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7-Methyl-3-adeninium Trichloro(7-methyladenine-*N*⁹)zinc(II) Hydrate

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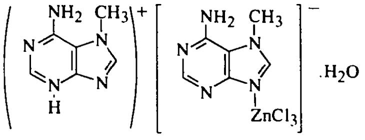
Abstract

The crystal structure of the title compound, ($C_6H_8N_5$)-[$ZnCl_3$($C_6H_7N_5$)].H_2O, contains 7-methyladeninium cations protonated at the N3 atom and trichloro(7-methyladenine)zinc(II) anions, with the Zn atom tetrahedrally coordinated by the N9 atom and three chlorine ligands. Both species are present as hydrogen-bonded centrosymmetric dimers stacked alternately in columns in the crystal.

Comment

The title compound, (1), was isolated in the course of an ongoing program of research into the metal complexes of heterocyclic bases. The N7 site of adenine is favoured for coordination of zinc when it is available, *e.g.* dichlorobis(purine)zinc(II) (Laity & Taylor, 1995), trichloro(adeninium)zinc(II) (Taylor, Vilkins & McCall, 1989) and trichloro(purinium)zinc(II) (Sheldrick, 1982), although N1 can also be a binding site, *e.g.* trichloro(9-methyladeninium)zinc(II) (McCall & Taylor, 1975). In this work, the intention was to study the coordination of zinc to adenine when the favoured N7 position is blocked.



(1)

The structure of (1) consists of trichloro(7-methyladenine)zinc(II) anions and protonated 7-methyladenine cations (Fig. 1). Zinc is coordinated *via* the N9 atom and its approximate tetrahedral stereochemistry is completed by three chlorine ligands. These metal–complex anions occur in the structure as centrosymmetric hydrogen-bonded dimers, with an N11—H···N1$^{\rm i}$ distance of 3.007 (3) Å [symmetry code: (i) $1-x$, $2-y$, $1-z$]. The Zn atom lies 0.382 (2) Å from the least-squares plane of the purine framework. The other 7-methyladenine moiety is protonated at the N3 position. This is a surprising result as N1 is the usual site of protonation in adenine and its derivatives, although N3 is protonated in 7-methyladenine dihydrochloride (Kistenmacher & Shigematsu, 1975). The internal angle at N3 shows an expansion of about 5° when compared with the corresponding angle in the coordinated base; this is characteristic of protonation of N in this ring (Table 2). In the crystal structure, these cations also occur as dimers, hydrogen bonded across another centre of symmetry, with an N3′—H···N9′$^{\rm ii}$ distance of 2.790 (3) Å [symmetry code: (ii) $-x$, $2-y$, $1-z$]. It is possible that the occurrence of these dimers leads to the N3(H) tautomer being the stable form in the solid. Hydrogen bonds link the moieties in the structure, *e.g.* N11′—H11′···Cl1$^{\rm iii}$ of length 3.492 (2) Å [symmetry code: (iii) $1-x$, $1-y$, $1-z$].

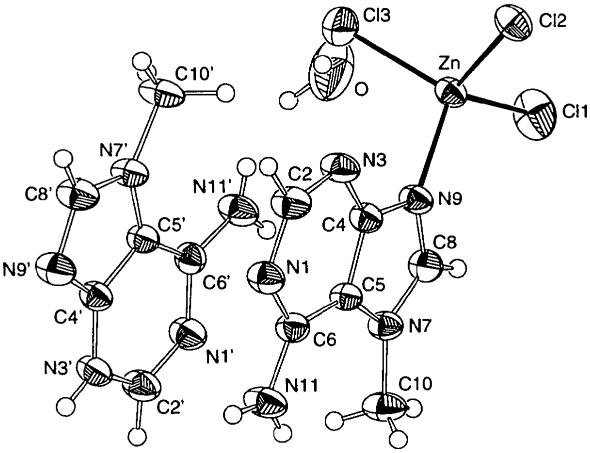


Fig. 1. A perspective drawing of the title compound showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are drawn as circles with arbitrary radii.

The dimeric cations and anions are alternately stacked in columns running parallel to the *a* axis (Fig. 2). The

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perpendicular distances between the bases are 3.500 (3) and 3.463 (3) Å. Weak hydrogen bonds to water connect the columns.

