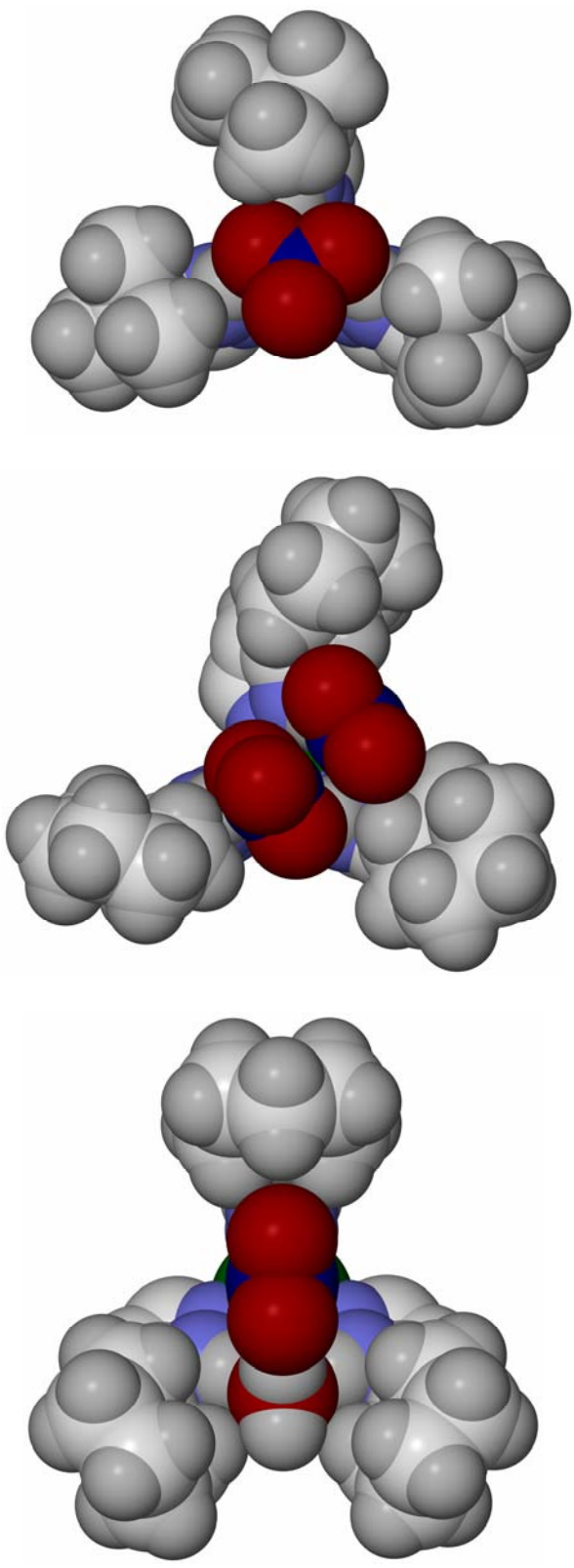

Figure S5 Comparative space-filling views of the guest-binding cavities in $[ZnCl(Hpz^{tBu})_3]NO_3$, containing one nitrate guest (top); half the dimeric capsule in $[ZnCl(Hpz^{Cy})_3]NO_3$, containing two nitrate ions (middle); and the monomeric unit in $[ZnBr(Hpz^{Cy})_3]NO_3{\cdot}H_2O$, containing a nitrate ion and water molecule (bottom). The views are parallel to the Zn–X ($X^- = Cl^-$ or Br^-) bond, and only one orientation of the disordered residues in the structures is shown. Colour code: C, white; H, grey; Cl or Br, yellow; N{pyrazole}, pale blue; N{nitrate}, dark blue; O, red; Zn, green.

Data for $[ZnCl(Hpz^{tBu})_3]NO_3$ are taken from ref. 15 of the main paper.

