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(μ_3-Trithiocyanurato-$\kappa^6N^1,S^2:N^3,S^4:N^5,S^6$)tris[($N,N,N',N'',N''$-pentamethyldiethylenetriamine-κ^3N,N',N'')zinc(II)] tris(perchlorate)

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Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.004 Å
Disorder in main residue
R factor = 0.023
wR factor = 0.076
Data-to-parameter ratio = 24.6

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

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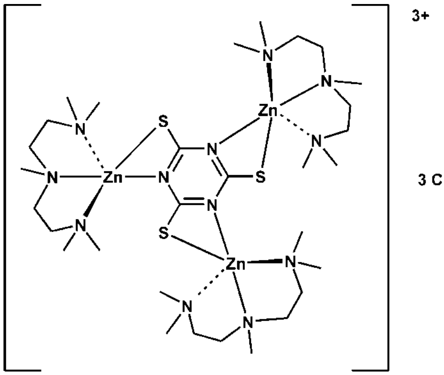
In the title compound, $[Zn_3(C_3N_3S_3)(C_9H_{23}N_3)_3](ClO_4)_3$, the three Zn^{II} centres, related by the body-diagonal threefold symmetry along [111], are bridged by a trithiocyanurate(3−) anion (ttc), with each centre having a distorted trigonal–bipyramidal geometry and bonded by three N atoms of a tridentate N,N,N',N'',N''-pentamethyldiethylenetriamine ligand, and one S and one N atoms of the ttc ligand. The secondary structure is stabilized by a variety of non-bonding C—H···O interactions, connecting the cation and perchlorate anions.

Comment

This paper represents a continuation of our systematic crystallographic study of Zn^{II} complexes bearing variously deprotonated trithiocyanuric acid (ttcH$_n$, n = 0–3) and an aliphatic polydentate amine (Marek *et al.*, 2003, 2007; Trávníček *et al.*, 2007). One of the goals of this study is to monitor the nuclearity of the prepared Zn^{II} complexes as a function mainly of the denticity of the amine used. Here, we report the synthesis and structure of the title compound, (I), which represents the first trinuclear Zn^{II} complex involving an anion of ttc as a ligand bridging three metal centres. Moreover, it is the first example of a Zn complex bearing both the ttc anion and N,N,N',N'',N''-pentamethyldiethylenetriamine (pmdien) which has bee prepared and structurally characterized in its mononuclear [Zn(pmdien)(ttcH)], (II) (Marek *et al.*, 2007), dinuclear [{Zn(pmdien)}$_2$(μ-ttc)](ClO$_4$)·H$_2$O, (III), (Trávníček *et al.*, 2007), and trinuclear forms, (I) (this work).



(I)

The molecular structure of the title compound, (I), is depicted in Fig. 1. The structure consists of a trinuclear Zn^{II} cation and three perchlorate anions. The three Zn^{II} metal centres are related by body-diagonal threefold symmetry along [111] and bridged by an essentially planar [out-of-plane

