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Dichlorobis(purine)zinc(II)

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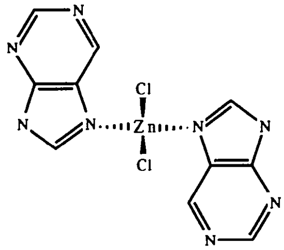
Abstract

In the crystal structure of the title compound, [$ZnCl_2(C_5H_4N_4)_2$], the Zn atom is found to be tetrahedrally coordinated by two Cl atoms and N7 of each of the two purine ligands, with Zn—Cl 2.222 (1) and 2.229 (2) Å, and Zn—N7 2.027 (3) and 2.033 (4) Å.

Comment

The title compound, (I), was prepared and its structure determined during the course of our ongoing study of nucleobases and their analogues (*e.g.* Cunane & Taylor, 1993). The complex exhibits tetrahedral coordination geometry typical of Zn ions, with two Cl atoms and N7 of each of two purine molecules being the ligating atoms. Table 2 shows that, although the ligands are crystallographically distinct, there are no significant differences between those corresponding bond lengths and angles that are expected to be chemically equivalent. The Zn atom is similarly coordinated to N7 in trichloropuriniumzinc(II) (Sheldrick, 1982) and apart from differences near the protonation site (N1), the bond lengths and angles in the two structures are similar.



(I)

Molecules are linked along the polar *a* axis by intermolecular hydrogen bonds as shown in Fig. 2 [N1···N9′($x + \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$) 2.797 (6) and N1′···N9($x - 1, y - 1, z - \frac{1}{2}$) 2.784 (5) Å].

This structure is one of a number of similar ones where the preferred coordination site of purine analogues to the Zn atom is N7. In solutions of purine,

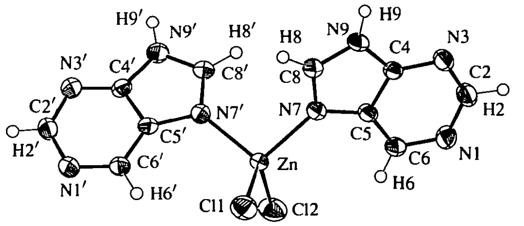


Fig. 1. A view of the molecule with displacement ellipsoids drawn at the 50% probability level. H atoms are drawn as circles of arbitrary radii.

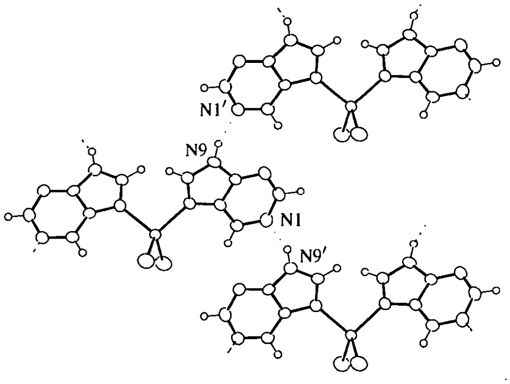


Fig. 2. A view of part of the structure showing hydrogen bonding.

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both N7 and N9 tautomers exist in equilibrium while the N7 tautomer occurs in the solid uncomplexed purine (Watson, Sweet & Marsh, 1965). It would appear that, while the opportunity for N9···Zn coordination is available in solution, under our reaction conditions the N7···Zn isomer is the least soluble.

Experimental

Crystals were obtained by slow evaporation of an aqueous solution that was 0.64 *M* in each of zinc(II) chloride, hydrochloric acid and purine. The density D_m was measured by flotation in a 1,2-dibromoethane/*N*,*N*-dimethylformamide mixture.

Crystal data

[$ZnCl_2(C_5H_4N_4)_2$]
$M_r = 376.50$
Monoclinic
Cc
$a = 6.591 (4)$ Å
$b = 12.222 (2)$ Å
$c = 17.254 (4)$ Å
$\beta = 96.78 (3)°$
$V = 1380.2 (9)$ Å^3
$Z = 4$
$D_x = 1.812$ Mg m^{-3}
$D_m = 1.81 (2)$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 10 reflections
$\theta = 10–12°$
$\mu = 2.17$ mm^{-1}
$T = 293$ K
Hexagonal prism
$0.40 \times 0.13 \times 0.08$ mm
Colourless

Data collection

CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: by integration from crystal shape
$T_{min} = 0.712$, $T_{max} = 0.864$
5491 measured reflections
2919 independent reflections
2603 observed reflections [$F^2 > 0$]

$R_{int} = 0.048$
$\theta_{max} = 32.51°$
$h = -9 \rightarrow 1$
$k = -18 \rightarrow 18$
$l = -25 \rightarrow 26$
8 standard reflections monitored every 50 reflections
intensity decay: <1%

Refinement

Refinement on *F*
$R = 0.040$
$wR = 0.033$
$S = 1.443$
2603 reflections
188 parameters
H-atom parameters not refined
$w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{max} = 0.02$
$\Delta\rho_{max} = 0.594$ e Å^{-3}
$\Delta\rho_{min} = -0.476$ 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)