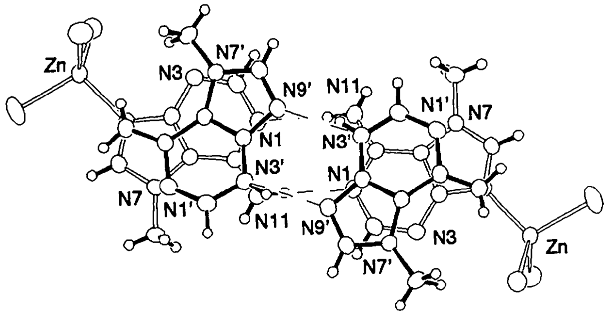

Fig. 2. A pair of dimeric cations and anions viewed down [100]. Hydrogen bonds are shown as broken lines.

The Zn—N9 bond length of 2.020 (2) Å can be compared with that of 2.091 Å for Zn—N7 in trichloro(adeninium)zinc(II) (Taylor, Vilkins & McCall, 1989) and 2.05 Å for Zn—N1 in trichloro(9-methyladeninium)zinc(II) (McCall & Taylor, 1975). In each of these structures, the Zn atom is tetrahedrally coordinated to an N atom and three Cl^- ions. In spite of the apparently significant differences in the Zn—N bond lengths, the bond-valence sum of zinc in each case is 2.06, 2.06 and 2.05, respectively (calculated according to Brown & Altermatt, 1985). This indicates that the differences in bond lengths to the heterocyclic bases are compensated for by concomitant differences in the Zn—Cl bond lengths.

Experimental

The heterocyclic base, 7-methyladenine, was prepared according to the method of Leonard, Fujii & Saito (1986), which involved blocking at the 3-position in order to achieve preferential methylation at the 7-position, followed by deblocking the 3-position. Crystals of the zinc(II) complex were prepared from 7-methyladenine (0.1 g, 0.667 mmol) dissolved in warm water (20 ml) and a 0.2 *M* zinc(II) chloride solution (7 ml, 0.19 mol). Slow evaporation gave long colourless single crystals. The density D_m was measured by flotation in 1,1,1-trichloroethane and 1,2-dibromoethane.

Crystal data

$(C_6H_8N_5)[ZnCl_3(C_6H_7N_5)].H_2O$
$M_r = 488.94$
Monoclinic
$P2_1/c$
$a = 7.214 (1)$ Å
$b = 16.437 (1)$ Å
$c = 16.180 (2)$ Å
$\beta = 97.378 (5)°$
$V = 1902.7 (4)$ Å^3
$Z = 4$
$D_x = 1.707$ Mg m^{-3}
$D_m = 1.71 (1)$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 11 reflections
$\theta = 30.01–31.97°$
$\mu = 5.91$ mm^{-1}
$T = 293$ K
Prism
0.305 × 0.246 × 0.186 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: by integration from crystal shape
$T_{min} = 0.1881$, $T_{max} = 0.4306$
3728 measured reflections
3599 independent reflections

3451 observed reflections $[F^2 > 0]$
$R_{int} = 0.012$
$\theta_{max} = 69.92°$
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 20$
$l = -19 \rightarrow 19$
1 standard reflection
frequency: 30 min
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.032$
$wR(F^2) = 0.07$
$S = 2.959$
3599 reflections
312 parameters
All H-atom parameters refined
Weighting scheme based on measured e.s.d.'s