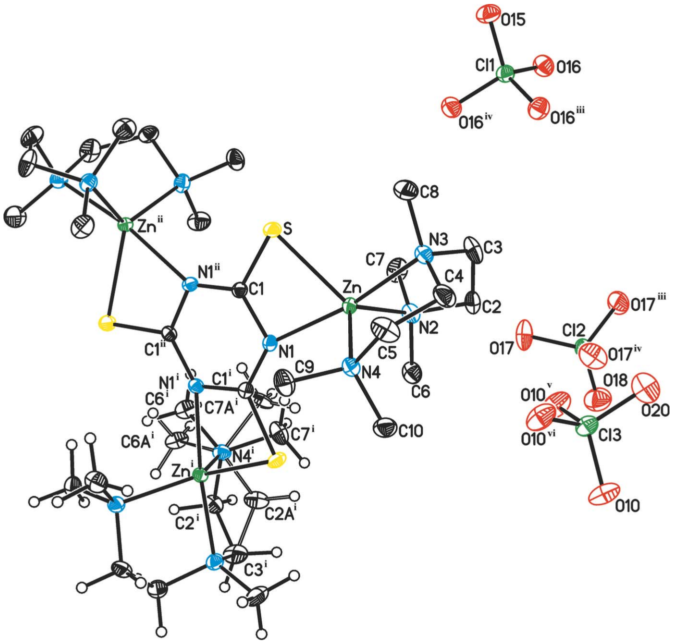


Figure 1

The molecular structure of (I). The non-H atoms are drawn as 50% probability displacement ellipsoids. Open lines indicate the minor (with occupation ~25%) disordered part of the pmdien fragment. Most of the H atoms and two of three disordered pmdien fragments have been omitted for clarity; the remaining H atoms are drawn as small spheres of arbitrary radius. [Symmetry codes: (i) y, z, x; (ii) z, x, y; (iii) $z - \frac{1}{2}, \frac{1}{2} - x, 1 - y$; (iv) $-y + \frac{1}{2}, -z + 1, x + \frac{1}{2}$; (v) $-z + 1, x + \frac{1}{2}, -y + \frac{3}{2}$; (vi) $y - \frac{1}{2}, -z + \frac{3}{2}, -x + 1$].

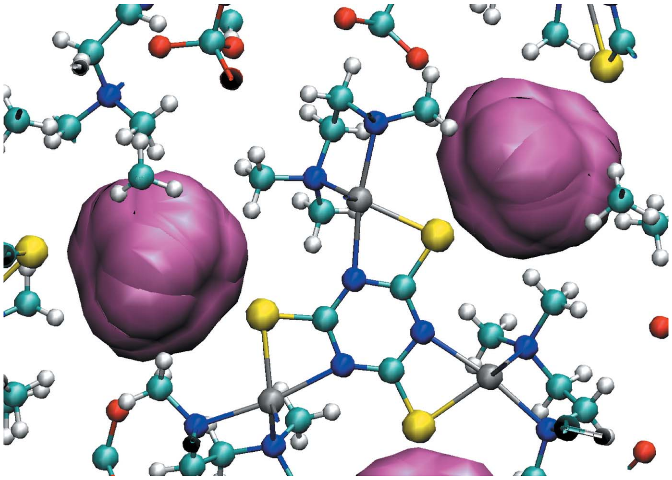


Figure 2

Part of the crystal structure of (I), showing the formation of voids. The cavities generated by *VMD* (Humphrey *et al.*, 1996) and a probe with radius 1.5 Å are shown in pink.

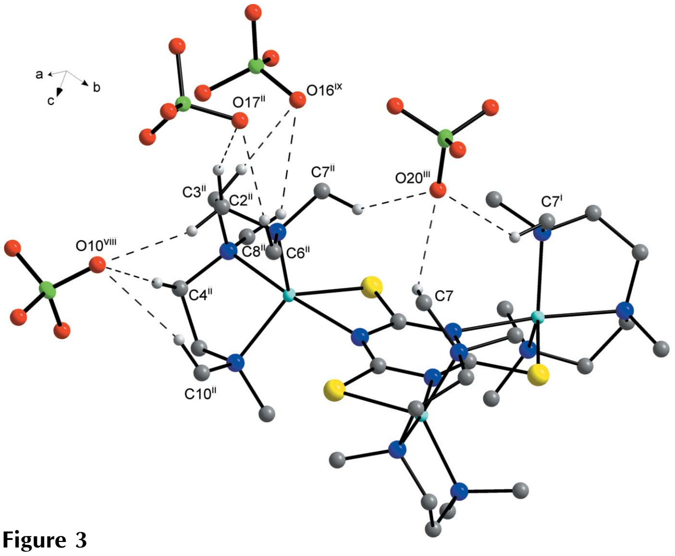


Figure 3

Part of the crystal structure of (I), showing C—H···O non-bonding interactions as dashed lines. [Symmetry codes: (i) y, z, x; (ii) z, x, y; (iii) $z - \frac{1}{2}, \frac{1}{2} - x, 1 - y$; (viii) $\frac{3}{2} - y, 1 - z, \frac{1}{2} + x$; (ix) $\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$]. Minor disordered pmdien fragments and H atoms not involved in hydrogen bonding have been omitted for clarity.

