Structure of Bis(2-amino-4,5-dihydro-3H^+-1,3-thiazolium) Tetrachlorozincate(II), 2C$_3$H$_7$N$_2$S$^+$.ZnCl$_4^{2-}$

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Abstract. $M_r = 413 \cdot 5$, monoclinic, $P2_1/c$, $a = 8 \cdot 691$ (3), $b = 12 \cdot 856$ (4), $c = 14 \cdot 230$ (5) Å, $\beta = 91 \cdot 78$ (5)°, $U = 1589 \cdot 2$ Å^3, $Z = 4$, $D_m = 1 \cdot 72$ (2), $D_x = 1 \cdot 73$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0 \cdot 71069$ Å, $\mu = 2 \cdot 49$ mm^{-1}, $F(000) = 832$, room temperature, final $R = 0 \cdot 042$ for 2551 reflections. The asymmetric unit consists of a ZnCl$_4^{2-}$ anion and two C$_3$H$_7$N$_2$S$^+$ (ATH$^+$) cations. There is no direct bonding between the metal atom and the ATH$^+$ cation. The distorted tetrahedral ZnCl$_4^{2-}$ anion is linked to ATH$^+$ cations through hydrogen bonding involving all H atoms attached to N. Both protonated ATH molecules have a similar conformation.

Introduction. Brugarolas & Gosálvez (1982) have reported that thiazoline-4-carboxylic acid (thiaproline) and 2-amino-4,5-dihydro-1,3-thiazole (ATH) hydrochloride are both potential inducers of the reverse transformation of tumour cells. Recent potentiometric and IR studies (Huang, May, Williams & Gosálvez, 1981) suggest that binding sites for metals are mainly the N donors for Zn, Mn, Ni and Cu, but in thiaproline there is some carboxylate involvement. The N atoms involved were suggested to be the secondary in thiaproline and the primary in ATH. Since the mechanism of anticancer action depends strongly on metal–ligand binding we have undertaken X-ray studies of several metal complexes with thiaproline and 2-amino-1,3-thiazoline. Crystallographic study of the Zn^{II}–thiaproline complex (Tatarowski, Kubiak, Głowiak, Morawiec, Kozłowski & Gosálvez, 1984) has shown that N and O donors are involved in metal-ion binding. Our recent studies on the Cu^{II}–ATH (Głowiak, Kubiak, Tatarowski, Kozłowski & Gosálvez, 1983) and Cd^{II}–ATH systems (Kubiak, Głowiak & Kozłowski, 1983) have shown that the ligand molecule does not bond directly with the metal ion.

To check the possibilities of metal–N bond formation by ATH we have studied also the interaction of Zn^{II} with this ligand and the X-ray structure of such a system is presented here.

Experimental. Clear, colourless crystal from 1:2 molar ratio of zinc(II) chloride and ATH.HCl at room temperature, dimensions $0 \cdot 15 \times 0 \cdot 10 \times 0 \cdot 20$ mm; D_m

by flotation in carbon tetrachloride/ethylene bromide; monoclinic from Weissenberg photographs, $P2_1/c$; Syntex $P2_1$ computer-controlled four-circle diffractometer, scintillation counter, Mo $K\alpha$ radiation, graphite monochromator; cell parameters by least squares from setting angles of 15 reflections; 2590 independent reflections; variable $\theta/2\theta$ scan, scan rate $2 \cdot 0$–$29 \cdot 3°$ min^{-1} (depending on intensity), $2\theta_{max} = 60°$; two standards measured every 30 reflections, no significant change; correction for Lorentz and polarization effects, not for absorption; 2551 reflections with $I > 1 \cdot 96\sigma(I)$ used for structure determination, index range h 0→11, k 0→16, l −18→18; calculations performed on a Nova 1200 computer with programs supplied by Syntex (1976); neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974). Structure solved by heavy-atom method. Full-matrix least-squares refinement minimizing $\sum w(|F_o| - |F_c|)^2$; $w = 1/\sigma^2(F)$; non-H atoms refined with anisotropic and amino-H atoms with isotropic temperature factors, remaining H atoms with fixed positional and thermal parameters; 170 variables; $(\Delta/\sigma)_{max} = 0 \cdot 1$; $(\Delta\rho)_{max} = 0 \cdot 3$ e Å^{-3}; $R = 0 \cdot 042$, $R_w = 0 \cdot 047$, $S = 4 \cdot 28$.