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

	x	y	z	U_{eq}
Zn	0.99548	0.41724 (4)	0.49892	0.0285 (2)
Cl1	1.1838 (2)	0.5670 (1)	0.52254 (7)	0.0458 (6)
Cl2	1.1771 (2)	0.2684 (1)	0.47846 (8)	0.0479 (6)
N1	0.8109 (7)	0.3334 (3)	0.2141 (2)	0.037 (2)
C2	0.6314 (7)	0.3773 (4)	0.1829 (2)	0.036 (2)
N3	0.5042 (6)	0.4363 (3)	0.2184 (2)	0.034 (2)
C4	0.5685 (6)	0.4495 (3)	0.2951 (2)	0.027 (2)
C5	0.7497 (6)	0.4081 (3)	0.3335 (2)	0.028 (2)
C6	0.8714 (7)	0.3481 (4)	0.2912 (2)	0.032 (2)
N7	0.7646 (6)	0.4401 (3)	0.4119 (2)	0.030 (2)
C8	0.5965 (7)	0.4983 (4)	0.4174 (2)	0.033 (2)
N9	0.4732 (6)	0.5051 (3)	0.3486 (2)	0.035 (2)
N1′	1.1042 (6)	0.3998 (3)	0.7883 (2)	0.036 (2)
C2′	0.9620 (7)	0.3445 (4)	0.8206 (2)	0.034 (2)
N3′	0.7882 (6)	0.3038 (3)	0.7849 (2)	0.034 (2)
C4′	0.7651 (6)	0.3235 (3)	0.7078 (2)	0.028 (2)
C5′	0.9042 (6)	0.3796 (3)	0.6681 (2)	0.027 (2)
C6′	1.0770 (7)	0.4197 (4)	0.7107 (2)	0.033 (2)
N7′	0.8317 (5)	0.3822 (3)	0.5885 (2)	0.031 (2)
C8′	0.6548 (7)	0.3294 (4)	0.5837 (2)	0.033 (2)
N9′	0.6081 (6)	0.2936 (3)	0.6535 (2)	0.035 (2)

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

Zn—Cl1	2.222 (1)	N7—C8	1.330 (6)
Zn—Cl2	2.229 (2)	C8—N9	1.360 (5)
Zn—N7	2.027 (3)	N1′—C2′	1.331 (6)
Zn—N7′	2.033 (4)	N1′—C6′	1.352 (5)
N1—C2	1.352 (6)	C2′—N3′	1.331 (6)
N1—C6	1.355 (5)	N3′—C4′	1.342 (5)
C2—N3	1.311 (6)	C4′—C5′	1.388 (6)
N3—C4	1.350 (5)	C4′—N9′	1.361 (5)
C4—C5	1.391 (5)	C5′—C6′	1.371 (6)
C4—N9	1.358 (5)	C5′—N7′	1.401 (5)
C5—C6	1.361 (6)	N7′—C8′	1.327 (6)
C5—N7	1.400 (5)	C8′—N9′	1.349 (5)
Cl1—Zn—Cl2	113.74 (6)	C5—N7—C8	104.7 (3)
Cl1—Zn—N7	112.1 (1)	N7—C8—N9	112.7 (4)
Cl1—Zn—N7′	111.7 (1)	C4—N9—C8	106.7 (3)
Cl2—Zn—N7	111.4 (1)	C2′—N1′—C6′	119.3 (4)
Cl2—Zn—N7′	107.0 (1)	N1′—C2′—N3′	127.2 (4)
N7—Zn—N7′	99.9 (1)	C2′—N3′—C4′	112.6 (4)
C2—N1—C6	118.7 (4)	N3′—C4′—C5′	124.9 (4)
N1—C2—N3	127.6 (4)	N3′—C4′—N9′	128.5 (4)
C2—N3—C4	112.3 (4)	C5′—C4′—N9′	106.6 (3)
N3—C4—C5	125.2 (4)	C4′—C5′—C6′	117.9 (3)
N3—C4—N9	127.5 (4)	C4′—C5′—N7′	109.0 (3)
C5—C4—N9	107.3 (3)	C6′—C5′—N7′	133.1 (4)
C4—C5—C6	117.8 (3)	N1′—C6′—C5′	118.1 (4)
C4—C5—N7	108.5 (3)	Zn—N7′—C5′	126.9 (3)
C6—C5—N7	133.6 (4)	Zn—N7′—C8′	126.7 (3)
N1—C6—C5	118.3 (4)	C5′—N7′—C8′	104.2 (3)
Zn—N7—C5	129.7 (3)	N7′—C8′—N9′	113.2 (3)
Zn—N7—C8	125.4 (3)	C4′—N9′—C8′	107.0 (4)

Systematic absences indicated that the space group was either *Cc* or *C*2/*c*. The structure was solved by Patterson and Fourier techniques. A satisfactory solution, that refined well, was found in *Cc*. The twofold axis apparent in the molecule is closely aligned with the crystallographic *a* axis. H atoms were located in difference maps but were placed at calculated positions 0.95 Å from the atoms on which they reside. Their positions were not recalculated after the final refinement cycles. The reflection data were averaged in point group *m*. The *x* and *z* coordinates of Zn were held constant. The coordinates in Table 1 are those for the correct hand of the crystal; refinement of the inverse set converged at $R = 0.049$, $wR = 0.045$.