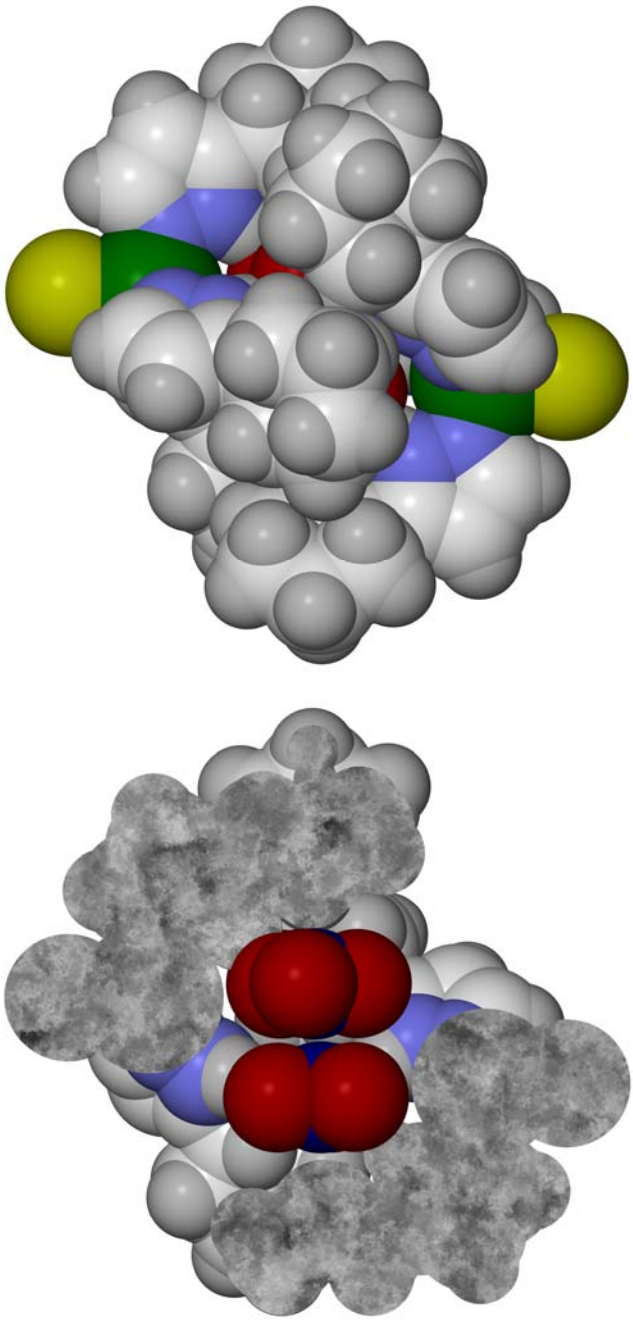

Figure S6 Space-filling (top) and cutaway (bottom) diagrams of the hydrogen-bonded dimer in $[ZnCl(Hpz^{Cy})_3]NO_3$, showing the pair of nitrate ions encapsulated by two $[ZnCl(Hpz^{Cy})_3]^+$ cations. Both views are the same as Fig. 3 of the main paper. Colour code: C, white; H, grey; Cl, yellow; N{pyrazole}, pale blue; N{nitrate}, dark blue; O, red; Zn, green.

