$1H^+$-Adeniniumtrichlorozinc(II) (Form i) – a Redetermination

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Abstract. [ZnCl$_3$(C$_5$H$_6$N$_5$)], $M_r = 307.9$, monoclinic, $P2_1/c$, $a = 10.844$ (4), $b = 5.931$ (2), $c = 15.718$ (6) Å, $\beta = 90.92$ (3)°, $V = 1010.8$ (6) Å^3, $Z = 4$, $D_m = 2.03$ (1), $D_x = 2.024$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 32.56$ cm^{-1}, $F(000) = 608$, $T = 295$ K, $R = 0.036$ for 4251 unique reflections. This work is a redetermination of a structure solved earlier from two-circle-diffractometer data [Taylor (1973). *Acta Cryst.* B29, 884–890], to obtain better coordinates for comparison with a neutron diffraction study. The complex exists as discrete adeniniumtrichlorozinc(II) molecules; the adenine moiety is protonated at N(1), while N(7) and the three Cl atoms are coordinated to Zn in a distorted tetrahedral arrangement. The Zn—N(7) coordination may serve as a model for bivalent-metal-ion interactions with nucleic acids. Hydrogen bonding is extensive, and is enhanced by intramolecular interactions and the significant non-planarity of the adeninium ligand.

Experimental. Crystals of the complex were grown as colourless plates by evaporation of a 16:1 acidified mixture of zinc chloride and adenine. D_m by flotation. Syntex $P2_1$ four-circle diffractometer at the Institute for Cancer Research, Philadelphia, USA, monochromated Mo $K\alpha$ radiation, $\omega/2\theta$-scan mode. Unit-cell parameters on crystal $0.283 \times 0.317 \times 0.167$ mm from 14 accurately centred reflections ($13.2 \le \theta \le 20.3°$). Total of 10328 reflections to $(\sin\theta)/\lambda = 0.81$ Å^{-1} in range $-17 \le h \le 17$, $0 \le k \le$

9, $-25 \le l \le 25$. Four standard reflections (060, 0,0,14, 32$\overline{4}$, 200) measured every 60 reflections. Only significant variation was for 200, decreased 6% in first 30 h, then steady. Lp and absorption corrections applied (Carrell, 1978), data merged to give 4251 unique reflections, $R_{int} = 3\%$, 224 unobserved ($I < 0$).

Structure solved by starting with non-H coordinates from previous refinement. H atoms located in difference map. Full-matrix least-squares refinement

Table 2. *Selected bond distances* (Å) *and angles* (°)

Zn—Cl(1)	2.255 (1)	Zn—Cl(2)	2.213 (1)
Zn—Cl(3)	2.232 (1)	Zn—N(7)	2.091 (1)
N(1)—C(2)	1.336 (2)	N(1)—C(6)	1.369 (2)
N(3)—C(2)	1.302 (2)	N(3)—C(4)	1.357 (2)
C(4)—C(5)	1.379 (2)	C(4)—N(9)	1.363 (2)
C(5)—C(6)	1.410 (2)	C(5)—N(7)	1.386 (2)
C(6)—N(6)	1.307 (2)	N(7)—C(8)	1.325 (2)
C(8)—N(9)	1.349 (2)		

Cl(1)—Zn—Cl(2)	111.14 (2)	Cl(1)—Zn—Cl(3)	111.14 (2)
Cl(1)—Zn—N(7)	104.19 (3)	Cl(2)—Zn—Cl(3)	118.78 (2)
Cl(2)—Zn—N(7)	107.39 (3)	Cl(3)—Zn—N(7)	102.75 (3)
C(2)—N(1)—C(6)	124.0 (1)	N(1)—C(2)—N(3)	125.0 (1)
C(2)—N(3)—C(4)	112.3 (1)	N(3)—C(4)—C(5)	127.3 (1)
N(3)—C(4)—N(9)	126.3 (1)	C(5)—C(4)—N(9)	106.4 (1)
C(4)—C(5)—C(6)	118.1 (1)	C(4)—C(5)—N(7)	109.5 (1)
C(6)—C(5)—N(7)	132.3 (1)	N(1)—C(6)—C(5)	113.1 (1)
N(1)—C(6)—N(6)	120.1 (1)	C(5)—C(6)—N(6)	126.7 (1)
Zn—N(7)—C(5)	135.8 (1)	Zn—N(7)—C(8)	116.8 (1)
C(5)—N(7)—C(8)	104.5 (1)	N(7)—C(8)—N(9)	112.7 (1)
C(4)—N(9)—C(8)	106.9 (1)		

