

The enrichment ratio of atomic contacts in the crystal structure of isomeric, triply protonated, 4'-functionalized terpyridine cations with $[\text{ZnCl}_4]^{2-}$ as counter-ion

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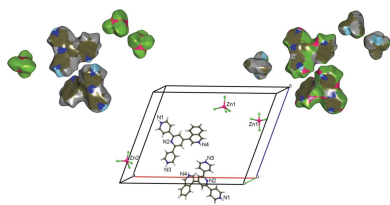
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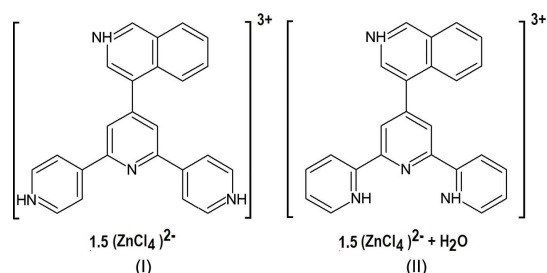
We report herein the synthesis, crystallographic analysis and a study of the non-covalent interactions observed in the new 4'-substituted terpyridine-based derivative bis[4'-(isoquinolin-2-ium-4-yl)-4,2':6',4''-terpyridine-1,1''-dium] tris[tetrachloridozincate(II)], $(\text{C}_{24}\text{H}_{19}\text{N}_4)_2[\text{ZnCl}_4]_3$ or $(44\text{TPH}_3)_2[\text{ZnCl}_4]_3$, where $(44\text{TPH}_3)^{3+}$ is the triply protonated cation 4'-(isoquinolinium-4-yl)-4,2':6',4''-terpyridinium. The compound is similar in its formulation to the recently reported 2,2':6',2''-terpyridinium analogue {bis[4'-(isoquinolin-2-ium-4-yl)-2,2':6',2''-terpyridine-1,1''-dium] tris[tetrachloridozincate(II)] monohydrate; Granifo *et al.* (2017). *Acta Cryst. C* **73**, 1121–1130}, although rather different and much simpler in its structural features, mainly in the number and type of non-covalent interactions present, as well as in the supramolecular structure they define.

1. Chemical context

We have recently reported the use of the 4'-pyridyl-substituted terpyridine 4'-(isoquinolin-4-yl)-2,2':6',2''-terpyridine (22TP) in the synthesis of the tetrachloridozincate salt $(22\text{TPH}_3)_2[\text{ZnCl}_4]_3 \cdot \text{H}_2\text{O}$ (II) containing the triply protonated cation $(22\text{TPH}_3)^{3+}$ (Granifo *et al.*, 2017). The structural study of (II) demonstrates the concerted way in which a series of non-covalent interactions, viz. hydrogen bonding, anion- π and π - π stacking, participate in the crystal packing. The repulsive nature of the π - π interaction between the triply protonated $(22\text{TPH}_3)^{3+}$ cations is counteracted by the $[\text{ZnCl}_4]^{2-}$ anions through abundant peripheral hydrogen bonding and anion- π interactions to the aromatic rings. A useful tool to highlight those contacts, which are statistically favored in a given structure, is the *enrichment ratios approach* (Jelsch *et al.*, 2014) based on the Hirshfeld surface, and whose application in the present case showed unexpectedly large enrichment ratios for the cationic $\text{C} \cdots \text{N}$ contacts in (II) as compared to those in the unprotonated base 22TP. This result was rationalized through the atomic and ring natural bond order charges (NBO), calculated by Maclagan and co-workers (Maclagan *et al.*, 2015) for a series of aromatic *N*-heterocyclic compounds. Concisely, in a protonated species, the hydrogen and nitrogen in the N-H group carry an almost constant charge q , with an average of $q(\text{H}) = 0.43 \pm 0.01$ and $q(\text{N}) = -0.46 \pm 0.1$. The other atoms in the aromatic rings, C and H, receive the



remaining positive charge, *i.e.* 0.57 ± 0.01 unit charge. A further remarkable result is that the $q(\text{N})$ values appear almost invariant when going from the neutral to the protonated base. Now, given that protonation leads to an increase on the positive charge in the C atoms and that the negative charge of the N atoms is almost invariant, a natural conclusion is that this ought to enrich the cationic $\text{C} \cdots \text{N}$ interactions. In an attempt to explore the effect of the position of the protonated N atoms on this type of interaction, we decided to protonate the already known isomeric base 4'-(isoquinolin-4-yl)-4,2':6',4''-terpyridine (44TP) (Granifo *et al.*, 2015) and to study the crystal structure of the new related compound $(44\text{TPH}_3)_2[\text{ZnCl}_4]_3$ (I).



2. Structural commentary

Fig. 1 shows the molecular geometry as well as atom and ring labelling for (I). There is one $(44\text{TPH}_3)^{3+}$ independent cationic moiety, protonated at N1 and N3 in the lateral pyridine rings (hereinafter py) and at N4 in the isoquinoline group (hereinafter, isq). The three negative charges required for charge balance are provided by one full independent $[\text{ZnCl}_4]^{2-}$ (tcz) anion in general position and a second one sitting on a twofold axis (thus providing only half of the charge). The general formulation is then $(44\text{TPH}_3)_2[\text{ZnCl}_4]_3$, similar to the 2,2':6',2'' analogue (II) but without water as solvent. In this respect, the analogy goes a bit further: the pseudosymmetry observed in (II), which linked both (otherwise independent) $(44\text{TPH}_3)^{3+}$ cations becomes genuine symmetry in (I), expressed through the crystallographic twofold operation through the tcz group at Zn2.

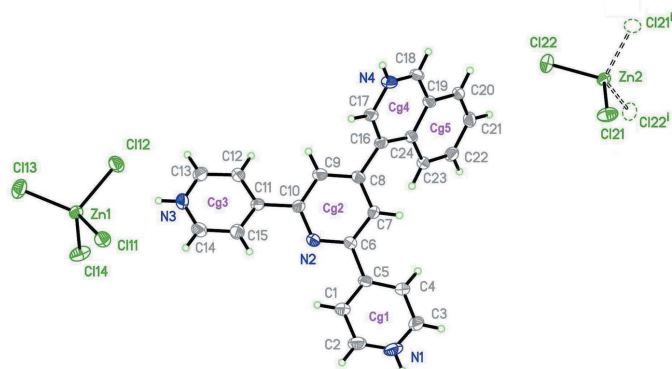


Figure 1

Molecular view of the asymmetric unit in (I), with displacement ellipsoids drawn at the 50% probability level. Atom Zn2 lays onto a twofold symmetry axis. Symmetry code: (i) $-x + 1, y, -z + \frac{3}{2}$.

