

C(42)	0.032 (1)	-0.1445 (5)	0.6459 (3)	6.8 (5)
C(43)	-0.093 (1)	-0.1341 (6)	0.6515 (3)	6.4 (6)
C(44)	-0.1446 (8)	-0.0644 (6)	0.6446 (3)	6.2 (5)
C(45)	-0.0719 (7)	-0.0044 (5)	0.6325 (2)	4.4 (4)
C(50)	0.1689 (6)	0.0566 (5)	0.5576 (2)	4.1 (3)
C(51)	0.1429 (8)	0.1120 (6)	0.5315 (2)	6.4 (5)
C(52)	0.141 (1)	0.100 (1)	0.4927 (3)	10 (1)
C(53)	0.166 (1)	0.031 (1)	0.4790 (3)	10 (1)
C(54)	0.192 (1)	-0.028 (1)	0.5025 (4)	11 (1)
C(55)	0.194 (1)	-0.0136 (6)	0.5423 (2)	7.1 (6)

Table 2. Selected geometric parameters (\AA , $^\circ$)

Pt—Cl	2.465 (2)	Pt—P(2)	2.322 (2)
Pt—P(1)	2.282 (2)	Pt—Si	2.321 (2)
Cl···H(C25 ⁱ)	2.96	C(34)···H(C12 ⁱⁱ)	2.91
C(32)···H(C23 ⁱⁱ)	2.93	C(23)···C(32 ⁱ)	3.50 (1)
Cl—Pt—P(1)	87.55 (7)	Pt—P(1)—C(17)	113.7 (4)
Cl—Pt—P(2)	85.73 (6)	Pt—P(2)—C(20)	107.9 (3)
Cl—Pt—Si	166.74 (7)	Pt—P(2)—C(26)	123.3 (3)
P(1)—Pt—P(2)	167.44 (7)	Pt—P(2)—C(27)	114.5 (3)
P(1)—Pt—Si	95.05 (7)	Pt—Si—C(30)	115.2 (2)
P(2)—Pt—Si	93.90 (6)	Pt—Si—C(40)	106.1 (2)
Pt—P(1)—C(10)	121.5 (3)	Pt—Si—C(50)	117.9 (2)
Pt—P(1)—C(16)	109.6 (3)		

Symmetry codes: (i) $\frac{1}{2} + x, y, \frac{3}{2} - z$; (ii) $x - \frac{1}{2}, y, \frac{3}{2} - z$;
 (iii) $x - \frac{1}{2}, \frac{1}{2} - y, 1 - z$.

Table 3. Comparison of some silyl compounds

Compounds: (a) *trans*-[PtCl(SiMePh₂)(PM₂Ph₂)] (McWeeny, Mason & Towel, 1969; Kapoor, 1968); (b) *trans*-[PtCl{SiMePh(1-naphthyl)}-(PM₂Ph₂)] (Hitchcock, 1976); (c) *trans*-[PtCl(SiPh₃)(PM₂Ph₂)] (this work); (d) *trans*-[PtCl{Si(OCH₂CH₂)₃N}(PM₂Ph₂)] (Eaborn, Odell, Pidcock & Scollary, 1976); (e) *trans*-[PtBr(SiMe₃)(PEt₃)₂] (Yamashita, Hayashi, Kobayashi, Tanaka & Goto, 1988).

Compound	Pt—Cl	Pt—Si	Pt—P
(a)	2.45 (1)	2.29	2.28, 2.28
(b)	2.462 (2)	2.317 (2)	2.292 (2), 2.306 (2)
(c)	2.465 (2)	2.321 (2)	2.282 (2), 2.323 (2)
(d)	2.471	2.292	2.300, 2.308
(e)	2.604 (6)*	2.330 (17)	2.296 (15), 2.299 (15)

* Pt—Br.

The H-atoms of all phenyl rings were placed in calculated positions and were included in the structure-factor calculations. x, y, z for the H-atoms on the methyl groups were refined except for those attached to C(16), which were not found.