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

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

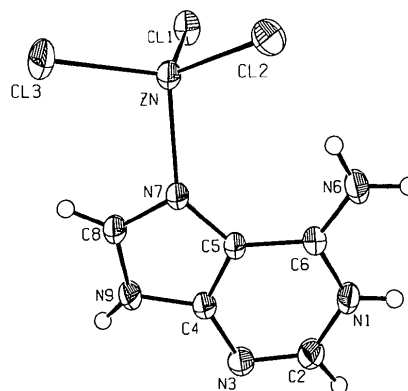|	x	y	z	U_{eq}
Zn	0.21431 (1)	0.76061 (3)	0.65463 (1)	0.0155
Cl(1)	0.07701 (3)	0.53388 (7)	0.71867 (2)	0.0170
Cl(2)	0.12005 (4)	1.01312 (6)	0.57288 (3)	0.0176
Cl(3)	0.35978 (4)	0.87713 (8)	0.74654 (3)	0.0371
N(1)	0.1937 (1)	0.2902 (2)	0.3764 (1)	0.0163
C(2)	0.2788 (1)	0.1231 (3)	0.3737 (1)	0.0152
N(3)	0.3689 (1)	0.0962 (2)	0.4286 (1)	0.0176
C(4)	0.3675 (1)	0.2532 (2)	0.4913 (1)	0.0147
C(5)	0.2864 (1)	0.4307 (2)	0.4994 (1)	0.0142
C(6)	0.1931 (1)	0.4568 (2)	0.4367 (1)	0.0154
N(6)	0.1104 (1)	0.6171 (2)	0.4327 (1)	0.0182
N(7)	0.3115 (1)	0.5445 (2)	0.5748 (1)	0.0160
C(8)	0.4063 (1)	0.4347 (3)	0.6092 (1)	0.0190
N(9)	0.4440 (1)	0.2606 (2)	0.5609 (1)	0.0157

Fig. 1. Molecular structure and atomic numbering scheme of adeniniumtrichlorozinc(II), with thermal ellipsoids drawn at the 50% probability level.

of 152 parameters based on F^2 using *XTAL*2.4 (Hall & Stewart, 1988). Scale factor, positional parameters for all atoms, anisotropic temperature factors for non-H atoms and isotropic temperature factors for H atoms refined. Also isotropic secondary-extinction correction applied and refined [final value 0·20 (1)]. On F^2, final $R = 0·042$, $wR = 0·067$, $w = 1·0/\{\sigma(F^2)\}^2$ where $\sigma(F^2) = \sigma(I)/(2·0|F|)$, $S = 1·47$. A structure-factor calculation after the refinement gave $R = 0·036$. $(\Delta/\sigma)_{max} = 0·01$, $\Delta\rho_{max} = 0·56$, $\Delta\rho_{min} = -0·50$ e Å^{-3}. Scattering factors from *International Tables for X-ray Crystallography* (1974), including those for bonded H atoms. Atomic parameters of non-H atoms are given in Table 1,* and selected

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and equations of, and deviations from, least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51905 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

bond lengths and angles are listed in Table 2. The molecular geometry is shown in Fig. 1.

Related literature. A different crystalline modification of this compound (form ii) has been reported by Muthiah, Mazumdar & Chaudhuri (1983). The molecules are identical within experimental error, except for some minor differences in the bonds to Zn.

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Structure of [P(CH₃)(C₆H₅)₃]₂[{IPd[CC(=O)(OCH₃)]₄}₂]

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Abstract. Methyltriphenylphosphonium di-μ-iodo-bis[(tetramethyl 1,2,3,4-buta-1,3-dienetetracarboxylate-C^1,C^4)palladium], [P(CH₃)(C₆H₅)₃]₂[{Pd(C₁₂H₁₂O₈)I}₂], $M_r = 1589·7$, triclinic, $P\bar{1}$, $a = 10·811$ (5), $b = 12·218$ (6), $c = 14·060$ (5) Å, $\alpha = 98·61$ (4), $\beta = 108·98$ (3), $\gamma = 106·90$ (4)°, $U = 1618$ (1) Å³, $Z = 1$, one-half molecule/asymmetric unit, $D_x = 1·631$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 15·96$ cm^{-1}, $F(000) = 788$, $T = 292$ K, $R = 0·0331$ for 5828 observed reflections. Each unit cell contains two triphenylmethylphosphonium cations and a dinuclear palladium complex dianion with the Pd atoms bridged by two μ-I atoms and each Pd atom chelated by a diacetylide dianion formed from dimethyl acetylenedicarboxylate. The Pd—I distances are 2·690 (1) and 2·677 (1) Å. The Pd structure coordination geometry is close to square planar

with I—Pd—C angles of 96·6 (1) and 175·9 (1)°, a C—Pd—C angle of 79·3 (1)°, and an I—Pd—I angle of 86·4 (1)°. The Pd atom is 0·006 Å out of the plane of the I and C atoms. The cation shows the expected tetrahedral configuration for a four-ligand phosphonium ion with an average C—P—C angle of 109·4 (1)°.

Experimental. The synthesis involved reaction of the known neutral metallocycle [Pd{C₄(CO₂CH₃)₄}-(PPh₃)₂]ₙ (Moseley & Maitlis, 1974) (91 mg, 0·1 mmol) with excess methyl iodide in chloroform at 296 K. Evaporation of the volatiles and recrystallization of the residue from acetone/diethyl ether provided [P(CH₃)(C₆H₅)₃]₂[{IPd[CC(=O)-(OCH₃)]₄}₂] in 78% isolated yield. ¹H NMR (CDCl₃): δ 7·6–7·7 (m, ~30H), 3·57 (s, 12H), 3·52 (s, 12H), 3·33 (d, $J_{Ph} = 12$ Hz, 6H). Crystals were obtained from slow diffusion of pentane into a CCl₄–