Bond distances and angles are unremarkable in the $(44\text{TPH}_3)^{3+}$ moiety, with only minor departures from commonly accepted values in general, and from those in (II) in particular. The most relevant features come from the dihedral angles involving the internal planar groups, and it is here where the molecular differences with (II) are more apparent. The terpyridine nucleus presents significant out-of-plane rotations of the lateral pyridinium groups with regard to the central py one, and similarly with the pendant isq rings [dihedral angles: 2, 1 = $15.87 (16)^\circ$; 2, 3 = $25.80 (16)^\circ$; 2, 4 = $48.49 (15)^\circ$, plane labels taken from their N heteroatoms]. This large rotation of the isq group is required to avoid 'bumping' between the otherwise colliding atoms H7 and H23. The experimental $d(\text{H7} \cdots \text{H23})$ distance is 2.36 \AA , while in a perfectly planar disposition this value would collapse down to $\approx 0.80 \text{ \AA}$. This 'anti-bumping' argument appears to be reinforced by the difference between the angles C16, [C24–C16–C8 = $124.7 (3)^\circ$ > C17–C16–C8 = $116.2 (3)^\circ$], suggesting some kind of an $\text{H7} \cdots \text{H23}$ repulsion.

3. Supramolecular features

As in (II), the most conspicuous aspect of the structure of (I) is its packing scheme, derived from a number of different intermolecular interactions, presented in Table 1 (N/C–H \cdots Cl), Table 2 (π – π) and Table 3 (Zn–Cl \cdots π/π^+), which for convenience of description have been assigned an individual 'code' or sequence number (from #1 to #17). Among these, hydrogen bonds are the most abundant and are clearly divided into two groups: stronger N–H \cdots Cl (#1 to #5) and weaker

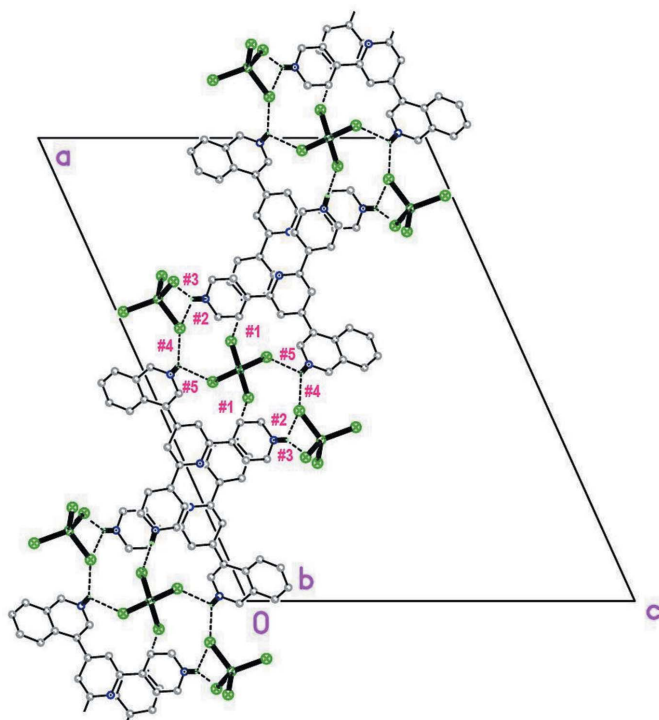


Figure 2

The broad (010) planar structure, shown sideways, along *b*.

Table 1
Hydrogen-bond geometry (Å, °) for (I).

Code	D—H...A	D—H	H...A	D...A	D—H...A
#1	N1—H1N...Cl21 ⁱ	0.846 (10)	2.27 (3)	3.085 (4)	161 (3)
#2	N3—H3N...Cl12 ⁱⁱ	0.846 (10)	2.71 (3)	3.291 (3)	127 (3)
#3	N3—H3N...Cl14 ⁱⁱⁱ	0.847 (10)	2.48 (4)	3.203 (4)	145 (3)
#4	N4—H4N...Cl12 ⁱⁱⁱ	0.850 (10)	2.41 (3)	3.125 (3)	142 (3)
#5	N4—H4N...Cl22 ^{iv}	0.850 (10)	2.74 (3)	3.264 (3)	121 (3)
#6	C4—H4...Cl14 ^v	0.93	2.72	3.316 (4)	123
#7	C7—H7...Cl14 ^v	0.93	2.73	3.589 (3)	155
#8	C13—H13...Cl12 ⁱⁱ	0.93	2.71	3.287 (4)	121
#9	C17—H17...Cl22 ^{iv}	0.93	2.77	3.320 (3)	119
#10	C23—H23...Cl11 ^{vii}	0.93	2.74	3.434 (4)	132

Symmetry codes: (i) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$; (ii) $x, y + 1, z$; (iii) $-x + 1, y, -z + \frac{1}{2}$; (iv) $-x + 1, -y + 1, -z + 1$; (v) $x, -y + 1, y + \frac{1}{2}$; (vi) $-x + \frac{3}{2}, y + \frac{1}{2}, -y + \frac{1}{2}$; (vii) $x, -y + 2, y + \frac{1}{2}$.

C—H...Cl bonds (#6 to #10). Interactions #1 to #6 serve to link the $(44\text{TPH}_3)^{3+}$ cations to the $[\text{ZnCl}_4]^{2-}$ anions as shown in Fig. 2, to form broad 2D structures parallel to $(10\bar{1})$. Fig. 3, in turn, presents a view of these planar arrays along the plane normal. The remaining interactions (hydrogen bonds #7–#10, π – π contacts #11–#14 and $\text{Cl}\cdots\pi$ interactions #15–#17) link the superimposed planes roughly along $[10\bar{1}]$, defining a well-connected 3D network. The so-called $\text{Cl}\cdots\pi$ interactions (Bauzá *et al.*, 2016; Gamez, 2014; Giese *et al.*, 2015, 2016) that

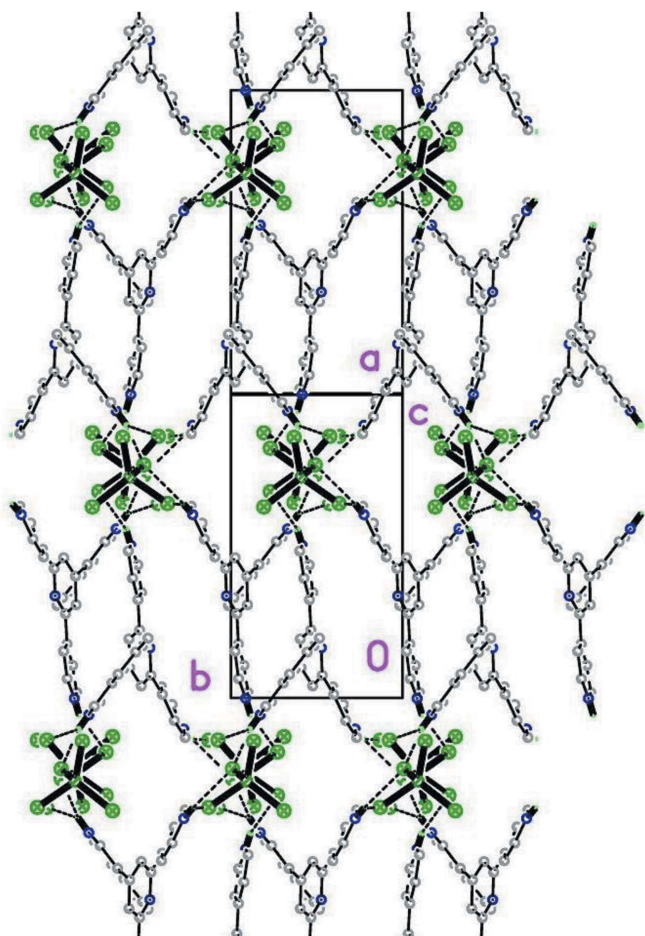


Figure 3
Same as Fig. 2, but shown along the plane normal, roughly $[10\bar{1}]$.