Data collection: CAD-4 Software (Enraf-Nonius, 1989). Cell refinement: Xtal3.2 LATCON (Schwarzenbach & King, 1992). All subsequent calculations were carried out using TEXSAN (Molecular Structure Corporation, 1989). The structure was determined from Patterson and difference Fourier maps and refined by full-matrix least squares.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1204). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Contrasting Structures of Two Adducts of Zinc Crotonate with Substituted Pyridines

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Abstract

Despite their closely similar empirical formulae and the very small difference in the substituted pyridine bases used in their syntheses, the structures of tetrakis(μ -crotonato- $O:O'$)bis(4-cyanopyridine- N)dizinc(II) (1), [Zn₂(C₄H₅O₂)₄(C₆H₄N₂)₂], and catena-poly[{(crotonato- O,O')(4-vinylpyridine- N)zinc}- μ -crotonato- $O:O'$] (2), [Zn(C₄H₅O₂)₂(C₇H₇N)], are markedly different. Compound (1) is dimeric with four crotonate ligands bridging a pair of Zn atoms, each of which car-

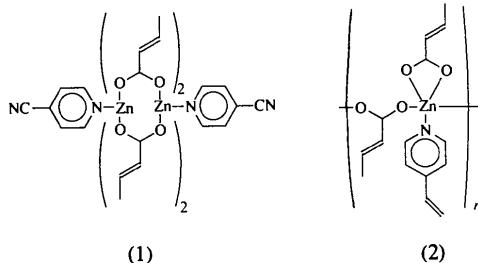
ries an axial 4-cyanopyridine ligand. There is no direct metal–metal bonding and the coordination of zinc is square pyramidal. Compound (2) forms a polymeric chain with a single crotonate bridge linking each Zn atom to the next. Each Zn atom also carries a chelating crotonate and a 4-vinylpyridine ligand to give a highly distorted five-coordinate geometry.

Comment

The structural chemistry of metal carboxylate complexes is rich and diverse. The variety of possible modes of bonding of carboxylate ligands to metals leads to many different kinds of structure, even for homoleptic complexes, and the incorporation of other ligands adds further to this diversity.

Homoleptic zinc carboxylate complexes have polymeric solid-state structures which include chains, sheets and three-dimensional networks (Clegg, Little & Straughan, 1986*a,b*, 1987; Guseinov, Musaev, Usualiev, Amiraslanov & Mamedov, 1984; Nakacho, Misawa, Fujiwara, Wakahara & Tomita, 1976; Clegg, Harbron, Hunt, Little & Straughan, 1990; Goldschmied, Rae & Stephenson, 1977; Blair, Howie & Wardell, 1993; Capilla & Aranda, 1979). The polymeric chain structure of zinc crotonate is broken up into dimeric molecules by treatment with neutral nitrogen bases such as pyridine and quinoline (Clegg, Little & Straughan, 1986*c*).

We have found that the use of different nitrogen bases does not always lead to the same type of binuclear molecular structure. The two structures reported here, (1) and (2), are completely different from each other even though the nitrogen bases used in their preparation differ only in a substituent group at a site not directly involved in the zinc binding and the synthetic method and conditions were essentially the same in each case.



Compound (1) results from treatment of zinc crotonate with 4-cyanopyridine. Its structure is molecular and dimeric, similar to that previously reported for the corresponding quinoline adduct (Clegg, Little & Straughan, 1986*c*). All four crotonate ligands act as symmetrical *syn-syn* bridges, holding the two Zn atoms in close proximity (Zn···Zn 2.910 Å); there is no evidence or requirement for direct metal–metal bonding in this complex. The square-pyramidal coordination of each Zn atom is completed by an axial 4-cyanopyridine ligand

bound through the pyridine N atom; the cyano group plays no part in metal coordination and there are no notably short intermolecular contacts. Presumably crystal packing, rather than any intramolecular interactions, is responsible for the non-linearity of the N–Zn···Zn–N unit and the orthogonality of the two pyridine ring planes, which are in contrast to the linearity and coplanarity observed in the bis(quinoline) complex (Clegg, Little & Straughan, 1986*c*).

