

A cationic zinc(II) complex of a new ligand based on *N,N,N',N'*-tetramethylstreptamine 2,4,6-orthoformate as the trichloro(pyridine)-zincate(II) salt

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Key indicators

Single-crystal X-ray study

$T = 143\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.005\text{ \AA}$

R factor = 0.029

wR factor = 0.068

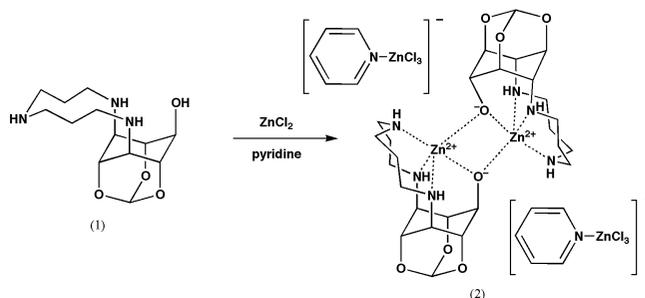
Data-to-parameter ratio = 13.8

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the title compound, *rac*-Bis[μ -(1*R*,2*S*,12*R*,13*S*,15*S*,17*S*,18*r*)-14,16,19-trioxa-3,7,11-triazatetracyclo[13.3.1.0^{2,13}.0^{12,17}]nonadecan-18-olato-1*k*³*N*³,*N*⁷,*N*¹¹:2*k*²*O*¹⁸]dizinc(II) bis[trichloro-(pyridine)zincate(II)], $[\text{Zn}_2(\text{C}_{13}\text{H}_{22}\text{N}_3\text{O}_4)_2][\text{ZnCl}_3(\text{C}_5\text{H}_4\text{N})]_2$, the cation displays crystallographic inversion symmetry. The geometry at zinc is trigonal bipyramidal. Three hydrogen bonds $\text{N}-\text{H}\cdots\text{Cl}-\text{Zn}$ lead to the formation of columns parallel to the *a* axis.

Comment

The previous communication (Jones *et al.*, 2003) described the crystal and molecular structure of a cationic zinc complex, of interest as a potential leaving group in models for certain aspects of catalysis in metalloenzymes. Crystal structures also contain a wealth of potential information about reactivity, but evidence from a single structure (which may be 'basically anecdotal'; Kirby, 1994) should be regarded with caution. We report here a second structure, (2), containing the same dication (but with a different counter-ion). The structure was determined because it was thought that a different, possibly monomeric form of the zinc complex might have been formed (see *Experimental*). However, the structure solution (Fig. 1) revealed the same dimeric dication, again with inversion symmetry, but with the complex anion $[\text{Zn}(\text{py})\text{Cl}_3]^-$ replacing chloride as counter-ion. The formation of the dimeric complex in two different structures with distinctly different counter-ions, and in the presence of a potentially competing ligand (pyridine), suggests that the species is relatively stable and not just the 'accidental' result of a compromise between packing forces in a specific structure.



The cations of the two compounds are structurally similar, as would be expected; the general comments of the previous paper are thus valid for the current structure (*e.g.* the inversion symmetry and the trigonal-bipyramidal geometry at zinc; however, some differences are presented below). We also have good spectroscopic evidence that the structures are similar in solution (Beckmann, 1998). A least-squares fit of the asymmetric unit of the two cations (Fig. 2) shows that the ZnNC_3N

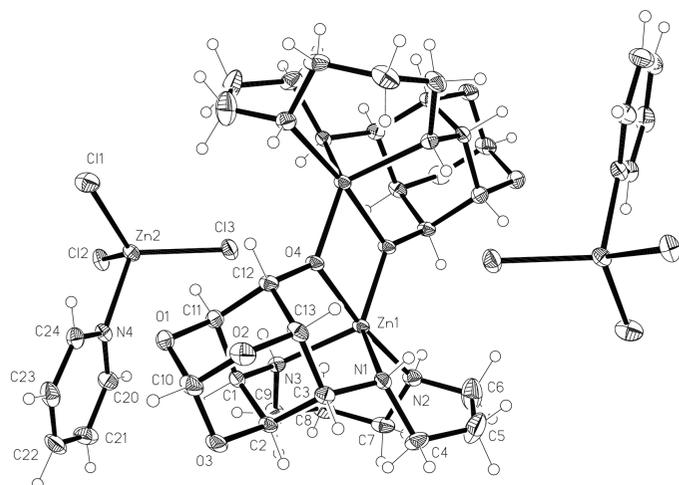


Figure 1
The structure of the title compound in the crystal. Ellipsoids are drawn at the 30% probability level. H-atom radii are arbitrary.