Table 2
 π – π contacts in (I).

Ring codes as in Fig. 1. ccd: centroid-to-centroid distance; da: dihedral angle between rings; ipd: interplanar distance, or (mean) distance from one plane to the neighbouring centroid. For details, see Janiak (2000)

Interaction code	Cg...Cg	ccd (Å)	da (°)	ipd (Å)
#11	Cg4...Cg5 ^{vii}	3.495 (2)	18.1 (15)	3.32 (2)
#12	Cg5...Cg5 ^{vii}	3.843 (2)	0.0	3.35 (2)
#13	Cg1...Cg3 ^{viii}	3.784 (2)	16.2 (14)	3.66 (2)
#14	Cg1...Cg2 ^{ix}	4.149 (2)	15.9 (16)	3.85 (2)

Symmetry codes: (vii) $-x + 1, -y + 2, -z + 1$; (viii) $-x + \frac{3}{2}, -y + \frac{5}{2}, -z + 1$; (ix) $-x + \frac{3}{2}, -y + \frac{3}{2}, -z + 1$.

Table 3
Anion... π and anion... π^+ interactions (Å, °) in (I).

d is the $\text{Cl}\cdots X$ distance where X is the atom in the ring nearest the Cl anion; α is the angle subtended by the $\text{Cl}-\text{Cg}$ vector to the ring normal; β is the angle subtended by the $X-\text{Cg}$ and $X-\text{Cg}$ vectors (for $\beta < 90^\circ$, the anion projects within the ring and for $90^\circ < \beta$, the anion projects outside the ring; n (in η^n) is the number of interacting atoms. NB according to standard requirements for anion... π interactions (Giese *et al.* 2015, 2016), β should be $< 100^\circ$.

Code	Zn—Cl...Cg	Cl...Cg	d	α	β	η^n
#15	Zn1—Cl12...Cg5 ^v	3.739 (2)	3.671	14.5	82.0	η^2
#16	Zn1—Cl13...Cg2 ^{xi}	3.760 (2)	3.829	8.60	76.5	η^1
#17	Zn1—Cl13...Cg4 ^{xiii}	4.084 (2)	3.748	23.9	94.3	η^1

Symmetry codes: (x) $x, -y + 1, z - \frac{1}{2}$; (xi) $x, -y + 2, z - \frac{1}{2}$; (xiii) $x, -y + 1, z - \frac{1}{2}$.

involve the aromatic ring systems, either neutral π or charged π^+ , and the Cl^- anions are presented in Fig. 4.

4. Hirshfeld surface and enrichment ratio

Calculations of the recently introduced enrichment ratio (ER) approach using the Hirshfeld surface methodology (Jelsch *et al.*, 2014) were performed with *MoProViewer* (Guillot *et al.*, 2014). Considering that the ER is the ratio between the actual contacts and those that should result from random ones, values larger than unity for any pair of elements mean they have a high tendency to form contacts in the crystal structure, the opposite happening for pairs with values lower than unity. The computed Hirshfeld surfaces and the corresponding contact ERs in the global structure of (I) are shown in Fig. 5 and Table 4, respectively. Since a tcz anion ($\text{Zn}2$) is located on a twofold axis, it was necessary to generate a dimer of the asymmetric unit in order to obtain the entire surface for each species (Fig. 5). As expected, the results show that the greatest contributions to the global surfaces (taking into account the inner and outer surfaces) are provided by C (27.56%), Cl (33.88%) and H_C (27.26%) atoms. On the other hand, visualization of the ERs discloses a remarkable increase in the $\text{C}\cdots\text{N}$ contacts in the $(44\text{TPH}_3)^{3+}$ cations (ER = 2.78; Table 4), as compared to those of neutral free 44TP (ER = 0.34; Table 5). As a way to specifically study the cation–cation interactions, the Hirshfeld surface and the respective ERs of the $(44\text{TPH}_3)^{3+}$ cation were computed. So, in Fig. 6, the coloured interior/exterior Hirshfeld surfaces shows, as in the global

Table 4

Hirshfeld contact surfaces and ERs for $(44\text{TPH}_3)_2[\text{ZnCl}_4]_3$ computed around the two $(44\text{TPH}_3)^{3+}$ cations and the three $[\text{ZnCl}_4]^{2-}$ anions.

The H atoms bound to carbon (H_C) and nitrogen (H_N) are differentiated. The first column corresponds to 'interior' atoms and the remaining columns to 'exterior' ones.

	C	N	Cl	Zn	H_C	H_N
Surface interior (%)	28.66	2.65	33.36	3.49	26.38	5.46
Surface exterior (%)	26.45	2.20	34.40	3.01	28.15	5.80
Enrichment ratios (reciprocal contacts merged)						
C	1.74					
N	2.78	0.24				
Cl	0.89	0.21	0.27			
Zn	0.92	0.00	0.10	0.00		
H_C	0.35	0.59	1.91	2.33	0.60	
H_N	0.49	0.00	2.36	1.40	0.07	0.00

Table 5

Hirshfeld contact surfaces and ERs for 44TP.

The first column corresponds to 'interior' atoms and the remaining columns to 'exterior' ones.