The structure of compound (2), obtained from zinc crotonate and 4-vinylpyridine, is chain-polymeric, but it bears little resemblance to the chain structure of the

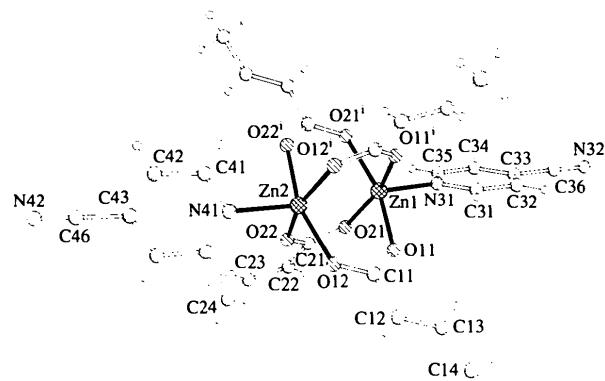


Fig. 1. Molecular structure of (1) with labels for the non-H atoms of the asymmetric unit and symmetry-equivalent atoms bonded to Zn. The crystallographic mirror plane contains the Zn atoms and the N31 ligand and bisects the N41 ligand. Atoms are represented by spheres of arbitrary radii.

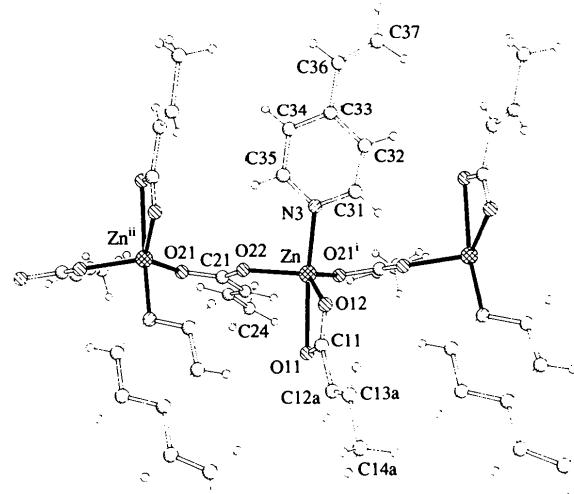


Fig. 2. A section of the polymeric chain structure of (2) with labels for the non-H atoms of the asymmetric unit and atoms bonded to them in adjacent units. Only the major disorder unit of the non-bridging crotonate ligand is shown. Atoms are represented by spheres of arbitrary radii.

parent zinc crotonate. The Zn atoms are well separated (4.860 Å), each Zn atom being linked to the next in the chain by a single *syn-anti* crotonate bridge. The five-coordination of zinc is attained by the binding of a 4-vinylpyridine ligand and a further crotonate ligand, which has a markedly unsymmetrical chelating mode. The narrow bite angle of the chelating ligand imposes an irregular five-coordinate geometry, which approximates to tetrahedral if this crotonate ligand is regarded as occupying a single coordination site.

Most other reported structures of zinc carboxylates with additional nitrogen or sulfur base ligands are molecular, generally mononuclear with approximately tetrahedral coordination geometry and monodentate carboxylate ligands (Horrocks, Ishley & Whittle, 1982a,b; Nadzhafov, Usubaliev, Amiraslanov, Movsumov & Mamedov, 1981; Cavalca, Gasparri, Andreotti & Domiano, 1967). A polymeric structure is found for the bis(hydrazine) adduct of zinc acetate because the nitrogen base here is bifunctional and acts as a bridge (Ferrari, Braibanti, Bigiardi & Lanfredi, 1965). Most hydrated zinc carboxylates are also mononuclear with coordination of zinc by either monodentate or chelating carboxylate ligands and by two, three or four water molecules [the Cambridge Structural Database contains almost 20 such structures (Allen, Davies, Galloy, Johnson, Kennard, Macrae, Mitchell, Mitchell, Smith, & Watson, 1991)], but, of interest in the context of the polymeric chain structure of compound (2), the monohydrated complex of zinc 2-ethoxybenzoate contains both bridging and terminal (but not chelating) carboxylates to produce a polymeric structure (Natarajan, Gowda & Cartz, 1974).

