

References

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Dichlorobis(5,7-dimethyl[1,2,4]triazolo[1,5-*a*]pyrimidine-*N*³)zinc(II)

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Abstract

The synthesis and crystal structure of the title compound, [ZnCl₂(C₇H₈N₄)₂], obtained by the reaction of zinc(II) chloride with 5,7-dimethyl[1,2,4]triazolo[1,5-*a*]pyrimidine (dmtp), are reported. The Zn atom is tetrahedrally coordinated by two Cl atoms at distances of 2.197 (1) and 2.2499 (8) Å and to two N3 atoms of two independent molecules of dmtp at distances of 2.058 (2) and 2.020 (2) Å. One of the dmtp ligand types is associated in couples by stacking interactions with an interplanar distance of 3.36 (1) Å.

Comment

5,7-Dimethyl[1,2,4]triazolo[1,5-*a*]pyrimidine (dmtp) is a ligand especially suited to mimicking purine rings, from which it differs mainly in having a pyrimidine N atom in a bridgehead position. Crystallographic studies carried out on metal–dmtp complexes have indicated that the N3 atom in the monodentate form is the most preferred binding site. This coordination mode has been found for [Cd(dmtp)₂(NCS)₂(H₂O)₂] and [Hg(dmtp)₂(SCN)₂]

(Dillen, Lenstra, Haasnoot & Reedijk, 1983), [Cu(dmtp)₂(SCN)₂]₂ and [Pt(dmtp)₄][Pt(SCN)₆] (Biagini-Cingi, Manotti-Lanfredi, Tiripicchio, Haasnoot & Reedijk, 1983), β-[Cu(dmtp)₂(SCN)₂]₂ (Haasnoot, Driessen & Reedijk, 1984), [CoHg(dmtp)₃(SCN)₄(H₂O)]₂ (Biagini-Cingi, Manotti-Lanfredi, Tiripicchio, Haasnoot & Reedijk, 1984), [FeHg(dmtp)₂(NCS)₄(H₂O)_{1.5}], [FeHg(dmtp)₂(NCS)₄(H₂O)] and [FeHg(dmtp)(NCS)₄(H₂O)₂(Me₂CO)] (Biagini-Cingi, Manotti-Lanfredi, Tiripicchio, Haasnoot & Reedijk, 1985), [Cu(dmtp)₄(H₂O)₂][PF₆]₂ (Favre, Haasnoot & Reedijk, 1986), [CuHg(dmtp)₂(μ-SCN)₃] (Biagini-Cingi, Manotti-Lanfredi, Tiripicchio, Haasnoot & Reedijk, 1986), [Ni(dmtp)₂(H₂O)₄](H₂O)₂I₂ and [Ni(dmtp)₄(H₂O)₂](dmtp)₂(I₃)₂ (Lenstra, Bruins, Beurskens, Haasnoot & Reedijk, 1989) and [Pd(dmtp)₂Br₂][CH₃OH] (Hage, Graaff, Haasnoot, Kieler & Reedijk, 1990). A different coordination mode *via* N3 and N4 has been found in the cluster [Cu₄(dmtp)₄Cl₂][Cu₂Cl₄] (Haasnoot, Favre, Hinrichs & Reedijk, 1988).

As part of our work on the coordination chemistry of purine analogues (Sirera, Romero, Salas, Sánchez & Moreno, 1991; Salas *et al.*, 1992; Romero, Salas, Quirós, Williams & Molina, 1993), we report here the synthesis and crystal structure of the metal complex [Zn(dmtp)₂Cl₂] (I).