	C	N	H_C
Surface interior (%)	42.44	10.43	47.13
Surface exterior (%)	40.81	10.44	48.74
Enrichment ratios (reciprocal contacts merged)			
C	1.28		
N	0.34	0.44	
H_C	0.90	1.69	0.94

situation, the relevance of the C (36.26%), Cl (25.08%) and H_C (27.34%) atoms, while values in Table 6 show that the C...N contacts are significantly enriched (ER = 2.15). When these results are compared with those obtained in (II), a very similar behavior is observed, *i.e.*, in spite of changing the position of the protonated pyridyl N atoms, the system reorients itself as to favour the C...N interactions, evidencing

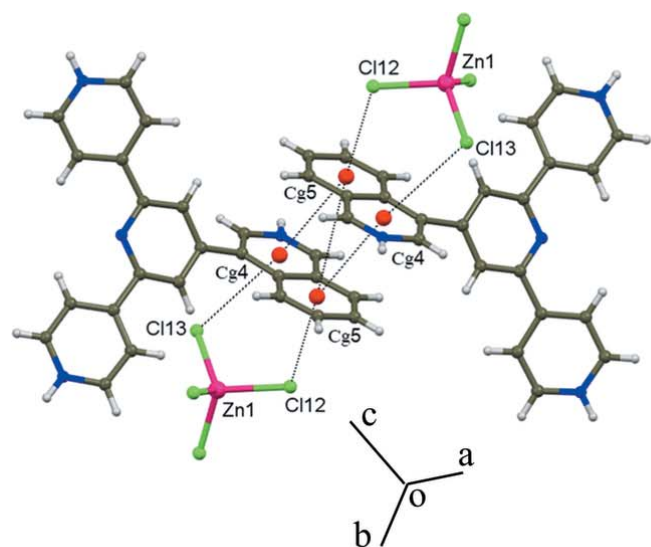


Figure 4
Anion... π interactions in (I) including the π -stacking involved.

Table 6

Hirshfeld contact surfaces and ERs for $(44\text{TPH}_3)^{3+}$.

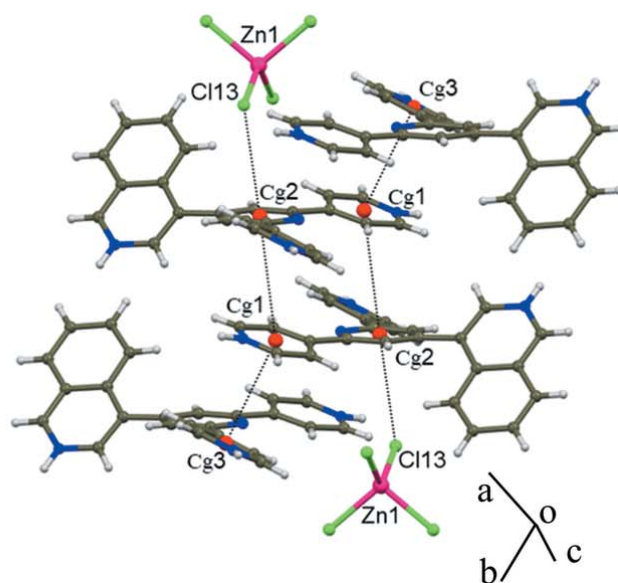
The H atoms bound to carbon (H_C) and nitrogen (H_N) are differentiated. The first column corresponds to 'interior' atoms and the remaining columns to 'exterior' ones.

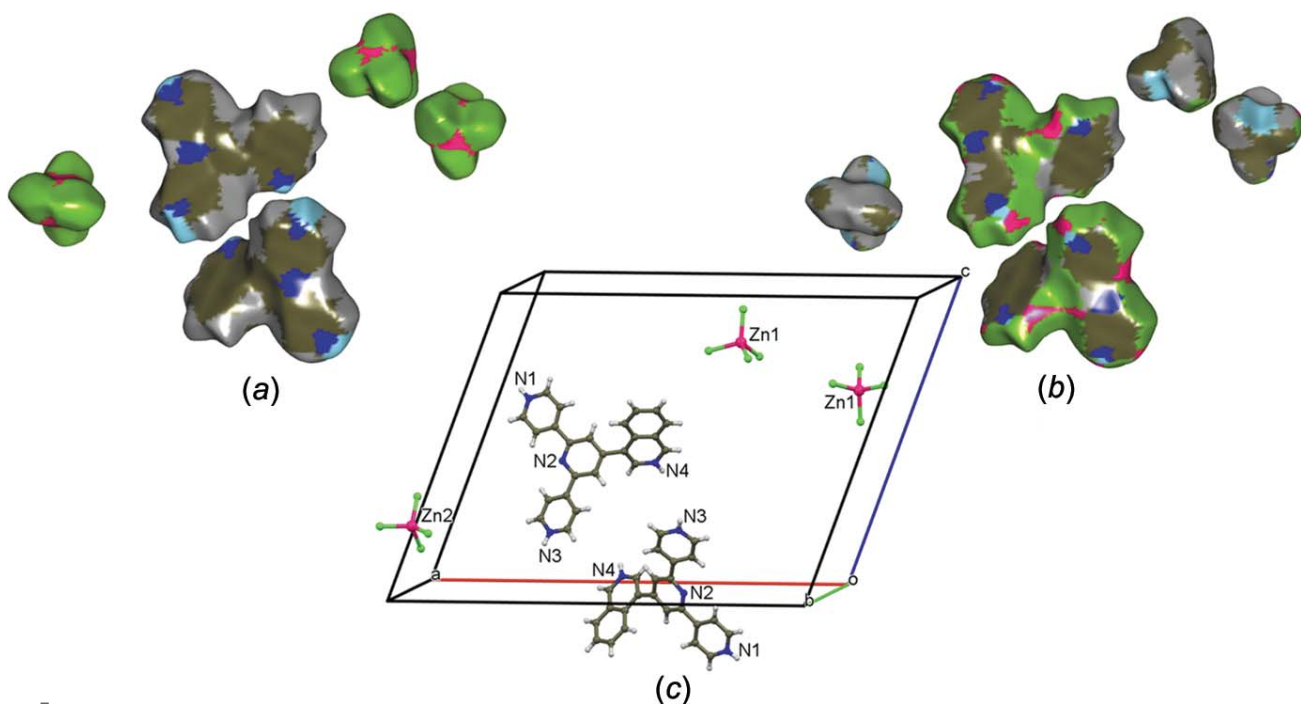
	C	N	Cl	Zn	H_C	H_N
Surface interior (%)	44.29	4.09	0.00	0.00	42.66	8.96
Surface exterior (%)	28.22	3.60	50.16	4.66	12.03	1.34
Enrichment ratios (reciprocal contacts merged)						
C	1.62					
N	2.15	0.43				
Cl	0.62	0.16	NaN			
Zn	0.76	0.00	NaN	NaN		
H_C	0.49	0.65	1.34	1.37	1.29	
H_N	0.73	0.00	1.64	0.88	0.18	0.00

the validity of the application of the criterion based on atomic charges.