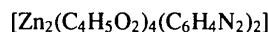
These results further underline the complexity of the structural chemistry of carboxylate complexes and the unpredictability of the structures given our present knowledge.

Experimental

Both of the title compounds were prepared by treatment of zinc crotonate with the corresponding substituted pyridine (1:1 molar ratio) in ethanol solution and recrystallized from ethanol solution by cooling.

Compound (1)

Crystal data



$M_r = 679.28$

Orthorhombic

Pnma

$a = 12.0761(6)$ Å

$b = 12.2729(6)$ Å

$c = 21.0414(14)$ Å

$V = 3118.5(3)$ Å³

$Z = 4$

$D_x = 1.447$ Mg m⁻³

Data collection

Stoe Siemens diffractometer

ω/θ scans with on-line

profile fitting (Clegg, 1981)

Absorption correction:

empirical

$T_{\min} = 0.308$, $T_{\max} = 0.384$

7471 measured reflections

2897 independent reflections

2341 observed reflections

$[I > 2\sigma(I)]$

$R_{\text{int}} = 0.0292$

$\theta_{\max} = 25.01^\circ$

$h = -14 \rightarrow 14$

$k = -14 \rightarrow 14$

$l = -25 \rightarrow 25$

3 standard reflections

frequency: 60 min

intensity decay: 37%

Refinement

Refinement on F^2

$R(F) = 0.0288$

$wR(F^2) = 0.0840$

$S = 1.062$

2896 reflections

214 parameters

$$w = 1/[\sigma^2(F_o^2) + (0.0398P)^2 + 1.2129P]$$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.351$ e Å⁻³

$\Delta\rho_{\min} = -0.231$ e Å⁻³

Extinction correction:

SHELXL93 (Sheldrick, 1993)

Extinction coefficient:

0.0007 (2)

Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (1)

	x	y	z	U_{eq}
Zn1	0.52447 (3)	1/4	0.69454 (2)	0.04667 (14)
Zn2	0.54234 (3)	1/4	0.55664 (2)	0.04710 (14)
O11	0.6424 (2)	0.3640 (2)	0.67509 (9)	0.0829 (7)
O12	0.6599 (2)	0.3657 (2)	0.57082 (8)	0.0735 (6)
C11	0.6866 (2)	0.3965 (2)	0.62527 (11)	0.0560 (6)
C12	0.7769 (2)	0.4772 (2)	0.63088 (11)	0.0663 (7)
C13	0.8213 (2)	0.5055 (3)	0.68502 (13)	0.0752 (8)
C14	0.9146 (3)	0.5826 (3)	0.6952 (2)	0.1075 (13)
O21	0.4072 (2)	0.3660 (2)	0.68095 (8)	0.0736 (6)
O22	0.4260 (2)	0.3669 (2)	0.57673 (8)	0.0751 (6)
C21	0.3833 (2)	0.4005 (2)	0.62659 (11)	0.0558 (6)
C22	0.2958 (3)	0.4835 (3)	0.62163 (12)	0.0736 (8)
C23	0.2511 (3)	0.5137 (3)	0.56796 (14)	0.0883 (10)
C24	0.1591 (4)	0.5937 (4)	0.5601 (2)	0.148 (2)
N31	0.5367 (2)	1/4	0.79180 (13)	0.0465 (6)
C31	0.6360 (3)	1/4	0.8185 (2)	0.0661 (11)
C32	0.6505 (3)	1/4	0.8835 (2)	0.0616 (10)
C33	0.5590 (3)	1/4	0.92135 (15)	0.0522 (8)
C34	0.4558 (3)	1/4	0.8942 (2)	0.0717 (12)
C35	0.4489 (3)	1/4	0.8294 (2)	0.0601 (10)
C36	0.5745 (4)	1/4	0.9900 (2)	0.0705 (11)
N32	0.5890 (4)	1/4	1.0429 (2)	0.109 (2)
N41	0.5090 (2)	1/4	0.46086 (12)	0.0465 (6)
C41	0.4909 (3)	0.1576 (2)	0.43024 (11)	0.0666 (7)
C42	0.4509 (3)	0.1538 (3)	0.36917 (11)	0.0732 (9)
C43	0.4288 (3)	1/4	0.3387 (2)	0.0568 (9)
C46	0.3808 (4)	1/4	0.2756 (2)	0.0783 (13)
N42	0.3411 (4)	1/4	0.2269 (2)	0.116 (2)