$(\Delta/\sigma)_{max} = 1.921$ for U_{iso} of H111; 0.31 for non-H atoms
$\Delta\rho_{max} = 0.444$ e Å^{-3}
$\Delta\rho_{min} = -0.366$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.2B and 2.3.1)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Zn	0.65067 (4)	0.58631 (2)	0.33875 (2)	0.0289 (1)
Cl1	0.7101 (1)	0.46601 (4)	0.40409 (5)	0.0570 (4)
Cl2	0.86876 (8)	0.61127 (4)	0.25470 (4)	0.0382 (3)
Cl3	0.36621 (9)	0.59079 (4)	0.26173 (4)	0.0476 (3)
N1	0.5606 (3)	0.9132 (1)	0.4343 (1)	0.036 (1)
C2	0.5913 (4)	0.8756 (2)	0.3639 (2)	0.039 (1)
N3	0.6234 (3)	0.7974 (1)	0.3513 (1)	0.036 (1)
C4	0.6258 (3)	0.7540 (1)	0.4218 (1)	0.029 (1)
C5	0.6001 (3)	0.7858 (1)	0.4989 (1)	0.027 (1)
C6	0.5639 (3)	0.8698 (1)	0.5049 (1)	0.030 (1)
N7	0.6114 (3)	0.7200 (1)	0.5536 (1)	0.0295 (9)
C8	0.6420 (3)	0.6543 (1)	0.5088 (1)	0.032 (1)
N9	0.6512 (3)	0.6708 (1)	0.4294 (1)	0.0314 (9)
C10	0.5922 (5)	0.7194 (2)	0.6428 (2)	0.041 (1)
N11	0.5285 (4)	0.9081 (1)	0.5737 (1)	0.044 (1)
N1′	0.1129 (3)	0.7506 (1)	0.5476 (1)	0.038 (1)
C2′	0.0732 (4)	0.8202 (2)	0.5807 (2)	0.039 (1)
N3′	0.0448 (3)	0.8905 (1)	0.5406 (1)	0.034 (1)
C4′	0.0635 (3)	0.8905 (1)	0.4583 (1)	0.030 (1)
C5′	0.1046 (3)	0.8195 (1)	0.4186 (1)	0.028 (1)
C6′	0.1282 (3)	0.7465 (1)	0.4648 (1)	0.030 (1)
N7′	0.1137 (3)	0.8432 (1)	0.3371 (1)	0.0316 (9)
C8′	0.0790 (4)	0.9231 (2)	0.3340 (2)	0.040 (1)
N9′	0.0480 (3)	0.9550 (1)	0.4063 (1)	0.039 (1)
C10′	0.1474 (5)	0.7932 (2)	0.2659 (2)	0.043 (1)
N11′	0.1683 (4)	0.6742 (1)	0.4359 (1)	0.041 (1)
O	0.1403 (5)	0.4508 (2)	0.3548 (2)	0.088 (2)

Table 2. *Selected geometric parameters (Å, °)*

Zn—Cl1	2.2572 (8)	N7—C10	1.467 (3)
Zn—Cl2	2.2456 (8)	C8—N9	1.322 (3)
Zn—Cl3	2.2612 (7)	N1′—C2′	1.311 (3)
Zn—N9	2.020 (2)	N1′—C6′	1.360 (3)
N1—C2	1.339 (3)	C2′—N3′	1.328 (3)
N1—C6	1.344 (3)	N3′—C4′	1.356 (3)
C2—N3	1.326 (3)	C4′—C5′	1.383 (3)
N3—C4	1.342 (3)	C4′—N9′	1.350 (3)

C4—C5	1.387 (3)	C5′—C6′	1.413 (3)
C4—N9	1.384 (3)	C5′—N7′	1.385 (3)
C5—C6	1.412 (3)	C6′—N11′	1.323 (3)
C5—N7	1.392 (3)	N7′—C8′	1.337 (3)
C6—N11	1.332 (3)	N7′—C10′	1.460 (3)
N7—C8	1.335 (3)	C8′—N9′	1.326 (3)
Cl1—Zn—Cl2	109.75 (3)	N7—C8—N9	113.1 (2)
Cl1—Zn—Cl3	113.02 (3)	Zn—N9—C4	128.8 (1)
Cl1—Zn—N9	106.22 (6)	Zn—N9—C8	124.7 (1)
Cl2—Zn—Cl3	108.49 (3)	C4—N9—C8	105.5 (2)
Cl2—Zn—N9	112.24 (6)	C2′—N1′—C6′	119.7 (2)
Cl3—Zn—N9	107.15 (6)	N1′—C2′—N3′	126.0 (2)
C2—N1—C6	119.5 (2)	C2′—N3′—C4′	116.8 (2)
N1—C2—N3	129.0 (2)	N3′—C4′—C5′	120.8 (2)
C2—N3—C4	111.6 (2)	N3′—C4′—N9′	126.9 (2)
N3—C4—C5	125.1 (2)	C5′—C4′—N9′	112.3 (2)
N3—C4—N9	126.1 (2)	C4′—C5′—C6′	119.3 (2)
C5—C4—N9	108.8 (2)	C4′—C5′—N7′	104.1 (2)
C4—C5—C6	118.5 (2)	C6′—C5′—N7′	136.6 (2)
C4—C5—N7	106.0 (2)	N1′—C6′—C5′	117.4 (2)
C6—C5—N7	135.4 (2)	N1′—C6′—N11′	116.3 (2)
N1—C6—C5	116.3 (2)	C5′—C6′—N11′	126.3 (2)
N1—C6—N11	118.4 (2)	C5′—N7′—C8′	106.3 (2)
C5—C6—N11	125.2 (2)	C5′—N7′—C10′	128.8 (2)
C5—N7—C8	106.5 (2)	C8′—N7′—C10′	124.9 (2)
C5—N7—C10	128.6 (2)	N7′—C8′—N9′	114.0 (2)
C8—N7—C10	124.8 (2)	C4′—N9′—C8′	103.3 (2)

