Refinement

Refinement on F

$R = 0.069$

$wR = 0.080$

$S = 24.27$

1457 reflections

253 parameters

Only H-atom U's refined

Unit weights applied

$(\Delta/\sigma)_{max} = 1.554$

$\Delta\rho_{max} = 1.07$ e Å^{-3}

$\Delta\rho_{min} = -0.70$ e Å^{-3}

Extinction correction: none

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$$B_{eq} = (32\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i.a_j.$$

	x	y	z	B_{eq}
Ni	0.21065 (19)	0.11407 (8)	0.18583 (23)	3.66 (9)
Cl(1)	0.2091 (4)	0.04717 (16)	−0.1707 (4)	5.27 (17)
Cl(2)	0.1336 (4)	0.34003 (17)	1.1477 (5)	5.87 (20)
O(11)	0.1381 (20)	0.0113 (6)	−0.0929 (16)	13.7 (12)
O(12)	0.1304 (15)	0.0713 (6)	−0.2922 (14)	11.3 (9)
O(13)	0.3007 (21)	0.0216 (8)	−0.2373 (24)	18.8 (15)
O(14)	0.2493 (11)	0.0850 (4)	−0.0599 (11)	6.8 (6)
O(21)	0.0989 (15)	0.2952 (5)	1.2252 (15)	10.2 (8)
O(22)	0.1205 (15)	0.3345 (6)	0.9875 (16)	11.7 (10)
O(23)	0.2684 (16)	0.3500 (9)	1.1711 (20)	18.1 (15)
O(24)	0.068 (3)	0.3797 (6)	1.193 (3)	21.5 (19)
N(1)	0.2612 (11)	0.0328 (4)	0.2617 (13)	5.5 (6)
N(2)	0.4220 (10)	0.1225 (4)	0.2176 (11)	4.4 (5)
N(3)	0.1844 (11)	0.1878 (4)	0.0690 (12)	4.8 (5)
N(4)	0.0024 (10)	0.0963 (4)	0.1741 (13)	4.7 (5)
N(5)	0.1725 (10)	0.1420 (4)	0.4184 (11)	4.4 (5)
C(1)	0.1804 (17)	−0.0040 (6)	0.3484 (20)	7.2 (9)
C(2)	0.4039 (15)	0.0350 (6)	0.3268 (18)	6.3 (8)
C(3)	0.4826 (14)	0.0710 (7)	0.2323 (19)	6.2 (8)
C(4)	0.4940 (14)	0.1565 (7)	0.1114 (18)	6.3 (9)
C(5)	0.4336 (15)	0.2090 (7)	0.0836 (20)	6.6 (8)
C(6)	0.3031 (18)	0.2076 (6)	−0.0166 (18)	6.5 (9)
C(7)	0.0621 (17)	0.1925 (6)	−0.0456 (19)	6.6 (9)
C(8)	−0.0699 (16)	0.1768 (7)	0.0238 (18)	6.3 (8)
C(9)	−0.0871 (12)	0.1193 (7)	0.0472 (18)	6.1 (8)
C(10)	−0.0441 (13)	0.1033 (7)	0.3397 (19)	6.5 (8)
C(11)	0.0227 (13)	0.1496 (6)	0.4187 (16)	5.6 (7)
C(12)	0.2410 (14)	0.1904 (6)	0.4847 (16)	6.0 (8)

Table 2. *Geometric parameters* (Å, °)