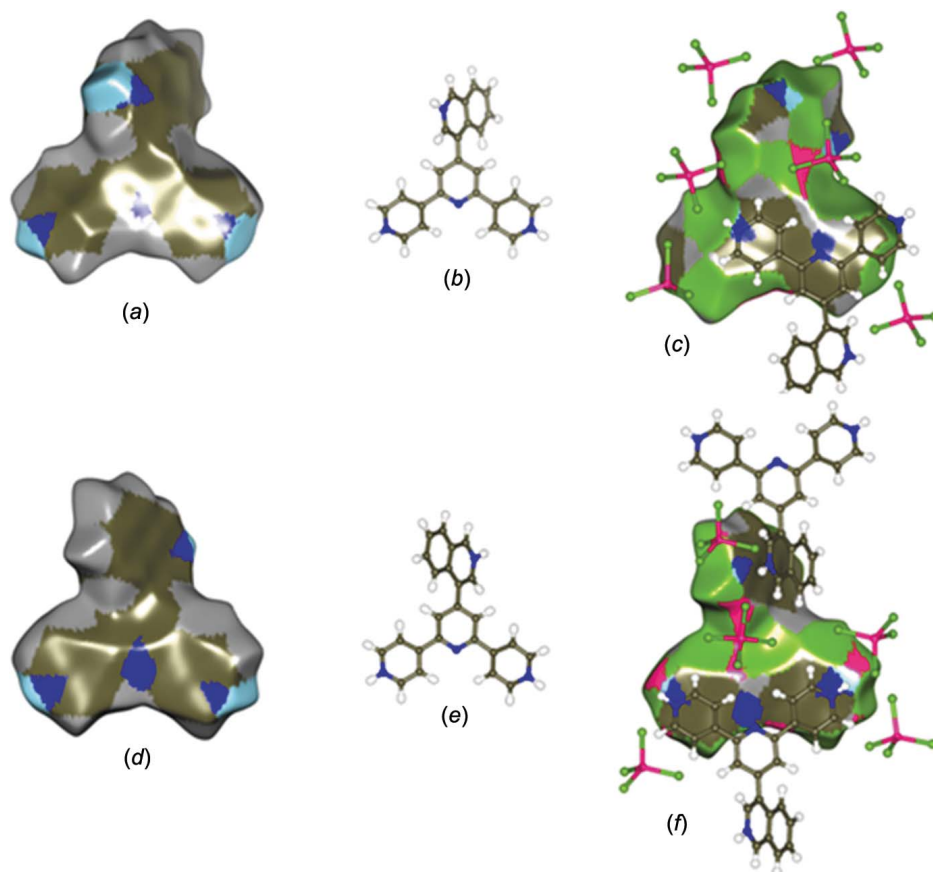
5. Database survey

A search of the Cambridge Structural Database (CSD version 5.39, November 2017, update 3, May 2018; Groom *et al.*, 2016) for recently published structures with triply protonated $(\text{LH}_3)^{3+}$ cations showed just a handful of entries, *viz.*: IRESII [2,4,6-tris(2-pyridinio)pyridine trinitrate; Padhi *et al.*, 2011]; LEMVAC {2,2'-[4-(pyridinium-4-yl)pyridine-2,6-diyl]dipyridinium trinitrate monohydrate; Seth *et al.*, 2013}; ODOHIA [trihydrogen 4'-(4-pyridyl)-2,2':6',2''-terpyridine trinitrate bis(nitric acid); Manna *et al.*, 2013]; LODHUI [2,6-bis-(pyridinium-2-yl)-4-(pyridinium-4-yl)pyridine tribromide trihydrate; Manna *et al.*, 2014a]; FOTRUD [4'-(pyridinium-4-yl)-3,2':6',3''-terpyridine-1,1''-diium triperchlorate monohydrate; Manna *et al.*, 2014b] and KEQYAJ [bis[4'-(isoquinolin-2-ium-4-yl)-2,2':6',2''-terpyridine-1,1''-diium] tris[tetra-chloridozincate(II)] monohydrate (II); Granifo *et al.*, 2017].




Figure 5

Right and left: Hirshfeld surfaces of the independent entities of (I) shown in (c) (conveniently set apart as to avoid overlapping) and colored in accordance with the species contributing most to the electron density on the surface; (a) surfaces coloured according to the interior atoms (b) surfaces coloured according to the exterior atoms. Colour key: H_C : grey, H_N : light blue, C: dark brown, N: blue, Cl: green, Zn: purple.


Figure 6

Hirshfeld surface of the $(44TPH_3)^{3+}$ cation coloured in accordance with the species contributing most to the electron density on the surface, showing (a)/(c) front and (d)/(f) back. In (a)/(d) the surface is coloured according to the interior atoms and in (c)/(f) the surface is coloured according to the exterior atoms. The orientation of the structure inside the surface is shown in (b)/(e). Colour key: H_C grey, H_N light blue, C dark brown, N blue, Cl green and Zn magenta.

Table 7
Experimental details.

Crystal data	
Chemical formula	(C ₂₄ H ₁₉ N ₄) ₂ [ZnCl ₄] ₃
<i>M_r</i>	1348.37
Crystal system, space group	Monoclinic, <i>C2/c</i>
Temperature (K)	295
<i>a</i> , <i>b</i> , <i>c</i> (Å)	30.642 (2), 8.0866 (4), 23.413 (2)
β (°)	114.316 (7)
<i>V</i> (Å ³)	5286.8 (7)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	2.00
Crystal size (mm)	0.34 × 0.20 × 0.14
Data collection	
Diffractometer	Oxford Diffraction Xcalibur, Sapphire3
Absorption correction	Multi-scan (<i>CrysAlis PRO</i> ; Rigaku OD, 2015)
<i>T_{min}</i> , <i>T_{max}</i>	0.58, 0.82
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	23819, 6416, 4482
<i>R_{int}</i>	0.065
($\sin \theta/\lambda$) _{max} (Å ⁻¹)	0.690
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, <i>S</i>	0.045, 0.106, 1.08
No. of reflections	6416
No. of parameters	330
No. of restraints	3
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.62, -0.60

Computer programs: *CrysAlis PRO* (Rigaku OD, 2015), *SHELXS97* and *SHELXTL* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015) and *PLATON* (Spek, 2009).

A characteristic found in these structures, in common with the case reported herein, is that only the N atoms of the three outermost pyridyl groups are protonated and that the lateral rings of the terpyridine portion adopt a *syn-syn* conformation with respect to the central pyridine ring. In most of the reported cases it was found that, in spite of the repulsive electrostatic nature between positively charged (LH₃)³⁺ cations, the π - π stacking interactions appear enhanced when the π -system is charged. Due to lack of reported information, quantitative comparison of the ERs could only be made with the (already discussed) structure (II).

6. Synthesis and crystallization

The tetrachloridozincate salt (44TPH₃)₂[ZnCl₄]₃ was prepared by the reaction of 4'-(isoquinolin-4-yl)-4,2':6',4''-terpyridine (44TP; Granifo *et al.*, 2015), ZnCl₂ and concentrated HCl (37%). 44TP (4.8 mg) was placed in a small beaker and dissolved with concentrated HCl (0.5 ml) and then 0.5 ml of water was added. To this solution was added an excess of ZnCl₂ (48.0 mg) and the resulting solution was stirred for 1.5 min. The clear solution was allowed to stand at room temperature for a few days to give colourless block-shaped

crystals, which were washed with methanol (3 × 1 ml) and then dried with hot air.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 7. H atoms were identified in an intermediate difference map, and treated differently in refinement: those attached to C were further idealized and finally allowed to ride with C—H = 0.93 Å, while those attached to N were refined with restrained N—H = 0.85 (1) Å. In all cases, H-atom displacement parameters were taken as $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{Host})$.

