

Structure of Trichloro(9-methyladeninium)zinc(II) Monohydrate

By J. MAIXNER

Central Laboratories, Institute of Chemical Technology, Praha 2, 166 28 Czechoslovakia

AND J. ZACHOVÁ

Institute of Physics, Charles University, Praha 2, Czechoslovakia

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Abstract. $[\text{ZnCl}_3(\text{C}_6\text{H}_8\text{N}_5)] \cdot \text{H}_2\text{O}$, $M_r = 339.9$, monoclinic, $P2_1/n$, $a = 6.334$ (1), $b = 14.204$ (1), $c = 14.215$ (1) Å, $\beta = 100.72$ (1)°, $V = 1256.6$ (5) Å³, $Z = 4$, $D_x = 1.796$ (1) Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 2.632$ mm⁻¹, $F(000) = 680$, $T = 293$ (1) K, $R = 0.020$, $wR = 0.025$ for 1594 observed reflections with $I > 3\sigma(I)$. The Zn atom is coordinated to three Cl atoms and to the N(7) of the adenine molecule in a distorted tetrahedral arrangement. This indicates that for nucleic acids N(7) is a possible coordination site for bivalent metal ions. The adenine molecule, which is protonated at N(1), is significantly non-planar with a dihedral angle of 4.4 (9)° between the imidazole and the pyrimidine rings.

Experimental. Crystals were grown by cooling a solution of 9-methyladenine and zinc chloride (molar ratio 2:1) in 2 M hydrochloric acid. The solution was saturated at about 308 K to give large isometric colourless crystals with very well developed faces and maximal crystal dimensions of 8 × 6 × 5 mm. A crystal of size 0.3 × 0.4 × 0.45 mm was selected and mounted on an Enraf–Nonius CAD-4 diffractometer. The unit-cell parameters were determined using a least-squares method to optimize the adjusted angular setting of 20 reflections with $18 < \theta < 20^\circ$ constrained to a monoclinic cell. The space group was determined by the systematic absences ($0k0$ with k odd, $h0l$ with $h+l$ odd) observed in the diffractometer-collected intensity data. Intensities were collected with graphite-monochromated Mo $K\alpha$ radiation. The ω - 2θ technique was used with scan width $(0.8 + 0.35\tan\theta)^\circ$ extended 25% on each side for background measurement. A set of 2068 unique reflections, 1594 of which had $I > 3\sigma(I)$, was obtained from 7874 reflections measured in the range $1 < 2\theta < 48^\circ$ [$-7 < h < 7$, $-16 < k < 16$, $-16 < l < 16$, $\sin(\theta/\lambda) < 0.5717$ Å⁻¹, $R_{\text{int}} = 0.018$]. The angular positions of three standard reflections (065, 579, 387) were checked after measuring 500 reflections, the intensities of two reflections (065, 579) were monitored after every 7200 s. The position of the crystal

was stable and the monitored intensity showed a slight decrease of about 2.8% after 13.4 h. Corrections were made for Lorentz and polarization effects but not for absorption.

The structure was solved by direct methods and refined on F by full-matrix least squares with anisotropic thermal motion for all non-H atoms. All H-atom positions were found from $\Delta\rho$ syntheses and included in the model. The final refinement cycle was performed with 186 variables including all positional parameters, anisotropic thermal parameters for the non-H atoms, isotropic thermal parameters for the H atoms, one scale factor and the extinction coefficient $g = 1.31$ (3) × 10⁻⁶, where the correction factor $(1 + gI_c)^{-1}$ was applied to F_c . The final agreement factors were $R = 0.020$, $wR = 0.025$ and $S = 1.39$. The ratio of the maximum least-squares shift to e.s.d. in the final refinement cycle was less than 0.06. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = 4F_o^2/\sigma^2(F_o^2)$. The final $\Delta\rho$ map was almost featureless with the highest peak at 0.22 (4) and the lowest peak at -0.19 (4) e Å⁻³. All calculations were carried out on PDP11/73 and PC/AT microcomputers using the SHELXS86 (Sheldrick, 1990) and PARST88 (Nardelli, 1988) programs and the Enraf–Nonius SDP (Frenz, 1985) software. Neutral-atom scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol IV). The fractional atomic coordinates and B_{eq} values are listed in Table 1* and the bond distances and angles are in Table 2. An ORTEP drawing of the title complex is shown in Fig. 1 with the packing in the unit cell in Fig. 2.