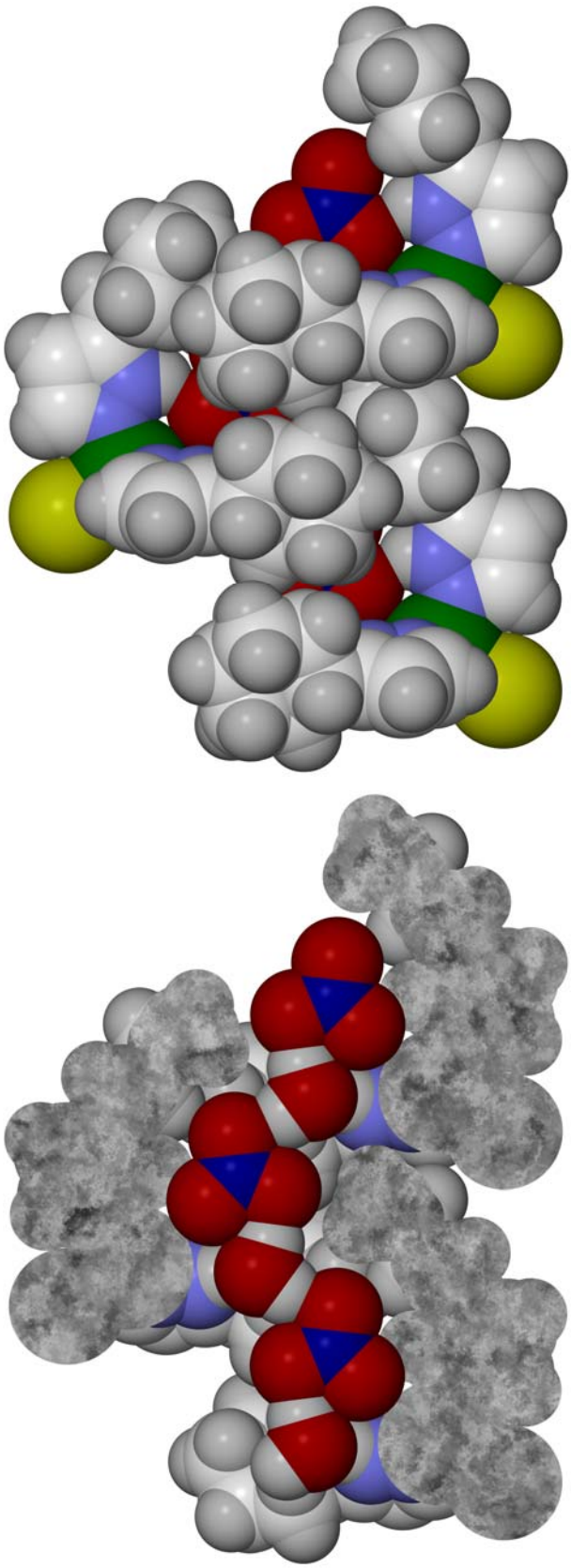

Figure S7 Partial space-filling (top) and cutaway (bottom) packing diagrams of $[ZnBr(Hpz^{Cy})_3]NO_3{\cdot}H_2O$, showing the $[NO_3{\cdot}H_2O]_n^{n-}$ chains sheathed by the $[ZnBr(Hpz^{Cy})_3]^+$ cations. Both views are the same as Fig. 5 of the main paper. Colour code: C, white; H, grey; Br, yellow; N{pyrazole}, pale blue; N{nitrate}, dark blue; O, red; Zn, green.