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supporting information

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The enrichment ratio of atomic contacts in the crystal structure of isomeric, triply protonated, 4'-functionalized terpyridine cations with $[\text{ZnCl}_4]^{2-}$ as counter-ion

Juan Granifo, Sebastián Suárez and Ricardo Baggio

Computing details

Data collection: *CrysAlis PRO* (Rigaku OD, 2015); cell refinement: *CrysAlis PRO* (Rigaku OD, 2015); data reduction: *CrysAlis PRO* (Rigaku OD, 2015); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015), *PLATON* (Spek, 2009).

Bis[4'-(isoquinolin-2-ium-4-yl)-4,2':6',4''-terpyridine-1,1''-dium] tris(tetrachloridozincate)

Crystal data

$(\text{C}_{24}\text{H}_{19}\text{N}_4)_2[\text{ZnCl}_4]_3$

$M_r = 1348.37$

Monoclinic, *C2/c*

$a = 30.642$ (2) Å

$b = 8.0866$ (4) Å

$c = 23.413$ (2) Å

$\beta = 114.316$ (7)°

$V = 5286.8$ (7) Å³

$Z = 4$

$F(000) = 2704$

$D_x = 1.694$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 4699 reflections

$\theta = 3.7\text{--}27.5^\circ$

$\mu = 2.00$ mm⁻¹

$T = 295$ K

Blocks, colourless

$0.34 \times 0.20 \times 0.14$ mm

Data collection

Oxford Diffraction Xcalibur, Sapphire3 diffractometer

Radiation source: fine-focus sealed X-ray tube, Enhance (Mo) X-ray Source

Graphite monochromator

ω scans

Absorption correction: multi-scan (CrysAlisPro; Rigaku OD, 2015)

$T_{\min} = 0.58$, $T_{\max} = 0.82$

23819 measured reflections

6416 independent reflections

4482 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.065$

$\theta_{\max} = 29.4^\circ$, $\theta_{\min} = 3.7^\circ$

$h = -39 \rightarrow 41$

$k = -10 \rightarrow 10$

$l = -30 \rightarrow 31$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.045$

$wR(F^2) = 0.106$

$S = 1.08$

6416 reflections

330 parameters

3 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0313P)^2 + 4.8559P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.002$

$$\Delta\rho_{\max} = 0.62 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.60 \text{ e } \text{\AA}^{-3}$$

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Zn1	0.65199 (2)	0.59124 (5)	0.12147 (2)	0.02480 (12)
Cl11	0.68969 (3)	0.80880 (11)	0.18160 (5)	0.0407 (3)
Cl12	0.58917 (3)	0.50894 (12)	0.14395 (5)	0.0419 (3)
Cl13	0.62471 (4)	0.63226 (13)	0.01753 (4)	0.0418 (2)
Cl14	0.70191 (3)	0.37027 (10)	0.15801 (4)	0.0325 (2)
Zn2	0.500000	0.40642 (7)	0.750000	0.02449 (14)
Cl21	0.56071 (3)	0.22938 (11)	0.76067 (5)	0.0384 (2)
Cl22	0.47311 (3)	0.57574 (10)	0.66606 (4)	0.0342 (2)
N1	0.84733 (11)	0.9147 (4)	0.65467 (16)	0.0383 (8)
H1N	0.8754 (6)	0.887 (4)	0.6794 (16)	0.046*
N2	0.70304 (9)	1.0267 (3)	0.46155 (13)	0.0257 (6)
N3	0.65260 (11)	1.2242 (4)	0.24416 (14)	0.0327 (7)
H3N	0.6521 (13)	1.273 (4)	0.2119 (11)	0.039*
N4	0.51052 (10)	0.6700 (3)	0.43396 (14)	0.0281 (7)
H4N	0.4922 (11)	0.609 (3)	0.4043 (12)	0.034*
C1	0.79534 (11)	0.9775 (4)	0.55141 (17)	0.0328 (9)
H1	0.790536	1.005648	0.510738	0.039*
C2	0.84084 (12)	0.9559 (5)	0.59660 (19)	0.0380 (9)
H2	0.867084	0.969995	0.586770	0.046*
C3	0.81105 (13)	0.9004 (4)	0.67238 (18)	0.0377 (10)
H3	0.816987	0.874321	0.713614	0.045*
C4	0.76494 (12)	0.9249 (4)	0.62865 (17)	0.0334 (9)
H4	0.739506	0.919950	0.640532	0.040*
C5	0.75647 (11)	0.9572 (4)	0.56675 (16)	0.0257 (8)
C6	0.70667 (11)	0.9661 (4)	0.51656 (15)	0.0233 (7)
C7	0.66782 (11)	0.9041 (4)	0.52621 (15)	0.0228 (7)
H7	0.672074	0.860642	0.564933	0.027*
C8	0.62267 (11)	0.9081 (4)	0.47714 (16)	0.0221 (7)
C9	0.61866 (11)	0.9763 (4)	0.42063 (16)	0.0251 (7)
H9	0.588853	0.984287	0.387052	0.030*
C10	0.65932 (11)	1.0322 (4)	0.41467 (15)	0.0230 (7)
C11	0.65678 (11)	1.0990 (4)	0.35449 (15)	0.0232 (7)
C12	0.61460 (12)	1.1688 (4)	0.31040 (16)	0.0285 (8)
H12	0.587272	1.172068	0.318353	0.034*
C13	0.61339 (13)	1.2323 (4)	0.25572 (17)	0.0313 (8)
H13	0.585546	1.280842	0.226775	0.038*