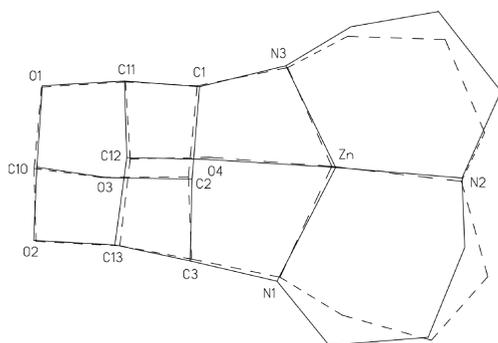


Figure 2
Least-squares fit of the chemically identical cations (asymmetric unit only, H atoms have been omitted) of the title compound (dashed bonds) and that of the previous paper (full bonds; Jones *et al.*, 2003).

rings differ in conformation between the two compounds; except for these three C atoms, however, the r.m.s. displacement is only 0.09 Å. Bond lengths and angles at zinc (see Table 1 for exact values and s.u.'s) differ appreciably for Zn—O_{4ax} (here 2.09, previously 2.16 Å) and O_{4eq}—Zn—N3 (here 124°, previously 107°).

The anion has distorted tetrahedral geometry at the central Zn atom. Three classical N—H...Cl—Zn hydrogen bonds (Table 2) are observed between anion and cation, the net effect of which is to form columns of anions and cations parallel to the *a* axis in the regions $x, y \simeq \frac{1}{2}$ (Fig. 3) and $x, y \simeq 0$. However, these interactions are appreciably longer than the N—H...Cl[−] of the previous structure, and are supplemented by a series of 'weak' C—H...X hydrogen bonds ($X = \text{Cl}$ and O; Table 2) of comparable lengths.

Experimental

Crystals of (2) were obtained fortuitously on adding pyridine to the combined 'waste' solutions from completed kinetic experiments (which had been retained for recycling) (Beckmann, 1998). Crystals began to grow from an aqueous solution (also containing *N*-ethylmorpholine buffer and KCl) some days after adding pyridine.

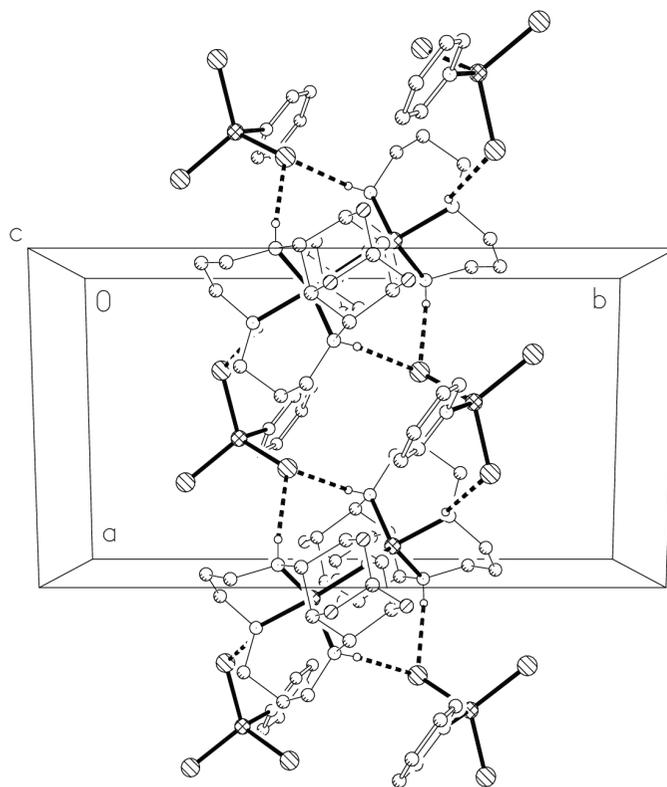


Figure 3
Packing diagram of the title compound, showing one column (see text). Hydrogen bonds are indicated by dashed lines. H atoms not involved in classical hydrogen bonds have been omitted.

Crystal data

[Zn₂(C₁₃H₂₂N₃O₄)₂]
[ZnCl₃(C₅H₄N)]₂
M_r = 1201.05
Monoclinic, *P*2₁/*c*
a = 9.5416 (15) Å
b = 17.491 (2) Å
c = 14.098 (3) Å
 β = 104.366 (10)°
V = 2279.2 (7) Å³
Z = 2

D_x = 1.750 Mg m^{−3}
Mo *K*α radiation
Cell parameters from 54 reflections
 θ = 10–11.5°
 μ = 2.49 mm^{−1}
T = 143 (2) K
Tablet, colourless
0.50 × 0.45 × 0.15 mm

Data collection

Stoe Stadi-4 diffractometer
 ω/θ scans
Absorption correction: ψ scans
(*XEMP*; Siemens, 1994)
*T*_{min} = 0.670, *T*_{max} = 0.984
8250 measured reflections
4031 independent reflections
3390 reflections with $I > 2\sigma(I)$

*R*_{int} = 0.035
 θ_{max} = 25.0°
h = −11 → 11
k = −20 → 20
l = 0 → 16
3 standard reflections
frequency: 60 min
intensity decay: 4%

Refinement

Refinement on *F*²
 $R[F^2 > 2\sigma(F^2)] = 0.029$
 $wR(F^2) = 0.069$
S = 1.04
4031 reflections
292 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0268P)^2 + 1.2592P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.47 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.38 \text{ e } \text{Å}^{-3}$

Table 1
Selected geometric parameters (Å, °).