Discussion. Final atomic parameters are given in Table 1.* The molecular geometry and atom numbering are shown in Fig. 1. Bond distances and angles are in Table 2.

The structure consists of a tetrachlorozincate anion and two protonated 2-amino-1,3-thiazolium cations held together by a combination of ionic and hydrogen-bonded contacts. As shown in Table 2, the coordination geometry of the tetrachlorozincate anion is distorted tetrahedral as found in other structures in which discrete ZnCl$_4^{2-}$ ions are present; for example, in the crystal structures of dicytosinium tetrachlozincate (Bourne & Taylor, 1983) and the cytosinium hemitetrachlorozincate–cytosine complex (Fujinami, Ogawa,

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* Lists of structure amplitudes, anisotropic thermal parameters, calculated H-atom parameters and H-bonding parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39669 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters and isotropic temperature factors with e.s.d.'s in parentheses*

For non-hydrogen atoms $B_{eq} = \frac{4}{3}\Sigma B_{ij}$.

	x	y	z	B_{eq}/B_{iso} (Å²)
Zn	0·22718 (6)	0·24941 (4)	0·23225 (4)	3·24 (3)
Cl(1)	0·4662 (1)	0·1855 (1)	0·1978 (1)	4·0 (1)
Cl(2)	0·1042 (1)	0·2942 (1)	0·0973 (1)	4·2 (1)
Cl(3)	0·0900 (2)	0·1298 (1)	0·3082 (1)	6·0 (1)
Cl(4)	0·2762 (1)	0·3867 (1)	0·3288 (1)	4·8 (1)
S(1)	0·2942 (2)	−0·0076 (1)	0·0606 (1)	4·6 (1)
S(2)	0·6777 (2)	0·3812 (1)	0·0695 (1)	4·8 (1)
N(1)	0·1259 (7)	−0·0955 (4)	−0·0763 (4)	5·1 (4)
N(2)	0·1098 (5)	−0·1605 (3)	0·0753 (3)	4·4 (3)
N(3)	0·4710 (6)	0·2608 (4)	−0·0174 (4)	5·4 (4)
N(4)	0·6081 (5)	0·3770 (3)	−0·1044 (3)	4·5 (3)
C(1)	0·1646 (5)	−0·0962 (3)	0·0130 (4)	3·7 (4)
C(2)	0·1523 (6)	−0·1405 (4)	0·1715 (4)	5·1 (5)
C(3)	0·2935 (6)	−0·0732 (4)	0·1733 (4)	4·7 (4)
C(4)	0·5732 (5)	0·3343 (4)	−0·0260 (3)	3·4 (3)
C(5)	0·7155 (6)	0·4644 (5)	−0·1001 (4)	5·2 (5)
C(6)	0·7955 (6)	0·4576 (4)	−0·0069 (4)	5·1 (5)
H(1N1)	0·175 (6)	−0·054 (4)	−0·107 (4)	4·7 (16)
H(2N1)	0·063 (7)	−0·133 (5)	−0·087 (4)	5·3 (20)
H(1N3)	0·452 (7)	0·240 (4)	0·053 (5)	8·1 (17)
H(2N3)	0·430 (6)	0·249 (4)	−0·067 (4)	4·2 (15)