(C_3N_3) deviations are 0.011 (3) Å for C1 and 0.008 (2) Å for N1 (Brandenburg, 2006)] trithiocyanurate(3−) anion (ttc). Each Zn^{II} ion adopts a distorted trigonal–bipyramidal geometry (τ = 0.82) (Addison *et al.*, 1984) and is bonded by three N atoms of pmdien, and one S and one N atoms of the ttc ligand. The separation Zn···Zn = 6.0283 (5) Å. For comparison, the Ru···Ru distances in a similar trinuclear Ru complex bridged also by the ttc ligand are in the range 5.838 (3)–5.894 (2) Å (Kar *et al.*, 2004). The Zn—N(pmdien) bond distances are in the range 2.083 (2)—2.159 (2) Å in (I), while Zn—N1(ttc) and Zn—S(ttc) are 2.206 (2) and 2.3793 (8) Å, respectively. The delocalization of the electron density within the bridging μ-ttc ligand is affected significantly by the coodination of ttc to metal centres *via* both N and S atoms. The main consequence of the last-mentioned fact is elongation of the S—C bond distances within the μ-ttc ligand when the S atom is coordinated to zinc. These bond lengths for the Zn-coordinated S atom are 1.711 (3) Å in (I), 1.732 (4) Å in (II), and 1.734 (2) and 1.724 (2) Å in (III). The C—S distances for the uncoordinated S atoms are 1.688 (4) and 1.700 (4) Å in (II), and 1.698 (2) Å in (III). For comparison, the average value of a C═S double bond is 1.655 (11) Å (Cambridge Structural Database, Version 5.27.1; Allen, 2002).

The arrangement of trinuclear cations and perchlorate anions causes the formation of approximately spherical voids in the crystal structure of (I) (Fig. 2). These cavities are at a distance of 3.8 Å from S1, and their volume is 63 (6) Å^3 (Spek, 2003). The secondary structure of (I) is stabilized by a variety of non-bonding interactions of the type C—H···O, connecting the cation and perchlorate anions (Table 1 and Fig. 3).

Experimental

N,*N*,*N*′,*N*″,*N*″-Pentamethyldiethylenetriamine (pmdien) (0.2 ml, 1 mmol) was added to an ethanol solution (60 ml) of zinc(II) perchlorate hexahydrate (0.37 g, 1 mmol) and stirred at room temperature. Trithiocyanuric acid (ttcH$_3$) (0.06 g, 0.33 mmol) and triethylamine (0.1 ml, 1 mmol), dissolved in 50 ml of ethanol, were added dropwise to this solution. A white precipitate formed after some time and the reaction mixture was stirred further for 1 h. The precipitate was filtered off and washed with several portions of ethanol. The mother liquor was left to stand for crystallization at

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room temperature. After several weeks, crystals suitable for X-ray analysis were obtained. Yield 63%. Elemental analysis (%) calculated for $C_{30}H_{69}Cl_3N_{12}O_{12}S_3Zn_3$: C 30.3, H 5.8, N 14.1; found: C 30.1, H 5.8, N 14.0.