Related literature. Trichloro(9-methyladeninium)-zinc(II) monohydrate was prepared as a model

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and geometry and least-squares-plane data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55730 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: LI1022]

Table 1. Fractional atomic coordinates for non-H atoms and their equivalent isotropic temperature factors (\AA^2)

$$B_{eq} = (4/3)\sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	x	y	z	B_{eq}
Zn	0.04078 (5)	0.45741 (3)	0.75453 (2)	2.395 (6)
Cl(1)	0.2611 (1)	0.33878 (6)	0.73139 (5)	3.32 (2)
Cl(2)	-0.1469 (1)	0.50038 (7)	0.61171 (6)	3.95 (2)
Cl(3)	-0.1422 (1)	0.43859 (6)	0.87288 (5)	3.87 (2)
Ow	0.4328 (4)	0.3001 (2)	0.5327 (1)	4.63 (6)
N(1)	0.6025 (4)	0.6837 (2)	0.6648 (2)	2.70 (5)
N(3)	0.7229 (4)	0.7087 (2)	0.8297 (2)	2.61 (5)
N(6)	0.3137 (4)	0.5931 (2)	0.4944 (2)	3.31 (6)
N(7)	0.2549 (4)	0.5644 (2)	0.8060 (2)	2.38 (5)
N(9)	0.4846 (4)	0.6352 (2)	0.9219 (2)	2.51 (5)
C(2)	0.7389 (5)	0.7209 (2)	0.7410 (2)	2.86 (7)
C(4)	0.5521 (4)	0.6549 (2)	0.8389 (2)	2.08 (6)
C(5)	0.4092 (4)	0.6115 (2)	0.7674 (2)	2.04 (6)
C(6)	0.4339 (4)	0.6262 (2)	0.6719 (2)	2.37 (6)
C(8)	0.3066 (5)	0.5817 (2)	0.8988 (2)	2.75 (6)
C(9)	0.5811 (5)	0.6695 (3)	1.0176 (2)	4.02 (8)

Table 2. Bond distances (\AA) and angles ($^\circ$) with *e.s.d.*'s in parentheses

Zn—Cl(1)	2.251 (1)	C(4)—C(5)	1.375 (4)
Zn—Cl(2)	2.238 (1)	C(5)—C(6)	1.411 (4)
Zn—Cl(3)	2.230 (1)	N(7)—C(5)	1.379 (4)
Zn—N(7)	2.077 (3)	N(7)—C(8)	1.322 (3)
N(1)—C(2)	1.360 (3)	N(9)—C(4)	1.357 (4)
N(1)—C(6)	1.362 (4)	N(9)—C(8)	1.348 (3)
N(3)—C(2)	1.295 (4)	N(9)—C(9)	1.467 (6)
N(3)—C(4)	1.350 (4)	C(6)—N(6)	1.305 (3)
Cl(1)—Zn—Cl(2)	108.10 (3)	C(8)—N(9)—C(9)	126.8 (2)
Cl(1)—Zn—Cl(3)	116.36 (3)	N(1)—C(2)—N(3)	124.7 (3)
Cl(1)—Zn—N(7)	102.57 (7)	N(3)—C(4)—N(9)	126.1 (2)
Cl(2)—Zn—Cl(3)	117.02 (3)	N(3)—C(4)—C(5)	127.7 (3)
Cl(2)—Zn—N(7)	108.76 (6)	N(9)—C(4)—C(5)	106.2 (2)
Cl(3)—Zn—N(7)	102.65 (7)	N(7)—C(5)—C(4)	110.0 (2)
Zn—N(7)—C(5)	132.8 (2)	N(7)—C(5)—C(6)	131.9 (2)
Zn—N(7)—C(8)	120.8 (2)	C(4)—C(5)—C(6)	117.9 (3)
C(2)—N(1)—C(6)	124.4 (2)	N(1)—C(6)—C(5)	112.9 (2)
C(2)—N(3)—C(4)	112.3 (2)	N(1)—C(6)—N(6)	119.7 (3)
C(5)—N(6)—C(8)	104.1 (2)	C(5)—C(6)—N(6)	127.4 (2)
C(4)—N(9)—C(8)	106.8 (2)	N(7)—C(8)—N(9)	112.8 (3)
C(4)—N(9)—C(9)	126.4 (2)		