Table 2. *Bond distances (Å) and angles (°) with e.s.d.'s in parentheses*

Zn—Cl(1)	2·301 (1)	Cl(1)—Zn—Cl(2)	108·59 (5)
Zn—Cl(2)	2·243 (1)	Cl(1)—Zn—Cl(3)	110·76 (5)
Zn—Cl(3)	2·244 (2)	Cl(1)—Zn—Cl(4)	104·65 (5)
Zn—Cl(4)	2·269 (1)	Cl(2)—Zn—Cl(3)	110·00 (6)
		Cl(2)—Zn—Cl(4)	113·21 (5)
		Cl(3)—Zn—Cl(4)	109·52 (6)
S(1)—C(1)	1·725 (5)	S(1)—C(1)—N(1)	121·6 (4)
S(1)—C(3)	1·811 (5)	N(1)—C(1)—N(2)	125·0 (5)
C(1)—N(1)	1·305 (7)	S(1)—C(1)—N(2)	113·4 (4)
C(1)—N(2)	1·312 (6)	C(1)—N(2)—C(2)	116·4 (4)
N(2)—C(2)	1·431 (7)	N(2)—C(2)—C(3)	107·8 (4)
C(2)—C(3)	1·501 (8)	C(3)—S(1)—C(1)	91·2 (2)
		C(2)—C(3)—S(1)	106·2 (4)
S(2)—C(4)	1·720 (5)	S(2)—C(4)—N(3)	121·5 (4)
S(2)—C(6)	1·807 (6)	N(3)—C(4)—N(4)	124·7 (5)
C(4)—N(3)	1·306 (7)	S(2)—C(4)—N(4)	113·7 (3)
C(4)—N(4)	1·287 (6)	C(4)—N(4)—C(5)	117·3 (4)
N(4)—C(5)	1·461 (7)	N(4)—C(5)—C(6)	105·9 (4)
C(5)—C(6)	1·480 (8)	C(5)—C(6)—S(2)	108·2 (4)
		C(6)—S(2)—C(4)	90·5 (2)
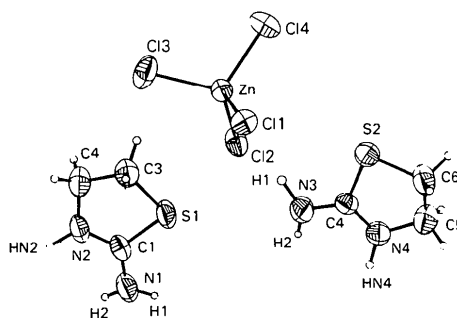
Arakawa, Shirotake, Fujii & Tomita, 1979). The spread in the Zn—Cl distances [2·243 (1)–2·301 (1) Å] and Cl—Zn—Cl angles [104·65 (5)–113·21 (5)°] may be partly due to the hydrogen bonds between the Cl atoms and the neighbouring ATH⁺ cations.

All bond distances and angles of both ATH⁺ cations fall in the expected range. They are in good agreement with values obtained from the structure determinations of 2-amino-1,3-thiazoline hydrochloride (Vedavathi & Vijayan, 1981) and $(ATH)_2CuCl_4$ (Głowiak *et al.*, 1983) and $(ATH)CdCl_3$ (Kubiak *et al.*, 1983). These bond distances indicate extensive electron delocalization in the N_{exo}—CS—N_{endo} moiety.

The two independent cations are very similar in their geometry and conformation. The dihydrothiazole rings are nonplanar with the methylene C atoms situated on opposite sides of the NCSN planes at −0·155, 0·216 (5) Å and −0·130, 0·212 (6) Å, respectively. All H atoms attached to N atoms lie in the NCSN planes. The conformations of the rings are similar to those in $(ATH)_2CuCl_4$ and $(ATH)CdCl_3$, but differ from the envelope-like conformation observed in aminothiazoline hydrochloride.

The unit-cell contents, plus some neighbouring molecules included to display the hydrogen-bonding system, are shown in Fig. 2; details of the individual hydrogen bonds have been deposited.*

All H atoms bonded to N participate in the hydrogen-bonding network. There are six kinds of hydrogen bonds, each having a Cl atom as acceptor. Cl(1) is hydrogen bonded to the N atom of a neighbouring thiazoline ring translated by *c*-glide symmetry, consequently forming an infinite chain along **c**. The chains are connected by hydrogen bonds from Cl(4) to the amino groups of the two ligand molecules. Cl(2) acts as a double acceptor from the amino and heterocyclic NH groups of the one ligand molecule. Of the four Cl atoms, three participate in hydrogen bonds, and the remaining one, Cl(3), with a relatively short Zn—Cl distance, does not.

* See deposition footnote.