Crystal data

$[Zn_3(C_3N_3S_3)(C_9H_{23}N_3)_3](ClO_4)_3$
M_r = 1188.61
Cubic, $P2_13$
a = 17.32348 (16) Å
V = 5198.83 (8) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 1.71 mm^{-1}
T = 120 (2) K
0.30 × 0.30 × 0.20 mm

Data collection

Kuma KM-4 CCD diffractometer
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2006)
$T_{\min}$ = 0.829, $T_{\max}$ = 1.000 (expected range = 0.589–0.710)
39533 measured reflections
5689 independent reflections
5055 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.030

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.023
$wR(F^2)$ = 0.076
S = 1.03
5689 reflections
231 parameters
51 restraints
H-atom parameters constrained
$\Delta\rho_{\max}$ = 0.71 e Å^{-3}
$\Delta\rho_{\min}$ = −0.61 e Å^{-3}
Absolute structure: Flack (1983), 2562 Friedel pairs
Flack parameter: −0.028 (9)

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

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2A···O17	0.99	2.85	3.659 (4)	140
C6—H6C···O17	0.98	2.55	3.475 (4)	157
C6—H6C···O17	0.98	2.55	3.475 (4)	157
C7—H7A···O17	0.98	2.91	3.752 (4)	144
C2—H2B···O10$^{\rm i}$	0.99	2.42	3.358 (4)	158
C4—H4B···O10$^{\rm i}$	0.99	2.52	3.506 (4)	177
C5—H5B···O18$^{\rm i}$	0.99	2.79	3.515 (3)	130
C10—H10B···O10$^{\rm i}$	0.98	2.69	3.652 (3)	167
C8—H8C···O16$^{\rm ii}$	0.98	2.83	3.556 (4)	132
C3—H3B···O16$^{\rm ii}$	0.99	2.45	3.417 (9)	165
C7—H7C···O20$^{\rm iii}$	0.98	2.71	3.438 (4)	131
C7A—H7E···O20$^{\rm iii}$	0.98	2.61	2.888 (10)	96

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

A part of the pmdien ligand has been refined as disordered between two positions defined by an approximately 33–43° angular rotation of the disordered fragment around the Zn—N2 bond. All H atoms were located in a difference map and refined using the riding model with C—H distances of 0.98 ($C_{\rm methyl}$) and 0.99 Å (CH_2), and with $U_{\rm iso}$(H) values of $1.2U_{\rm eq}(C_{CH_2})$ or $1.5U_{\rm eq}(C_{\rm methyl})$. C2, C3, C6, C7 and N2 are disordered over two positions; the site occupancy factors refined to 0.758 (6) and 0.242 (6).

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Johnson & Burnett, 1996), *VMD* (Version 1.8.5; Humphrey *et al.*, 1996) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *SHELXL97*, *PLATON* (Spek, 2003) and *DIAMOND*.

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References

Addison, A. W., Rao, T. N., Reedijk, J., Rijin, J. V. & Verchoor, G. C. (1984). *J. Chem. Soc. Dalton Trans.* pp. 1349–1356.
Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Brandenburg, K. (2006). *DIAMOND*. Release 3.1d. Crystal Impact GbR, Bonn, Germany.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Humphrey, W., Dalke, A. & Schulten, K. (1996). *J. Mol. Graph.* **14**, 33–38.
Johnson, C. K. & Burnett, M. N. (1996). *ORTEPIII*. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
Kar, S., Pradhan, B., Sinha, R. K., Kundu, T., Kodgire, P., Rao, K. K., Puranik, V. G. & Lahiri, G. K. (2004). *Dalton Trans.* pp. 1752–1760.
Marek, J., Kopel, P. & Trávníček, Z. (2003). *Acta Cryst.* C**59**, m558–m560.
Marek, J., Trávníček, Z. & Čermáková, Š. (2007). *Acta Cryst.* E**63**, m725–m727.
Oxford Diffraction (2006). *CrysAlis CCD* and *CrysAlis CCD*. Versions 1.171.31.7. Oxford Diffraction Ltd, Abingdon, Oxfordshire, England.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Trávníček, Z., Marek, J. & Čermáková, Š. (2007). *Acta Cryst.* E**63**, m795–m797.

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