The title structure was solved using Patterson and Fourier techniques. The H atoms were observed in a difference map but placed at calculated positions using *BONDAT* (*Xtal*3.2; Hall, Flack & Stewart, 1992), except for those on the methyl groups, where one was positioned from the difference map and the others calculated from this. The positions of the H atoms on the water molecule were taken from the difference map. Refinement of an extinction correction parameter was attempted, but this did not give a physically realistic value for the parameter and was subsequently omitted.

Data reduction: *Xtal*3.2 *DIFDAT ADDREF ABSORB SORTRF*. Program(s) used to solve structure: *Xtal*3.2. Program(s) used to refine structure: *Xtal*3.2 *CRYLSQ*. Molecular graphics: *Xtal*3.2. Software used to prepare material for publication: *Xtal*3.2 *BONDLA CIFIO*.

The authors thank Mr Don Craig of the University of New South Wales for collecting the data.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KH1103). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis(pyridine-2-thione)-2κS;3κS-tetra-μ-sulfido-1:2$\kappa^4 S$;1:3$\kappa^4 S$-bis(triphenylphosphine)-2κP;3κP-dicoppermolybdenum Bis(dichloromethane) Solvate

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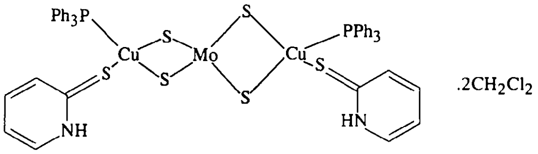
Abstract

The structure determination of $[Cu_2MoS_4(C_5H_5NS)_2(C_{18}H_{15}P)_2].2CH_2Cl_2$ is reported. The compound contains a linear $[CuS_2MoS_2Cu]$ cluster core, with each Cu atom having a distorted tetrahedral coordination involving two S atoms of a tetradentate MoS_4^{2-} moiety, one S atom of a pyridine-2-thione ligand and one P atom of a triphenylphosphine ligand.

Comment

Several linear clusters have been prepared over the past two decades, for example, $[MS_4M'_2(PPh_3)_3]$ (M = Mo, W; M' = Cu, Ag; Müller, Bőgge & Schimanski, 1983) and the heterometallic trinuclear clusters $(Et_4N)[(PPh_3)_2AgS_2MS_2Cu(CN)]$ (M = Mo, W; Du, Zhu, Chen, Wu & Lu, 1992*a*,*b*). The title compound, (I), also has a linear $[CuS_2MoS_2Cu]$ core, but one in which both Cu atoms are tetrahedrally coordinated by mixed ligands.



(I)

The Mo atom in (I) has tetrahedral coordination, MoS_4^{2-}, and each Cu atom is coordinated by a distorted tetrahedron involving two S atoms of the tetradentate MoS_4^{2-} moiety, one S atom of C_5H_5NS and one P atom of PPh_3 (Fig. 1). The average Cu···Mo, μ-S—Mo and μ-S—Cu distances of 2.7347 (7), 2.199 (2) and 2.298 (2) Å, respectively, are comparable with the corresponding values of 2.710 (3), 2.208 (5) and 2.267 (5) Å found in $[Cu_2MoS_4(PPh_3)_3].0.8CH_2Cl_2$. The Cu—S($C_5H_5NS$) bond length of 2.348 (2) Å is longer than that of 2.284 (2) Å in $[Cu_2(C_5H_5NS)_6]Cl_2$ (Con-

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