C14	0.69363 (13)	1.1557 (5)	0.28393 (18)	0.0366 (9)
H14	0.719948	1.150150	0.273842	0.044*
C15	0.69625 (13)	1.0939 (4)	0.33971 (17)	0.0321 (8)
H15	0.724803	1.048051	0.368031	0.039*
C16	0.57945 (11)	0.8377 (4)	0.48229 (15)	0.0225 (7)
C17	0.55171 (11)	0.7358 (4)	0.43484 (16)	0.0270 (8)
H17	0.561020	0.710850	0.402698	0.032*
C18	0.49493 (11)	0.7020 (4)	0.47743 (16)	0.0253 (8)
H18	0.466264	0.655910	0.474464	0.030*
C19	0.52111 (11)	0.8044 (4)	0.52799 (16)	0.0236 (7)
C20	0.50381 (11)	0.8408 (4)	0.57389 (16)	0.0262 (8)
H20	0.475249	0.794643	0.571249	0.031*
C21	0.52914 (12)	0.9435 (4)	0.62180 (16)	0.0301 (8)
H21	0.518261	0.966419	0.652638	0.036*
C22	0.57181 (12)	1.0155 (4)	0.62503 (16)	0.0283 (8)
H22	0.588456	1.087141	0.657908	0.034*
C23	0.58967 (11)	0.9837 (4)	0.58143 (15)	0.0243 (7)
H23	0.617993	1.033407	0.584754	0.029*
C24	0.56479 (11)	0.8747 (4)	0.53117 (15)	0.0218 (7)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.0216 (2)	0.0276 (2)	0.0238 (2)	0.00225 (15)	0.00800 (17)	0.00170 (16)
Cl11	0.0324 (5)	0.0322 (5)	0.0413 (6)	0.0011 (4)	-0.0012 (4)	-0.0048 (4)
Cl12	0.0251 (5)	0.0506 (6)	0.0529 (6)	0.0114 (4)	0.0190 (4)	0.0275 (5)
Cl13	0.0453 (6)	0.0558 (6)	0.0245 (5)	0.0109 (5)	0.0146 (4)	0.0042 (4)
Cl14	0.0280 (4)	0.0315 (5)	0.0396 (5)	0.0075 (3)	0.0156 (4)	0.0052 (4)
Zn2	0.0206 (3)	0.0297 (3)	0.0206 (3)	0.000	0.0060 (2)	0.000
Cl21	0.0251 (5)	0.0401 (5)	0.0431 (6)	0.0051 (4)	0.0071 (4)	-0.0101 (4)
Cl22	0.0450 (5)	0.0337 (5)	0.0243 (5)	0.0047 (4)	0.0147 (4)	0.0039 (4)
N1	0.0213 (16)	0.0404 (19)	0.040 (2)	0.0015 (14)	-0.0010 (15)	0.0030 (16)
N2	0.0209 (14)	0.0291 (15)	0.0278 (17)	-0.0009 (12)	0.0107 (12)	0.0032 (13)
N3	0.0368 (18)	0.0399 (18)	0.0223 (17)	-0.0082 (14)	0.0132 (14)	0.0010 (14)
N4	0.0220 (15)	0.0294 (16)	0.0305 (18)	-0.0063 (12)	0.0084 (13)	-0.0068 (13)
C1	0.0209 (18)	0.045 (2)	0.031 (2)	-0.0024 (16)	0.0089 (15)	0.0016 (17)
C2	0.0211 (18)	0.050 (2)	0.039 (2)	0.0001 (16)	0.0088 (17)	-0.0028 (19)
C3	0.033 (2)	0.040 (2)	0.030 (2)	-0.0108 (17)	0.0027 (17)	0.0060 (17)
C4	0.0229 (18)	0.044 (2)	0.028 (2)	-0.0078 (15)	0.0058 (15)	0.0030 (17)
C5	0.0185 (16)	0.0262 (17)	0.030 (2)	-0.0052 (13)	0.0075 (14)	0.0007 (15)
C6	0.0211 (17)	0.0260 (17)	0.0235 (18)	-0.0026 (14)	0.0097 (14)	0.0004 (14)
C7	0.0221 (17)	0.0276 (17)	0.0182 (17)	-0.0003 (13)	0.0079 (13)	0.0005 (14)
C8	0.0210 (16)	0.0231 (16)	0.0243 (18)	-0.0029 (13)	0.0115 (14)	-0.0044 (14)
C9	0.0181 (16)	0.0290 (18)	0.0266 (19)	0.0004 (13)	0.0077 (14)	-0.0016 (15)
C10	0.0191 (16)	0.0286 (17)	0.0208 (18)	0.0022 (13)	0.0078 (13)	0.0013 (14)
C11	0.0196 (16)	0.0270 (17)	0.0224 (18)	-0.0011 (13)	0.0081 (14)	-0.0032 (14)
C12	0.0246 (18)	0.0316 (19)	0.029 (2)	-0.0014 (14)	0.0109 (15)	0.0060 (16)
C13	0.029 (2)	0.0311 (19)	0.028 (2)	-0.0032 (15)	0.0059 (16)	0.0028 (16)

C14	0.028 (2)	0.052 (2)	0.033 (2)	-0.0050 (17)	0.0166 (17)	-0.0026 (18)
C15	0.0273 (19)	0.041 (2)	0.029 (2)	0.0041 (16)	0.0129 (16)	0.0056 (17)
C16	0.0168 (16)	0.0243 (17)	0.0235 (18)	0.0017 (13)	0.0053 (13)	0.0014 (14)
C17	0.0194 (17)	0.0365 (19)	0.0259 (19)	0.0008 (14)	0.0101 (14)	0.0000 (15)
C18	0.0175 (16)	0.0268 (18)	0.031 (2)	-0.0029 (13)	0.0093 (14)	0.0032 (15)
C19	0.0172 (16)	0.0250 (17)	0.0270 (19)	0.0016 (13)	0.0075 (14)	0.0060 (14)
C20	0.0198 (17)	0.0330 (19)	0.0262 (19)	0.0012 (14)	0.0099 (14)	0.0091 (15)
C21	0.0289 (19)	0.040 (2)	0.026 (2)	0.0048 (16)	0.0157 (16)	0.0060 (16)
C22	0.0294 (19)	0.0300 (19)	0.0220 (18)	-0.0021 (15)	0.0071 (15)	-0.0008 (15)
C23	0.0221 (17)	0.0263 (17)	0.0233 (18)	-0.0029 (13)	0.0080 (14)	0.0025 (14)
C24	0.0183 (16)	0.0226 (16)	0.0247 (18)	0.0029 (13)	0.0091 (13)	0.0052 (14)

Geometric parameters (Å, °)

Zn1—C113	2.2485 (10)	C7—H7	0.9300
Zn1—C111	2.2521 (10)	C8—C9	1.391 (5)
Zn1—C114	2.2775 (9)	C8—C16	1.491 (4)
Zn1—C112	2.2935 (10)	C9—C10	1.385 (4)
Zn2—C122	2.2545 (9)	C9—H9	0.9300
Zn2—C122 ⁱ	2.2545 (9)	C10—C11	1.481 (5)
Zn2—C121	2.2782 (9)	C11—C15	1.389 (5)
Zn2—C121 ⁱ	2.2783 (9)	C11—C12	1.399 (4)
N1—C2	1.333 (5)	C12—C13	1.366 (5)
N1—C3	1.342 (5)	C12—H12	0.9300
N1—H1N	0.846 (10)	C13—H13	0.9300
N2—C10	1.338 (4)	C14—C15	1.369 (5)
N2—C6	1.339 (4)	C14—H14	0.9300
N3—C13	1.337 (5)	C15—H15	0.9300
N3—C14	1.338 (5)	C16—C17	1.363 (4)
N3—H3N	0.847 (10)	C16—C24	1.423 (5)
N4—C18	1.316 (4)	C17—H17	0.9300
N4—C17	1.362 (4)	C18—C19	1.396 (5)
N4—H4N	0.850 (10)	C18—H18	0.9300
C1—C2	1.371 (5)	C19—C20	1.411 (5)
C1—C5	1.388 (5)	C19—C24	1.427 (4)
C1—H1	0.9300	C20—C21	1.354 (5)
C2—H2	0.9300	C20—H20	0.9300
C3—C4	1.376 (5)	C21—C22	1.405 (5)
C3—H3	0.9300	C21—H21	0.9300
C4—C5	1.388 (5)	C22—C23	1.367 (5)
C4—H4	0.9300	C22—H22	0.9300
C5—C6	1.496 (4)	C23—C24	1.416 (4)
C6—C7	1.393 (4)	C23—H23	0.9300
C7—C8	1.388 (4)		
C113—Zn1—C111	115.32 (4)	C10—C9—H9	120.2
C113—Zn1—C114	114.53 (4)	C8—C9—H9	120.2
C111—Zn1—C114	106.61 (4)	N2—C10—C9	123.0 (3)