Table 2. Selected geometric parameters (Å, °) for (1)

Zn1—O21	2.029 (2)	Zn2—O12	2.030 (2)
Zn1—O11	2.038 (2)	Zn2—O22	2.052 (2)
Zn1—N31	2.052 (3)	Zn2—N41	2.055 (3)
O21—Zn1—O21 ⁱ	89.16 (13)	O12—Zn2—O12 ⁱ	88.75 (13)
O21—Zn1—O11	88.73 (10)	O12—Zn2—O22	87.68 (9)
O21 ⁱ —Zn1—O11	160.30 (8)	O12 ⁱ —Zn2—O22	159.65 (7)

O11—Zn1—O11 ⁱ	86.70 (14)	O22—Zn2—O22 ⁱ	88.74 (13)	C33	0.6928 (6)	0.0217 (3)	0.5488 (7)	0.0701 (15)
O21—Zn1—N31	101.01 (7)	O12—Zn2—N41	106.33 (7)	C34	0.6249 (6)	0.0400 (3)	0.3946 (6)	0.076 (2)
O11—Zn1—N31	98.62 (7)	O22—Zn2—N41	93.90 (8)	C35	0.5703 (6)	0.1094 (3)	0.3496 (6)	0.0723 (15)
Symmetry code: (i) $x, \frac{1}{2} - y, z$.								

Compound (2)*Crystal data*[Zn(C₄H₅O₂)₂(C₇H₇N)] $M_r = 340.67$

Monoclinic

 $P2_1/c$ $a = 10.343$ (2) Å $b = 18.329$ (3) Å $c = 9.671$ (2) Å $\beta = 117.38$ (2) $^\circ$ $V = 1628.0$ (5) Å³ $Z = 4$ $D_x = 1.390$ Mg m⁻³*Data collection*

Stoe Siemens diffractometer

 w/θ scans with on-line

profile fitting (Clegg, 1981)

Absorption correction:

empirical

 $T_{\min} = 0.444$, $T_{\max} = 0.986$

5582 measured reflections

2698 independent reflections

Mo K α radiation $\lambda = 0.71073$ Å

Cell parameters from 32 reflections

 $\theta = 10\text{--}12.5^\circ$ $\mu = 1.522$ mm⁻¹ $T = 295$ (2) K

Plate

0.60 × 0.35 × 0.02 mm

Colourless

1685 observed reflections [$|I| > 2\sigma(I)$] $R_{\text{int}} = 0.0733$ $\theta_{\max} = 25.01^\circ$ $h = -12 \rightarrow 12$ $k = -21 \rightarrow 21$ $l = -11 \rightarrow 11$