Ni—O(14)	2.242 (9)	N(2)—C(3)	1.43 (2)
Ni—N(1)	2.20 (1)	N(2)—C(4)	1.45 (2)
Ni—N(2)	2.10 (1)	N(3)—C(6)	1.49 (2)
Ni—N(3)	2.11 (1)	N(3)—C(7)	1.51 (2)
Ni—N(4)	2.11 (1)	N(4)—C(9)	1.47 (2)
Ni—N(5)	2.13 (1)	N(4)—C(10)	1.50 (2)
N(1)—C(1)	1.44 (2)	N(5)—C(11)	1.49 (2)
N(1)—C(2)	1.49 (2)	N(5)—C(12)	1.49 (2)
O(14)—Ni—N(1)	85.1 (4)	Ni—N(1)—C(1)	128.5 (9)
O(14)—Ni—N(2)	86.3 (4)	Ni—N(1)—C(2)	105.6 (8)
O(14)—Ni—N(3)	83.3 (4)	C(1)—N(1)—C(2)	112 (1)
O(14)—Ni—N(4)	95.7 (4)	Ni—N(2)—C(3)	109.2 (8)
O(14)—Ni—N(5)	179.5 (4)	Ni—N(2)—C(4)	119.8 (8)
N(1)—Ni—N(2)	81.2 (4)	C(3)—N(2)—C(4)	112 (1)
N(1)—Ni—N(3)	167.7 (4)	Ni—N(3)—C(6)	116.0 (8)
N(1)—Ni—N(4)	91.3 (4)	Ni—N(3)—C(7)	116.1 (8)
N(1)—Ni—N(5)	95.2 (4)	C(6)—N(3)—C(7)	107 (1)
N(2)—Ni—N(3)	93.9 (4)	Ni—N(4)—C(9)	120.2 (9)
N(2)—Ni—N(4)	172.1 (4)	Ni—N(4)—C(10)	106.1 (7)
N(2)—Ni—N(5)	94.1 (4)	C(9)—N(4)—C(10)	115 (1)
N(3)—Ni—N(4)	93.9 (4)	Ni—N(5)—C(11)	105.4 (7)
N(3)—Ni—N(5)	96.4 (4)	Ni—N(5)—C(12)	121.1 (8)
N(4)—Ni—N(5)	84.0 (4)	C(11)—N(5)—C(12)	109 (1)

N(1)—H(N1)···O(11)	3.21 (2)	N(4)—H(N4)···O(11^{iii})	3.11 (2)
N(2)—H(N2)···O(22^i)	3.12 (2)	N(5)—H(N5)···O(12^{iv})	3.06 (2)
N(3)—H(N3)···O(21^{ii})	3.15 (2)		

Symmetry codes: (i) $\frac{1}{2} + x$, $\frac{1}{2} - y$, $-\frac{1}{2} + z$; (ii) x, y, $-1 + z$; (iii) $-x$, $-y$, $-z$; (iv) x, y, $1 + z$.

The structure was solved and refined by direct and Fourier methods with full-matrix least-squares refinement; H atoms were found by the difference Fourier method and theoretical calculation. The high value of $(\Delta/\sigma)_{max}$ results from the presence of the disordered perchlorate groups. Program used was *NRCVAX* (Gabe, Le Page, White & Lee, 1987).

References

Gabe, E. J., Le Page, Y., White, P. S. & Lee, F. L. (1987). *Acta Cryst.* A43, C-294.

Lu, T. H., Wu, D. T. & Chung, C. S. (1986). *J. Chem. Soc. Dalton Trans.* pp. 1999–2001.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A24, 351–359.

Richman, J. E. & Atkins, T. J. (1974). *J. Am. Chem. Soc.* 96, 2268–2270.

Structure of Diiodobis(1-pyrroline)zinc(II)

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Abstract

The bis(4,5-dihydro-3H-pyrrole)diiodozinc(II) molecule sits on a mirror plane with the Zn atom at $y = 0.25$, one pyrroline ring lying in the plane of the mirror and the other perpendicular to it. The I atom is in a general position. Zn—I and Zn—N distances are 2.557 (1) Å, and 2.029 (7) and 2.025 (7) Å, respectively.

Comment

The title compound was prepared as described previously (Baxter, Melville & Robins, 1991) and recrystallized from chloroform.

4,5-Dihydro-3H-pyrrole (1-pyrroline) is a useful intermediate in the synthesis of some phenanthroindolizidine alkaloids (Cragg, Herbert, Jackson, Moody & Nicholson, 1982). The major drawbacks to its organic synthesis are its volatility and its tendency to trimerize in solution. We have shown that 1-pyrroline forms a stable crystalline complex with zinc iodide (Baxter, Melville & Robins, 1991). Regeneration of the 1-pyrroline can be achieved when required by treatment of the complex with ammonia.

The Zn atom is in the centre of an approximately tetrahedral arrangement of two I atoms (one reflected in the mirror plane) [Zn—I 2.557 (1) Å] and two independent N atoms [Zn—N 2.029 (7) and 2.025 (7) Å] from the pyrroline rings. The Zn—I and Zn—N distances are almost identical to the values [2.553 (2), 2.05 (1) and 2.06 (1) Å, respectively] found in diiodobis(pyridine)zinc(II) (Le Querler, Borel & Leclaire, 1977). The Zn—N distances are also analogous to those found in other tetrahedral zinc complexes {2.046 (5) and 2.052 96) Å for [ZnCl$_2$(C$_5$H$_5$N)$_2$] (Steffen & Palenik, 1976) and 1.99 and 2.10 Å for [ZnCl(C$_2$H$_4$N$_4$)$_2$] (Baenziger & Schultz, 1971)}.