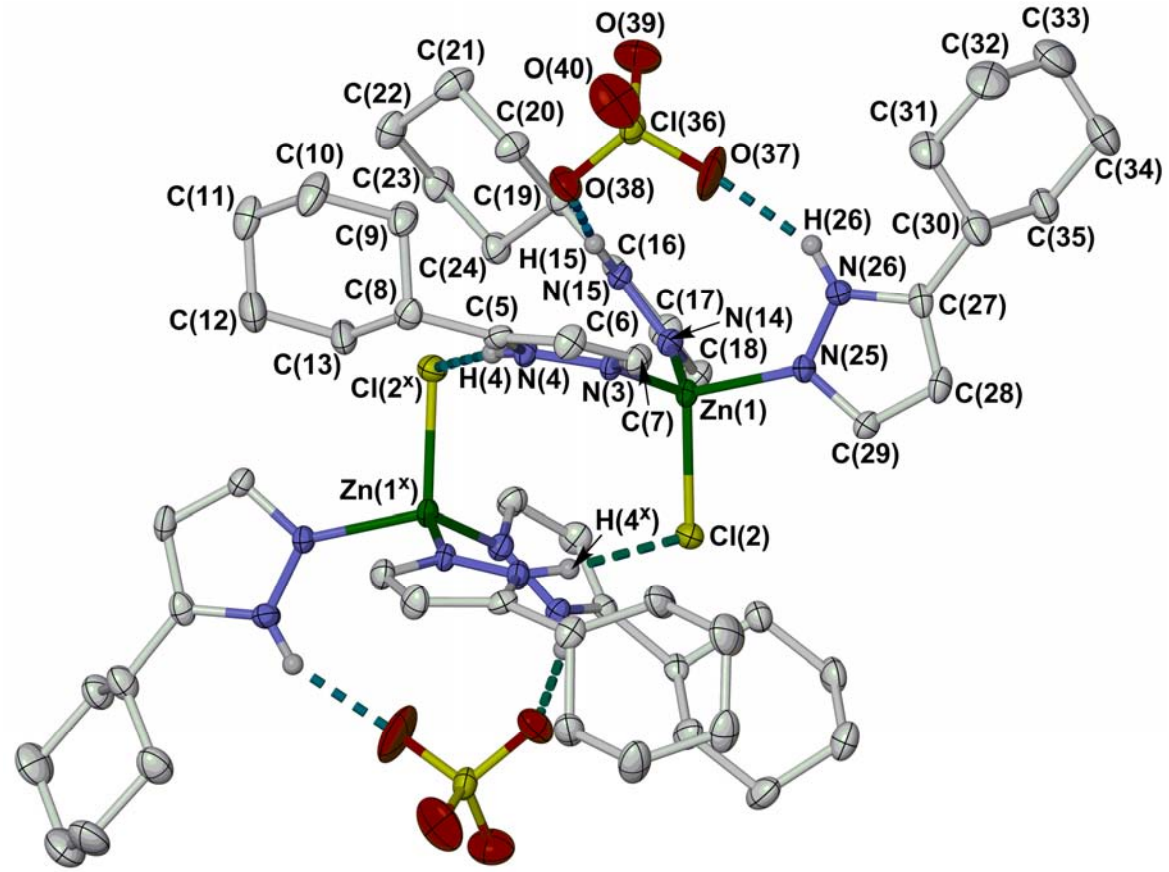

Figure S8 View of the hydrogen-bonded dimer in the crystal structure of $[ZnCl(Hpz^{Cy})_3]ClO_4$. All H atoms not involved in hydrogen bonding have been omitted for clarity, and displacement ellipsoids are at the 50% probability level. Symmetry code: (x) *–x*, *y*, ½*–z*. Colour code: C, white; H, grey; Cl, yellow; N, blue; O, red; Zn, green.

Table S4 Selected bond lengths and angles in the crystal structure of $[ZnCl(Hpz^{Cy})_3]ClO_4$ (Å, °).

Zn(1)–Cl(2)	2.3075(9)
Zn(1)–N(3)	2.031(2)
Zn(1)–N(14)	2.020(2)
Zn(1)–N(25)	2.051(2)
Cl(2)–Zn(1)–N(3)	111.12(6)
Cl(2)–Zn(1)–N(14)	103.39(7)
Cl(2)–Zn(1)–N(25)	103.61(6)
N(3)–Zn(1)–N(14)	122.78(8)
N(3)–Zn(1)–N(25)	102.60(9)
N(14)–Zn(1)–N(25)	111.98(9)