Zn1—O4 ⁱ	1.9590 (19)	Zn2—N4	2.070 (2)
Zn1—N1	2.082 (2)	Zn2—Cl1	2.2314 (9)
Zn1—N3	2.083 (3)	Zn2—Cl2	2.2496 (9)
Zn1—O4	2.0860 (19)	Zn2—Cl3	2.2615 (9)
Zn1—N2	2.106 (3)		
O4 ⁱ —Zn1—N1	133.76 (9)	Cl1—N3—C9	111.5 (2)
O4 ⁱ —Zn1—N3	123.80 (10)	Cl1—N3—Zn1	112.41 (18)
N1—Zn1—N3	98.10 (10)	C9—N3—Zn1	119.17 (19)
O4 ⁱ —Zn1—O4	76.99 (8)	Cl2—O4—Zn1 ⁱ	135.25 (17)
N1—Zn1—O4	86.78 (9)	Cl2—O4—Zn1	121.35 (16)
N3—Zn1—O4	88.04 (9)	Zn1 ⁱ —O4—Zn1	103.01 (8)
O4 ⁱ —Zn1—N2	96.93 (9)	N4—Zn2—Cl1	103.78 (7)
N1—Zn1—N2	95.22 (10)	N4—Zn2—Cl2	102.62 (7)
N3—Zn1—N2	98.26 (10)	Cl1—Zn2—Cl2	117.04 (4)
O4—Zn1—N2	173.04 (9)	N4—Zn2—Cl3	108.25 (7)
C3—N1—C4	111.2 (2)	Cl1—Zn2—Cl3	113.08 (4)
C3—N1—Zn1	112.64 (18)	Cl2—Zn2—Cl3	110.89 (3)
C4—N1—Zn1	112.96 (19)	C20—N4—C24	118.3 (3)
C7—N2—C6	115.0 (3)	C20—N4—Zn2	119.5 (2)
C7—N2—Zn1	118.0 (2)	C24—N4—Zn2	122.0 (2)
C6—N2—Zn1	110.3 (2)		

Symmetry code: (i) 2 - x, 1 - y, 1 - z.

Table 2
Hydrogen-bonding 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—H01...Cl3 ⁱ	0.81 (2)	2.66 (2)	3.449 (3)	165 (3)
N2—H02...Cl2 ⁱⁱ	0.80 (2)	2.72 (3)	3.356 (3)	138 (3)
N3—H03...Cl3	0.82 (2)	2.52 (2)	3.325 (3)	172 (3)
C3—H3...Cl1 ⁱⁱⁱ	1.00	2.70	3.664 (3)	162
C23—H23...Cl1 ^{iv}	0.95	2.75	3.638 (3)	156
C24—H24...Cl1	0.95	2.90	3.483 (3)	121
C4—H4A...Cl2 ^v	0.99	2.73	3.653 (4)	155
C7—H7A...Cl2 ^v	0.99	2.90	3.856 (3)	164
C7—H7B...Cl2 ⁱⁱ	0.99	2.85	3.514 (3)	125
C5—H5B...O1 ⁱⁱⁱ	0.99	2.48	3.257 (4)	135
C20—H20...O2 ^{vi}	0.95	2.47	3.203 (4)	134

Symmetry codes: (i) 2 - x, 1 - y, 1 - z; (ii) 1 - x, 1 - y, 1 - z; (iii) 2 - x, ½ + y, ½ - z; (iv) x, ½ - y, z - ½; (v) 1 - x, ½ + y, ½ - z; (vi) x - 1, y, z.

H atoms of NH groups were identified in difference syntheses and refined freely, but with a common N—H distance restraint. Other H atoms were included using a riding model with fixed C—H bond lengths of 1.00 (CH) or 0.99 Å (CH₂); *U*_{iso}(H) values were fixed at 1.2*U*_{eq} of the parent atom. One curious feature of the structure is the very short bond C5—C6, which at 1.442 (5) Å is much shorter than the corresponding bond in the previous paper, 1.524 (3) Å. We attribute this to libration effects arising from the appreciably higher *U* values of C5 and C6, or to a slight disorder of these atoms.

Data collection: *DIF4* (Stoe & Cie, 1992); cell refinement: *DIF4*; data reduction: *REDU4* (Stoe & Cie, 1992); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *SHELXL97*.

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