system for the study of nucleic acid–metal interactions by Raman spectroscopy. Although the occurrence of zinc in the human body is high (similar to iron), its role has not yet been fully explained. It has been shown that Zn^{2+} is essential for the activity of DNA and RNA polymerases, which are the catalysts of replication and transcription of DNA (Mildvan & Loeb, 1979). Shin & Eichhorn (1968) postulated that Zn^{2+} is bound to the bases when it participates in the reversible unwinding of DNA.

The most preferred adenine binding site for transition-metal coordination is N(9) or a bridging position between atoms N(9) and N(3) according to the data obtained from crystallographic studies. However, it is N(7), and to a lesser extent N(1), in the case of adenosine derivatives. Therefore 9-methyladenine, where the glycosidic bond site is blocked, is a simple model system for studies of

nucleic-acid interactions. Coordination to metal ions leaves the geometry about the liganded N atoms practically unchanged (Saenger, 1984).

The most favourable protonation site for the adenine molecule has been deduced as N(1) by Taylor & Kennard (1982) from a consideration of structural data retrieved from the Cambridge Structural Database. They found significant changes in the geometry of the purine skeleton caused by protonation, and in particular the change of the C(6)—N(1)—C(2) angle from $118.8(2)^\circ$ in the neutral adenine molecule to $123.2(2)^\circ$ in the protonated one.

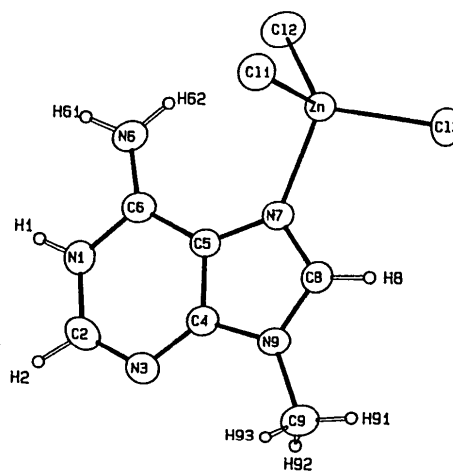


Fig. 1. ORTEP drawing (Johnson, 1976) of trichloro(9-methyladeninium)zinc(II). Thermal ellipsoids are drawn at the 50% probability level.

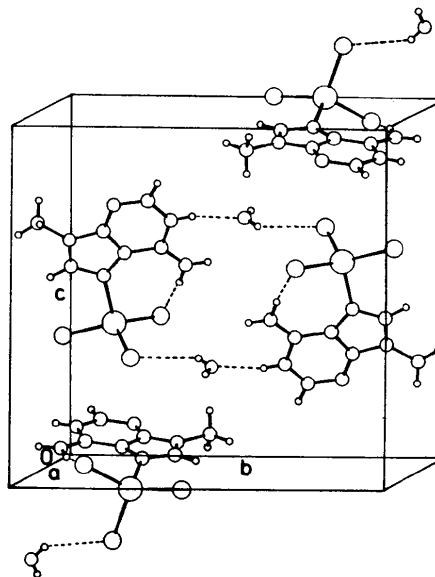


Fig. 2. Packing of the molecules in $[\text{ZnCl}_3(\text{C}_6\text{H}_8\text{N}_5)] \cdot \text{H}_2\text{O}$. Dashed lines indicate hydrogen bonding.