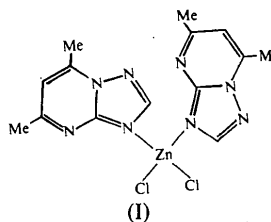


Fig. 1 shows a projection of the molecule with the atomic numbering scheme. The crystal structure of the title compound consists of monomeric Zn(dmtp)₂Cl₂ units. The coordination polyhedron around the Zn atom is a distorted tetrahedron which involves two N atoms of two independent dmtp ligands and two Cl atoms. The dmtp ligands act in a monodentate manner through N3. The Zn–N3 distances of 2.058 (2) (N3A) and 2.020 (2) Å (N3B) are in agreement with those found for the analogous complex dibromobis([1,2,4]triazolo[1,5-*a*]pyrimidine-*N*³)zinc(II) hemihydrate (Sanni *et al.*, 1986). The Zn–Cl distances of 2.197 (1) (Zn–Cl1) and 2.2499 (8) Å (Zn–Cl2) are in the expected range for metal complexes with ZnN₂Cl₂ distorted tetrahedral environments (Preston & Kennard, 1969; Baenziger & Schultz, 1971; Steffen & Palenik, 1977; Beauchamp, 1984; Cariati *et al.*, 1983; Bharadwaj, Schugar & Potenza, 1991).

The structural parameters of the two independent dmtp molecules are quite regular; both are planar

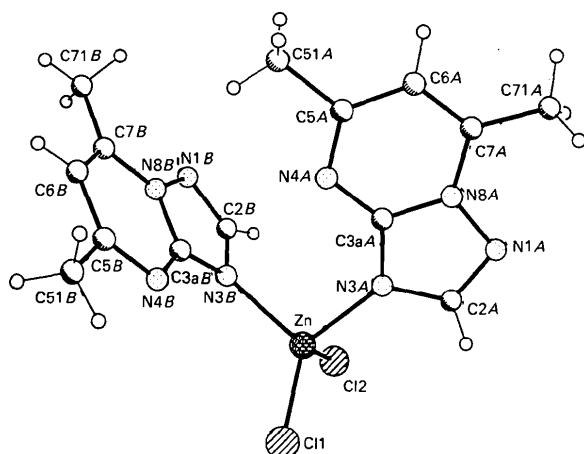


Fig. 1. A perspective view of the $\text{Zn}(\text{dtmp})_2\text{Cl}_2$ complex. The type A ligand is numbered N1A–N8A.

[maximum deviations from the mean planes through the two molecules are 0.013 (3) for C3aA and 0.011 (3) Å for C7B]. The dihedral angle between these planes is 101.8 (1)°.

A stereoscopic view of the unit-cell contents is shown in Fig. 2. The dtmp ligands of type A are associated in couples by stacking interactions, the two molecules being related by an inversion centre with a distance between them of 3.36 (1) Å.

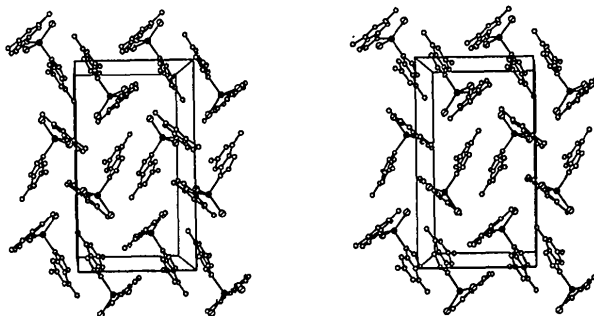


Fig. 2. Stereoscopic packing diagram of $\text{Zn}(\text{dtmp})_2\text{Cl}_2$.

Experimental

$[\text{Zn}(\text{dtmp})_2\text{Cl}_2]$ was prepared as colourless crystals by slow evaporation at room temperature of an aqueous solution containing 2 mmol of dtmp and 1 mmol of ZnCl_2 in 40 ml water.

Crystal data

$[\text{ZnCl}_2(\text{C}_7\text{H}_8\text{N}_4)_2]$

$M_r = 432.6$

Orthorhombic

Pbca

$a = 10.521$ (1) Å

$b = 18.425$ (3) Å

$c = 18.449$ (2) Å

Mo $K\alpha$ radiation

$\lambda = 0.7107$ Å

Cell parameters from 25 reflections

$\theta = 7.42$ – 21.73°

$\mu = 1.72$ mm^{-1}

$T = 295$ K

$V = 3576$ (1) Å³

$Z = 8$

$D_x = 1.608$ Mg m^{-3}

$D_m = 1.60$ Mg m^{-3}

$0.45 \times 0.40 \times 0.30$ mm

Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer

ω - $5/3\theta$ scans

Absorption correction:

from ψ scans of high χ reflections

$T_{\min} = 0.89$, $T_{\max} = 1.00$

4173 measured reflections

4173 independent reflections

2613 observed reflections

$[I > 3\sigma(I)]$

$\theta_{\max} = 28^\circ$

$h = 0 \rightarrow 13$

$k = 0 \rightarrow 24$

$l = 0 \rightarrow 21$

3 standard reflections

frequency: 60 min

intensity variation: 3.2%

Refinement

Refinement on F

$R = 0.026$

$wR = 0.027$

$S = 1.50$

2613 reflections

275 parameters

Only coordinates of H atoms

refined

$w = 1/\sigma^2(F_o)$

$(\Delta/\sigma)_{\max} = 0.12$

$\Delta\rho_{\max} = 0.3$ e \AA^{-3}

$\Delta\rho_{\min} = -0.25$ e \AA^{-3}

Atomic scattering factors

from *International Tables*

for X-ray Crystallography

(1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

	$B_{\text{eq}} = (4/3)\sum_i \sum_j \beta_{ij} a_i \cdot a_j \cdot$			
	x	y	z	B_{eq}
Zn	0.18655 (3)	0.14762 (2)	0.10492 (2)	2.465 (5)
Cl1	0.30474 (9)	0.24541 (5)	0.11490 (5)	5.05 (2)
Cl2	0.05785 (8)	0.11995 (5)	0.19831 (4)	3.60 (2)
N1A	0.4122 (2)	−0.0403 (1)	0.1342 (1)	3.34 (5)
C2A	0.3588 (3)	0.0219 (2)	0.1509 (2)	3.20 (6)
N3A	0.2982 (2)	0.0565 (1)	0.0951 (1)	2.70 (4)
C3aA	0.3155 (3)	0.0121 (1)	0.0386 (1)	2.33 (5)
N4A	0.2774 (2)	0.0209 (1)	−0.0298 (1)	2.50 (4)
C5A	0.3105 (3)	−0.0316 (2)	−0.0752 (2)	2.68 (5)
C51A	0.2664 (3)	−0.0236 (2)	−0.1520 (2)	3.59 (7)
C6A	0.3812 (3)	−0.0928 (2)	−0.0534 (2)	3.13 (6)
C7A	0.4192 (3)	−0.1016 (2)	0.0163 (2)	2.95 (6)
C71A	0.4938 (3)	−0.1627 (2)	0.0467 (2)	4.25 (8)
N8A	0.3841 (2)	−0.0464 (1)	0.0619 (1)	2.54 (4)
N1B	−0.0624 (2)	0.0808 (1)	−0.0565 (1)	2.84 (5)
C2B	−0.0215 (3)	0.0937 (2)	0.0092 (2)	2.81 (5)
N3B	0.0761 (2)	0.1413 (1)	0.0156 (1)	2.48 (4)
C3aB	0.0997 (3)	0.1605 (1)	−0.0531 (1)	2.17 (5)
N4B	0.1879 (2)	0.2064 (1)	−0.0780 (1)	2.70 (4)
C5B	0.1902 (3)	0.2146 (2)	−0.1497 (2)	2.85 (5)
C51B	0.2885 (3)	0.2652 (2)	−0.1786 (2)	4.31 (8)
C6B	0.1056 (3)	0.1787 (2)	−0.1967 (2)	2.90 (6)
C7B	0.0157 (3)	0.1329 (2)	−0.1703 (2)	2.58 (5)
C71B	−0.0817 (3)	0.0926 (2)	−0.2123 (2)	3.77 (7)
N8B	0.0165 (2)	0.1245 (1)	−0.0970 (1)	2.19 (4)

Table 2. Selected geometric parameters (Å, °)