The I—Zn—I angle of 120.3 (1)° is very large, in order to minimize I⋯I interactions. This large value is mimicked in the iodide and chloride structures [ZnI$_2$(C$_5$H$_5$N)$_2$] [120.32 (8)°], [ZnCl$_2$(C$_5$H$_5$N)$_2$] [121.8 (1)°] and [ZnCl$_2$(C$_2$H$_4$N$_4$)$_2$] [118.4 (2)°]. The N—Zn—N angle of 105.0 (3)° is also comparable to the referenced structures and reflects the larger I—Zn—I angle.

The packing arrangement is such that in alternate molecules the pyrroline rings are stacked parallel and perpendicular on top of each other along the b axis.
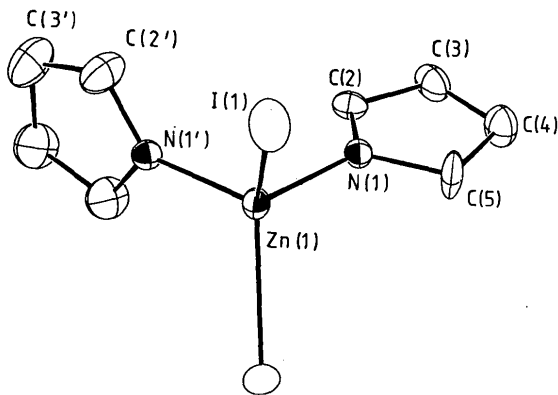

Fig. 2. Perspective packing diagram, viewed approximately down the b axis.

Experimental

Crystal data

[ZnI$_2$(C$_4$H$_7$N)$_2$]	Cell parameters from 25
M_r = 457.4	reflections
Orthorhombic	θ = 10–15°
$Pnma$	μ = 6.43 mm^{-1}
a = 11.351 (2) Å	T = 120 K
b = 9.734 (2) Å	Irregular
c = 12.090 (2) Å	0.5 × 0.3 × 0.3 mm
V = 1335.8 (5) Å^3	Colourless
Z = 4	Crystal source: recrystallized
D_x = 2.27 Mg m^{-3}	from chloroform
Mo $K\alpha$ radiation	
λ = 0.7107 Å	

Data collection

Enraf–Nonius CAD-4 diffractometer	1257 observed reflections [$I > 3.0\sigma(I)$]
$\omega/2\theta$ scans	θ_{max} = 27°
Absorption correction: empirical (Walker & Stuart, 1983)	h = 0 → 14
	k = 0 → 15
	l = 0 → 12
T_{min} = 0.86, T_{max} = 1.46	2 standard reflections
1703 measured reflections	frequency: 120 min
1545 independent reflections	intensity variation: 2%

Refinement

Refinement on F	w = 1/$\sigma^2(F)$
R = 0.034	$(\Delta/\sigma)_{max}$ = 0.06
wR = 0.060	$\Delta\rho_{max}$ = 0.83 e Å^{-3}
S = 3.2	$\Delta\rho_{min}$ = −2.04 e Å^{-3}

Fig. 1. Perspective view of the molecule showing the numbering scheme used (ORTEPII; Johnson, 1976).

1257 reflections
71 parameters
H-atom parameters not refined

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Mallinson, P. R. & Muir, K. W. (1985). *J. Appl. Cryst.* **18**, 51–53.
Steffen, W. L. & Palenik, G. L. (1976). *Acta Cryst.* **B32**, 298–300.
Walker, N. & Stuart, D. (1983). *Acta Cryst.* **A39**, 158–166.

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(1)	0.01069 (7)	0.25000	0.34742 (7)	0.020
I(1)	0.02501 (4)	0.02219 (5)	0.24298 (4)	0.034
N(1)	0.1443 (5)	0.2500	0.4588 (6)	0.021
N(1')	−0.1383 (6)	0.2500	0.4396 (5)	0.021
C(2)	0.1350 (7)	0.2500	0.5643 (7)	0.024
C(3)	0.2534 (9)	0.2500	0.6245 (8)	0.035
C(4)	0.3422 (8)	0.2500	0.5296 (8)	0.035
C(5)	0.2676 (7)	0.2500	0.4203 (7)	0.035
C(2')	−0.1972 (6)	0.1333 (8)	0.4744 (6)	0.043
C(3')	−0.3024 (7)	0.1713 (9)	0.5409 (7)	0.053