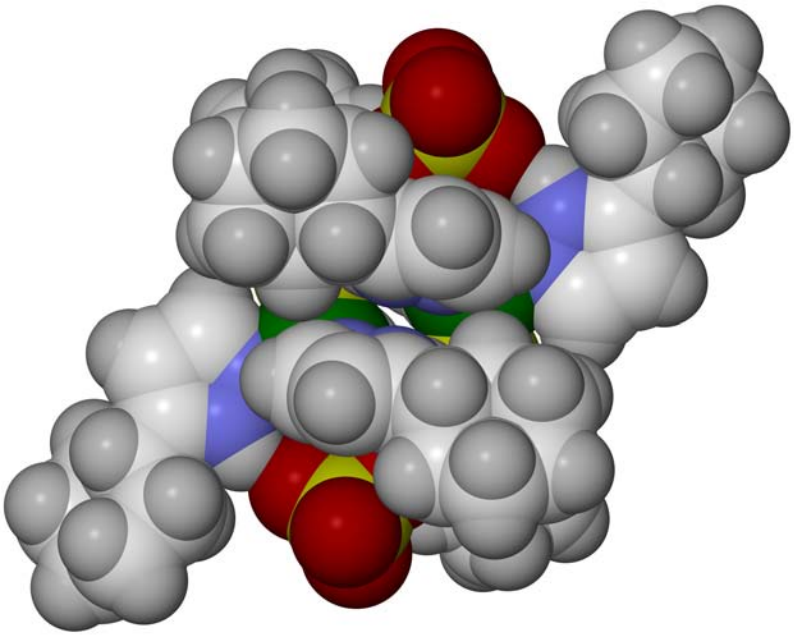

Figure S9 Space-filling view of the hydrogen-bonded dimer in the crystal structure of $[ZnCl(Hpz^{Cy})_3]ClO_4$. The view is the same as in Fig. S6, and Fig. 6 of the main paper. Colour code: C, white; H, grey; Cl, yellow; N, blue; O, red; Zn, green.

Table S5 Metric parameters for hydrogen bonds in the $[ZnY(Hpz^{R})_3]X$ structures (Å, °). Symmetry codes: (vi) 1–*x*, –*y*, –*z*; (viii) ½+*x*, ½–*y*, $^3/_2$–*z*; (x) –*x*, *y*, ½–*z*.

	D–H (D = N, O)	H…A (A = O, Cl)	D…A	D–H…A
$[ZnCl(Hpz^{Ph})_3]Cl$				
N(4)–H(4)…Cl(36)	0.88	2.37	3.2058(18)	158.4
N(15)–H(15)…Cl(36)	0.88	2.34	3.1428(16)	152.2
N(26)–H(26)…Cl(36)	0.88	2.29	3.1332(15)	161.5
$[ZnCl(Hpz^{Cy})_3]NO_3$				
N(4)–H(4)…O(37)	0.88	1.99	2.834(3)	160.7
N(15)–H(15)…O(38)	0.88	1.97	2.813(3)	160.7
N(26)–H(26)…O(39^{A})	0.88	2.04	2.913(3)	172.4
$[ZnBr(Hpz^{Cy})_3]NO_3 \cdot H_2O$				
N(4)–H(4)…O(27)	0.88	2.01	2.874(3)	166.5
N(15)–H(15)…O(24)	0.88	2.07	2.865(5)	149.4
O(27)–H(27A)…O(25^{viii})[a]	0.99	2.55	3.321(4)	134.3
O(27)–H(27A)…O(26^{viii})[a]	0.99	1.91	2.887(4)	169.2
O(27)–H(27B)…O(24)[a]	0.99	2.31	2.822(4)	111.2
O(27)–H(27B)…O(25)[a]	0.99	1.76	2.739(4)	171.2
$[ZnCl(Hpz^{Cy})_3]ClO_4$				
N(4)–H(4)…Cl(2^{x})	0.88	2.44	3.298(2)	165.3
N(15)–H(15)…O(38)	0.88	2.08	2.919(3)	159.8
N(26)–H(26)…O(37)	0.88	2.02	2.830(3)	152.9

[a]The long bonds O(27)–H(27A) and O(27)–H(27B) are an artefact of the refinement procedure, and metric parameters involving these H atoms should be treated with caution. See the main paper for more details.