Zn—Cl1	2.197 (1)	C7A—C71A	1.483 (4)
Zn—Cl2	2.2499 (8)	C7A—N8A	1.369 (4)
Zn—N3A	2.058 (2)	N1B—C2B	1.308 (4)
Zn—N3B	2.020 (2)	N1B—N8B	1.376 (3)
N1A—C2A	1.313 (4)	C2B—N3B	1.356 (4)
N1A—N8A	1.373 (3)	N3B—C3aB	1.339 (3)
C2A—N3A	1.368 (4)	C3aB—N4B	1.336 (3)
N3A—C3aA	1.337 (3)	C3aB—N8B	1.365 (3)
C3aA—N4A	1.334 (3)	N4B—C5B	1.332 (4)
C3aA—N8A	1.367 (3)	C5B—C51B	1.491 (5)

N4A—C5A	1.326 (4)	C5B—C6B	1.408 (4)
C5A—C51A	1.497 (4)	C6B—C7B	1.358 (4)
C5A—C6A	1.410 (4)	C7B—C71B	1.484 (4)
C6A—C7A	1.356 (4)	C7B—N8B	1.362 (3)
Cl1—Zn—Cl2	117.54 (4)	N1A—N8A—C3aA	110.8 (2)
Cl1—Zn—N3A	110.72 (7)	N1A—N8A—C7A	126.9 (2)
Cl1—Zn—N3B	116.17 (7)	C3aA—N8A—C7A	122.4 (2)
Cl2—Zn—N3A	103.05 (7)	C2B—N1B—N8B	101.5 (2)
Cl2—Zn—N3B	105.41 (7)	N1B—C2B—N3B	116.5 (3)
N3A—Zn—N3B	102.09 (9)	Zn—N3B—C2B	122.9 (2)
C2A—N1A—N8A	102.0 (2)	Zn—N3B—C3aB	130.6 (2)
N1A—C2A—N3A	115.4 (3)	C2B—N3B—C3aB	103.3 (2)
Zn—N3A—C2A	125.4 (2)	N3B—C3aB—N4B	128.4 (2)
Zn—N3A—C3aA	130.2 (2)	N3B—C3aB—N8B	108.3 (2)
C2A—N3A—C3aA	103.9 (2)	N4B—C3aB—N8B	123.4 (2)
N3A—C3aA—N4A	128.6 (2)	C3aB—N4B—C5B	115.2 (2)
N3A—C3aA—N8A	108.0 (2)	N4B—C5B—C51B	116.1 (3)
N4A—C3aA—N8A	123.4 (2)	N4B—C5B—C6B	123.1 (3)
C3aA—N4A—C5A	115.5 (2)	C51B—C5B—C6B	120.8 (3)
N4A—C5A—C51A	116.4 (3)	C5B—C6B—C7B	120.7 (3)
N4A—C5A—C6A	122.8 (3)	C6B—C7B—C71B	127.2 (3)
C51A—Zn—C6A	120.8 (3)	C6B—C7B—N8B	115.1 (2)
C5A—C6A—C7A	121.4 (3)	C71B—C7B—N8B	117.7 (2)
C6A—C7A—C71A	127.2 (3)	N1B—N8B—C3aB	110.5 (2)
C6A—C7A—N8A	114.5 (3)	N1B—N8B—C7B	127.0 (2)
C71A—C7A—N8A	118.3 (3)	C3aB—N8B—C7B	122.5 (2)

Computing was by means of the Enraf-Nonius SDP system (B. A. Frenz & Associates, Inc., 1982) on a DEC MicroVAX II computer at the Centre de Diffractométrie Automatique, Université Lyon I.

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates and geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71613 (42 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1080]

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(5,5-Dimethyl-4,7-diazadecane-1,10-diamine-*N,N',N'',N'''*)(perchlorato-*O*)copper(II) Perchlorate

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Abstract

The Cu^{II} ion in the title complex, [Cu(ClO₄)₂(C₁₀H₂₆N₄)]ClO₄, is five-coordinate with four N atoms equatorial and one perchlorato O atom axial. The two asymmetric N atoms are of the same *R* or *S* configuration. Each six-membered ring is in a stable chair conformation and the central five-membered ring is in a skew form. Hydrogen bonds help stabilize the crystal structure.

Comment

The thermodynamic and kinetic properties of complexes in which linear tetraamines surround a Cu^{II} ion have been studied extensively. Previously we have reported the crystal structure of [*N,N'*-bis(3-