Data reduction: *Xtal DIFDAT*, *ADDREF*, *ABSORB*, *SORTRF* (Hall, Flack & Stewart, 1992). Program(s) used to solve structure: *Xtal*. Program(s) used to refine structure: *Xtal CRYLSQ*. Molecular graphics: *Xtal*. Software used to prepare material for publication: *Xtal BONDLA*, *CIFIO*.

The authors are very grateful to Associate Professor A. H. White of The University of Western Australia for collecting the data.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1031). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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μ_3-Oxo-tris[(triisopropylphosphine)gold(I)] Tetrafluoroborate

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Abstract

μ_3-Oxo-tris[(triisopropylphosphine)gold(I)] tetrafluoroborate, $[Au_3O(C_9H_{21}P)_3]BF_4$, crystallizes with C_{3v}-symmetrical cations and anions. The cations show intramolecular Au···Au bonding, but any intermolecular aggregation, as detected in other homologues, is prevented by the bulky phosphine ligands.

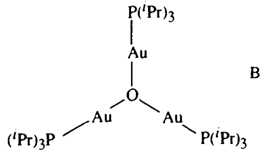
Comment

Trigoldoxonium salts $(LAu)_3O^+.X^-$ are of considerable interest as reagents in gold-cluster chemistry (Ramamoorthy & Sharp, 1990; Perevalova, Smyslova, Dyadchenko, Grandberg & Nesmeyanov, 1980; Zeller, Beruda, Kolb, Bissinger, Riede & Schmidbaur, 1991). Moreover, they provide direct evidence for the influence of Au···Au interactions on the structure of gold(I) compounds. These interactions between closed-shell metal atoms (Au $5d^{10}$) are based largely on relativistic effects (Pyykkö, 1988), which reach a local maximum in the Periodic Table for gold. All previously described structures of trigoldoxonium compounds show a nearly trigonal array of Au atoms, with Au···Au distances close to 3.1 Å, capped by an O atom.

Depending on the size of the phosphine ligands coordinated to the Au atoms, the cations undergo intermolecular aggregation to form dimers of the form $[(R_3PAu)_6O_2]^{2+}$. With the smallest tertiary phosphine ligand Me_3P (*i.e.* R = Me), dications with a tetrahedral Au_4 core are formed, with each bridging Au atom bonded to four neighbouring Au atoms (Angermaier & Schmidbaur, 1994*a*). In contrast, the corresponding oxonium salts having the somewhat larger phosphines Ph_2MeP (R_3 = Ph_2Me) (Yi, Ramamoorthy & Sharp, 1993) and Ph_3P (R = Ph) (Nesmeyanov, Perevalova, Struchkov, Antipin, Grandberg & Dyadchenko, 1980) are less intimately aggregated and form a square Au_4 unit, with each of the Au atoms bonded to only three neighbouring metal atoms. To date, it is only in the complex $[\{(o\text{-tolyl})_3PAu\}_3O]BF_4$, with its more bulky $(o\text{-tolyl})_3P$ ligand, that isolated monomeric cations have been detected (Yi, Ramamoorthy & Sharp, 1993).

Similar results have been obtained for the corresponding sulfonium systems $(LAu)_3S^+.X^-$, where both monocationic as well as oligo- or even polycationic species are observed, but with a different degree and mode of aggregation for a given ligand L (Angermaier & Schmidbaur, 1994*b*; Schmidbaur, Kolb, Zeller, Schier & Beruda, 1993; Jones, Sheldrick & Hädicke, 1980).

The present investigation is part of a more extended study of the influences exerted by the donor ligands, L, on the intermolecular aggregation of mono- or polynuclear gold(I) compounds. $[(^iPr_3PAu)_3O]BF_4$, (I), crystallizes in the trigonal space group $R\bar{3}$, with the central O atom of the cation and one of the B—F bonds of the anion situated on threefold rotation axes. The anion is found to be disordered, with the B atom located on a centre of inversion, resulting in a split model of two BF_4 ions with site occupancy factors of 0.5.



(I)

In the cations $[(^iPr_3PAu)_3O]^+$, an Au_3 triangle is capped by an O atom. The coordination geometry of the Au atoms is found to be nearly linear with an O—Au—P angle of 176.4 (2)°. While the Au—O and Au—P distances [2.030 (3) and 2.228 (2) Å, respectively] are in good agreement with literature values, the Au···Au distances [3.198 (1) Å] are remarkably larger than the Au···Au distances found in the only other monomeric $(LAu)_3O^+$ cation, $[\{(o\text{-tolyl})_3PAu\}_3O]BF_4$ (average 3.086 Å). This widening of the Au···Au distance leads to an Au—O—Au angle of 103.7 (2)°, as compared to an average value of 97.8° in the p-tolyl homologue. The bulky $^iPr_3P$ ligands thus not only preclude intermolecular Au···Au interactions, but also significantly reduce the intramolecular stabilization of the oxonium cation by direct-cluster bonding.