Fig. 1. The molecular geometry and atom numbering.
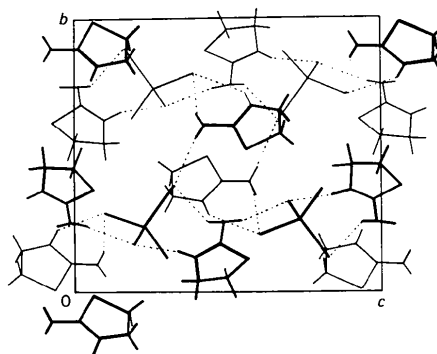
Fig. 2. Projection of the unit cell along **a**.

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Structure of *trans*-Diiodotetrakis(pyridine)cadmium(II)–Pyridine (1/2), [CdI₂(C₅H₅N)₄].2C₅H₅N

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Abstract. $M_r = 840.8$, orthorhombic, *Ccca*, $a = 11.620$ (2), $b = 15.847$ (2), $c = 17.245$ (4) Å, $V = 3175$ (1) Å³, $Z = 4$, $D_m = 1.7$ (1) (1,2-dichloroethane/1,2-dibromoethane), $D_x = 1.759$ Mg m⁻³, λ(Mo $K\alpha$) = 0.7107 Å, $\mu = 11.88$ mm⁻¹, $F(000) = 1624$, $T = 298$ K, final $R = 0.058$ for 1589 unique observed reflections. Cd is octahedrally coordinated with the N atoms of four pyridine molecules and two I⁻ ions in *trans* positions at average distances of 2.411 (7) and 2.9693 (7) Å, respectively. The crystal structure consists of layers perpendicular to **c**, built up of *trans*-CdI₂(py)₄ units linked together by van der Waals interactions between the ligating pyridine(py) molecules. The guest pyridine molecules are enclathrated in the cavities formed between the layers.

Introduction. A series of complexes of the type MP_4X_2 (where M is a divalent transition metal, P a pyridine derivative and X a halide or thiocyanate ion) form clathrate compounds with various guest molecules (Schaeffer, Dorsey, Skinner & Christian, 1957).

There has been no report on cadmium–pyridine complexes except for the early work of Paulus (1969) on Cd(py)₂Cl₂ which possesses a pseudooctahedral polymeric structure with bridging halide ligands. The crystal structure of the new clathrate compound, diiodotetrakis(pyridine)cadmium(II), which contains enclathrated pyridine guest molecules, has been determined.

Experimental. Cadmium iodide was dissolved in a pyridine–ethanol (1:1) mixture at 360 K. The colorless plate-like crystals immediately precipitated after cooling at room temperature. The crystal specimen for X-ray work was sealed in a Lindemann-glass capillary along with a small amount of mother liquid, since the crystals tend to lose pyridine easily. The large experimental error in density measurements is due to deterioration of the crystal in solution. Approximate dimensions of crystal $0.67 \times 0.45 \times 0.40$ mm. Rigaku AFC-5 automated four-circle diffractometer, graphite monochromator. Cell parameters refined by least-squares method on the basis of 20 2θ values, Mo $K\alpha$ radiation ($35° < 2\theta < 40°$). Intensity measurement performed to $2\theta = 70°$ (+h, +k, +l set), ω–2θ scan technique, scan speed 2° min⁻¹(θ). Mean ratio of structure factors of five standard reflections $0.95 < \sum(|F_o|/|F_o|_{initial})/5 \leq 1.00$. 2824 reflections measured, 1235 unobserved, 1589 unique [$|F_o| > 3\sigma(|F_o|)$]. Corrections for Lp and absorption (min. and max. transmission factors 0.118 and 0.307). Patterson map revealed the positions of I atoms; remaining non-H atoms found by successive Fourier syntheses and refined by block-diagonal least squares with anisotropic thermal parameters using the *UNICS*III computation program system (Sakurai & Kobayashi, 1979); six H atoms of coordinated pyridine molecules were found from difference density maps and refined isotropically; $\sum w ||F_o| - |F_c||^2$ minimized, $w^{-1} = \sigma^2(|F_o|) + (0.015|F_o|)^2$; final $R = 0.058$, wR