Table 2. *Geometric parameters* (Å, °)

Zn(1)—I(1)	2.557 (1)	N(1)—C(2)	1.280 (11)
Zn(1)—N(1')	2.025 (7)	N(1')—C(2')	1.384 (9)
N(1)—C(5)	1.474 (10)	C(3)—C(4)	1.528 (14)
C(2)—C(3)	1.528 (13)	C(2')—C(3')	1.486 (11)
C(4)—C(5)	1.569 (13)	C(3')—C(3')*	1.533 (13)
Zn(1)—N(1)	2.029 (7)		
I(1)—Zn(1)—N(1)	106.3 (1)	Zn(1)—N(1)—C(2)	126.8 (6)
N(1)—Zn(1)—N(1')	105.0 (3)	C(2)—N(1)—C(5)	113.2 (7)
Zn(1)—N(1)—C(5)	120.0 (6)	N(1)—C(2)—C(3)	113.7 (8)
Zn(1)—N(1')—C(2')	124.8 (4)	C(3)—C(4)—C(5)	106.0 (7)
C(2)—C(3)—C(4)	102.9 (8)	N(1')—C(2')—C(3')	110.4 (7)
N(1)—C(5)—C(4)	104.3 (7)	C(2')—N(1')—C(2')*	110.4 (7)
I(1)—Zn(1)—N(1')	108.9 (1)		

* Symmetry-generated atoms.

The crystal was cooled to 120 K using an Oxford Cryosystems device. Structure solution was obtained by direct methods using the program *MITHRIL* (Gilmore, 1984). Reliable H-atom positions could not be found from difference Fourier syntheses. Since the H-atom contributions were minimal, calculated positions were also excluded from the least-squares refinement. Calculations were performed using the Glasgow *GX* package (Mallinson & Muir, 1985).

References

Baenziger, N. C. & Schultz, R. J. (1971). *Inorg. Chem.* **10**, 661–666.
Baxter, G., Melville, J. C. & Robins, D. J. (1991). *Synlett*, pp. 359–360.
Cragg, J. E., Herbert, R. B., Jackson, F. B., Moody, C. J. & Nicholson, I. T. (1982). *J. Chem. Soc. Perkin Trans.* 1, pp. 2477–2485.
Gilmore, C. J. (1984). *J. Appl. Cryst.* **17**, 42–46.
Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Le Querler, J. F., Borel, M. M. & Leclaire, A. (1977). *Acta Cryst.* **B33**, 2299–2300.

Structure of [(CH3)3CNH3]2[ZnCl4].(CH3)3CNH3Cl

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Abstract

The structure of bis(*tert*-butylammonium) tetrachlorozincate-*tert*-butylammonium chloride (1/1) consists of $(CH_3)_3CNH_3^+$, $ZnCl_4^{2-}$ and Cl^- ions. The distorted tetrahedral $ZnCl_4^{2-}$ ion is surrounded by six cations with $Cl\cdots N$ distances of 3.19 (1)–3.38 (1) Å, while the isolated Cl^- ion is surrounded by four cations with $Cl\cdots N$ distances of 3.21 (1)–3.33 (1) Å. These short distances imply that the packing is stabilized by hydrogen bonds formed between the N and Cl atoms.

Comment

The title compound was investigated as part of a study on hydrogen bonding in alkylammonium tetrachlorozincates(II). Crystals of the title compound were obtained from an aqueous solution of $(CH_3)_3CNH_3Cl$ and $ZnCl_2$ in the molar ratios 3:1 or 2:1. To our knowledge, this is the first structural report of a double salt formed from an alkylamine–$ZnCl_2$–H_2O system; the crystal structure of $(NH_4)_2ZnCl_4.NH_4Cl$ from the NH_3–$ZnCl_2$–H_2O system has been reported (Klug & Alexander, 1944; Ohba, Shiokawa & Saito, 1987).

Cl(1), Cl(2) and Cl(4) in the $ZnCl_4^{2-}$ ion are each considered to exhibit two hydrogen-bond contacts to the N atoms of the cations with the $Cl\cdots N$ distance of 3.19 (1)–3.38 (1) Å, while Cl(3) does not seem to show any $Cl\cdots H$—N hydrogen-bond contacts; the shortest $Cl(3)\cdots N$ distance is 3.88 (1) Å. Cl(3) has the shortest Zn—Cl bond in the $ZnCl_4^{2-}$ ion; the anion is a distorted tetrahedron.