Cl13—Zn1—Cl12	108.54 (4)	N2—C10—C11	115.8 (3)
Cl11—Zn1—Cl12	110.25 (4)	C9—C10—C11	121.2 (3)
Cl14—Zn1—Cl12	100.58 (4)	C15—C11—C12	117.6 (3)
Cl22—Zn2—Cl22 ⁱ	105.21 (5)	C15—C11—C10	121.1 (3)
Cl22—Zn2—Cl21	117.78 (4)	C12—C11—C10	121.3 (3)
Cl22 ⁱ —Zn2—Cl21	107.29 (3)	C13—C12—C11	120.3 (3)
Cl22—Zn2—Cl21 ⁱ	107.30 (3)	C13—C12—H12	119.9
Cl22 ⁱ —Zn2—Cl21 ⁱ	117.77 (4)	C11—C12—H12	119.9
Cl21—Zn2—Cl21 ⁱ	102.14 (5)	N3—C13—C12	119.4 (3)
C2—N1—C3	122.8 (3)	N3—C13—H13	120.3
C2—N1—H1N	117 (3)	C12—C13—H13	120.3
C3—N1—H1N	120 (3)	N3—C14—C15	118.9 (4)
C10—N2—C6	117.4 (3)	N3—C14—H14	120.5
C13—N3—C14	123.0 (3)	C15—C14—H14	120.5
C13—N3—H3N	118 (3)	C14—C15—C11	120.8 (3)
C14—N3—H3N	119 (3)	C14—C15—H15	119.6
C18—N4—C17	122.8 (3)	C11—C15—H15	119.6
C18—N4—H4N	115 (3)	C17—C16—C24	119.0 (3)
C17—N4—H4N	122 (3)	C17—C16—C8	116.2 (3)
C2—C1—C5	119.6 (4)	C24—C16—C8	124.7 (3)
C2—C1—H1	120.2	N4—C17—C16	120.7 (3)
C5—C1—H1	120.2	N4—C17—H17	119.6
N1—C2—C1	119.7 (4)	C16—C17—H17	119.6
N1—C2—H2	120.1	N4—C18—C19	120.5 (3)
C1—C2—H2	120.1	N4—C18—H18	119.8
N1—C3—C4	119.0 (4)	C19—C18—H18	119.8
N1—C3—H3	120.5	C18—C19—C20	120.3 (3)
C4—C3—H3	120.5	C18—C19—C24	118.6 (3)
C3—C4—C5	119.8 (4)	C20—C19—C24	121.0 (3)
C3—C4—H4	120.1	C21—C20—C19	119.5 (3)
C5—C4—H4	120.1	C21—C20—H20	120.3
C1—C5—C4	118.8 (3)	C19—C20—H20	120.3
C1—C5—C6	119.8 (3)	C20—C21—C22	120.1 (3)
C4—C5—C6	121.4 (3)	C20—C21—H21	119.9
N2—C6—C7	123.3 (3)	C22—C21—H21	119.9
N2—C6—C5	115.3 (3)	C23—C22—C21	122.1 (3)
C7—C6—C5	121.2 (3)	C23—C22—H22	118.9
C8—C7—C6	119.0 (3)	C21—C22—H22	118.9
C8—C7—H7	120.5	C22—C23—C24	119.6 (3)
C6—C7—H7	120.5	C22—C23—H23	120.2
C7—C8—C9	117.7 (3)	C24—C23—H23	120.2
C7—C8—C16	122.7 (3)	C23—C24—C16	124.0 (3)
C9—C8—C16	119.6 (3)	C23—C24—C19	117.6 (3)
C10—C9—C8	119.6 (3)	C16—C24—C19	118.3 (3)

Symmetry code: (i) $-x+1, y, -z+3/2$.

Hydrogen-bond geometry (Å, °)

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N1—H1 <i>N</i> ···C121 ⁱⁱ	0.85 (1)	2.27 (2)	3.084 (3)	161 (3)
N3—H3 <i>N</i> ···C112 ⁱⁱⁱ	0.85 (1)	2.71 (3)	3.291 (3)	127 (3)
N3—H3 <i>N</i> ···C114 ⁱⁱⁱ	0.85 (1)	2.47 (2)	3.203 (3)	144 (3)
N4—H4 <i>N</i> ···C112 ^{iv}	0.85 (1)	2.41 (2)	3.125 (3)	142 (3)
N4—H4 <i>N</i> ···C122 ^v	0.85 (1)	2.74 (3)	3.264 (3)	121 (3)
C2—H2···C113 ^{vi}	0.93	2.87	3.551 (4)	131
C3—H3···C111 ^{vii}	0.93	2.94	3.823 (4)	158
C4—H4···C114 ^{viii}	0.93	2.72	3.316 (4)	123
C7—H7···C114 ^{viii}	0.93	2.73	3.589 (3)	155
C12—H12···C122 ^{ix}	0.93	2.88	3.607 (4)	136
C13—H13···C112 ⁱⁱⁱ	0.93	2.71	3.287 (4)	121
C14—H14···C111 ^{vi}	0.93	2.83	3.548 (4)	135
C15—H15···C114 ^{vi}	0.93	2.93	3.588 (4)	129
C17—H17···C122 ^v	0.93	2.77	3.320 (4)	119
C18—H18···C112 ^{iv}	0.93	2.85	3.335 (3)	114
C18—H18···C113 ^{iv}	0.93	2.88	3.759 (3)	159

Symmetry codes: (ii) $-x+3/2, y+1/2, -z+3/2$; (iii) $x, y+1, z$; (iv) $-x+1, y, -z+1/2$; (v) $-x+1, -y+1, -z+1$; (vi) $-x+3/2, y+1/2, -z+1/2$; (vii) $-x+3/2, -y+3/2, -z+1$; (viii) $x, -y+1, z+1/2$; (ix) $-x+1, -y+2, -z+1$.