There are two (9-methyladenine)zinc complexes reported in the Cambridge Structural Database by McCall & Taylor (1975, 1976) obtained from the same slightly acid solution. The (9-methyladenine)-zinc complex $[\text{ZnCl}_3(\text{C}_6\text{H}_7\text{N}_5)]^- \cdot [\text{C}_6\text{H}_8\text{N}_5]^+ \cdot \text{H}_2\text{O}$ shows that the N(1) site of one adenine molecule is protonated, while the N(1) site of the second molecule is strongly bound by Zn (McCall & Taylor, 1975) and the *catena*-dichloro- μ -(9-methyladenine)-zinc(II) complex exhibits two coordination sites, N(1) and N(7), bridging neighbouring adenine molecules (McCall & Taylor, 1976).

In addition, Taylor (1973) has published the crystal structure of (trichloroadeninium)zinc(II) crystallized from hydrochloric acid solution. The Zn ion is coordinated to N(7) and the adenine ring is protonated at N(1) and is significantly non-planar with a dihedral angle of $4.3(1)^\circ$ between the adenine moieties. The complex presented in this work is very similar to the latter compound as shown in Table 3.

The structure may mimic the way in which the zinc cation can interact with an adenine molecule in nucleic acids.

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Structure of Tris(η^5 -cyclopentadienyl)uranium Thiocyanate

BY MARIE-ROSE SPIRLET,* JEAN REBIZANT AND CHRISTOS APOSTOLIDIS

Commission of the European Communities, Joint Research Centre, Institute for Transuranium Elements, Postfach 2340, D-7500 Karlsruhe, Germany

AND BASIL KANELLAKOPOULOS

Institut für Heisse Chemie, Kernforschungszentrum Karlsruhe, Postfach 3640, D-7500 Karlsruhe, Germany

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Abstract. Tris(η^5 -cyclopentadienyl)(thiocyanato-*N*)-uranium, $[\text{U}(\text{NCS})(\text{C}_5\text{H}_5)_3]$, $M_r = 491.40$, orthorhombic, $Pca2_1$, $a = 15.427(2)$, $b = 8.323(3)$, $c = 11.772(5)$ Å, $V = 1511(1)$ Å³, $Z = 4$, $D_x = 2.159$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 103.0$ cm⁻¹, $F(000) = 904$, $T = 295(1)$ K, $R = 0.043$ for 902 reflections [$I > 3\sigma(I)$]. The U atom is surrounded by three η^5 -covalently bonded cyclopentadienyl rings and by one thiocyanate N atom in a

Table 3. Comparison of selected bond distances (Å) and angles ($^\circ$) in (adenine)zinc(II) complexes

	Protonation			
	site	Zn—N	C(5)—N(7)—C(8)	C(6)—N(1)—C(2)
$\text{C}_6\text{H}_{10}\text{Cl}_3\text{N}_5\text{OZn}^a$	N(1)(H ⁺)	2.077 (3)	104.1 (2)	124.4 (2)
$\text{C}_3\text{H}_6\text{Cl}_3\text{N}_5\text{Zn}^b$	N(1)(H ⁺)	2.094 (5)	104.2 (3)	124.6 (3)
$\text{C}_{17}\text{H}_{17}\text{Cl}_3\text{N}_{10}\text{OZn}^c$	N(1)	2.05 (2)		120 (1)
	N(1)(H ⁺)			124 (1)
$\text{C}_6\text{H}_7\text{Cl}_3\text{N}_5\text{OZn}^d$	N(1)	2.068 (2)		119.6 (2)
	N(7)	2.040 (2)	104.7 (2)	

References: (a) Present work; (b) Taylor (1973); (c) McCall & Taylor (1975); (d) McCall & Taylor (1976).

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* On leave from University of Liège, Belgium.

distorted tetrahedral configuration. The U—C bond distances average 2.73 (4) Å, in agreement with the values previously reported for tris(cyclopentadienyl)uranium compounds. These distances do not appear to be influenced by the nature of the basic ligand. The U—N bond length, 2.34 (4) Å, is, as expected, shorter than the corresponding distance observed in the adduct $[\text{U}(\text{C}_5\text{H}_5)_3(\text{NCS})(\text{NCCH}_3)]$.

Experimental. The title compound was prepared by reaction of tris(cyclopentadienyl)uranium chloride