3 standard reflections

frequency: 60 min

intensity decay: 54%

*Refinement*Refinement on F^2 $R(F) = 0.0396$ $wR(F^2) = 0.1129$ $S = 1.078$

2693 reflections

209 parameters

 $w = 1/[\sigma^2(F_o^2) + (0.0171P)^2 + 0.5381P]$
where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} = 0.003$ $\Delta\rho_{\max} = 0.411$ e Å⁻³ $\Delta\rho_{\min} = -0.266$ e Å⁻³Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)**Table 3.** Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (2)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Zn	0.48651 (6)	0.26342 (3)	0.38405 (6)	0.0552 (2)
O11	0.4899 (7)	0.3914 (3)	0.3787 (7)	0.126 (2)
O12	0.6672 (5)	0.3235 (3)	0.5121 (5)	0.1002 (13)
C11	0.6183 (9)	0.3845 (4)	0.4779 (8)	0.082 (2)
C12A	0.6766 (14)	0.4585 (6)	0.5320 (17)	0.082 (4)
C13A	0.8033 (15)	0.4684 (8)	0.6338 (17)	0.106 (4)
C14	0.8632 (9)	0.5486 (4)	0.6856 (10)	0.147 (3)
C12B	0.7501 (22)	0.4349 (9)	0.5701 (26)	0.091 (5)
C13B	0.7347 (20)	0.5024 (8)	0.5682 (24)	0.097 (5)
O21	0.3069 (4)	0.2457 (2)	-0.0946 (3)	0.0611 (9)
O22	0.4296 (4)	0.2519 (2)	0.1585 (3)	0.0609 (9)
C21	0.3122 (5)	0.2553 (2)	0.0369 (5)	0.0482 (11)
C22	0.1755 (5)	0.2709 (3)	0.0433 (5)	0.0578 (12)
C23	0.0478 (6)	0.2683 (3)	-0.0727 (6)	0.079 (2)
C24	-0.0928 (7)	0.2856 (4)	-0.0689 (8)	0.116 (2)
N3	0.5807 (4)	0.1617 (2)	0.4502 (4)	0.0574 (10)
C31	0.6503 (6)	0.1443 (3)	0.6016 (5)	0.0664 (13)
C32	0.7078 (6)	0.0766 (3)	0.6555 (6)	0.0738 (15)

Table 4. Selected geometric parameters (Å, °) for (2)

Zn—O21 ⁱ	1.968 (3)	Zn—N3	2.065 (4)
Zn—O22	1.992 (3)	Zn—O11	2.347 (5)
Zn—O12	2.028 (5)		
O21 ⁱ —Zn—O22	106.74 (12)	O12—Zn—N3	97.5 (2)
O21 ⁱ —Zn—O12	129.14 (15)	O21 ⁱ —Zn—O11	96.4 (2)
O22—Zn—O12	116.8 (2)	O22—Zn—O11	94.7 (2)
O21 ⁱ —Zn—N3	102.96 (13)	O12—Zn—O11	56.7 (2)
O22—Zn—N3	95.93 (13)	N3—Zn—O11	154.1 (2)

Symmetry code: (i) $x, \frac{1}{2} - y, z$.

For both structures, isotropic H atoms were refined using a riding model with $U(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. For compound (2), twofold orientational disorder of one of the crotonate ligands was resolved and refined with the aid of restraints on the geometry (similarity) and anisotropic displacement parameters; the disorder consists of two alternative orientations within the same plane for the central double bond and was modelled by the splitting of atoms C12 and C13, together with their attached H atoms and the H atoms of C14, into two partial atoms each.

The data sets for both compounds consist of a complete unique set of reflections together with their Friedel opposites and part of a further equivalent set; the index limits given do not indicate a whole sphere of data.

For both compounds, data collection: *DIF4* (Stoe & Cie, 1988); cell refinement: *DIF4*; data reduction: local programs; program(s) used to solve structures: *SHELXTL/PC* (Sheldrick, 1990); program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *SHELXTL/PC*; software used to prepare material for publication: *SHELXL93* and local programs.

We thank EPSRC for financial support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, together with unlabelled displacement ellipsoid plots of both structures, have been deposited with the IUCr (Reference: MU1144). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis(*n*-heptylammonium) Tetrachlorozincate

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Abstract

The crystal structure of $(C_7H_{18}N)_2[ZnCl_4]$ is composed of alternating layers of inorganic ions and paraffinic chains. It differs from the structures of analogous compounds that have a hydrocarbon chain containing an even number of C atoms. This may explain the odd–even effects observed in differential scanning calorimetry (DSC) measurements on these compounds.

Comment

Alkylammonium tetrahalometallates of general formula $(n-C_nH_{2n+1}NH_3)_2[MX_4]$ ($M = Mn, Cu, Cd, etc.; X = Cl, Br$) are known to form crystal structures in which

hydrocarbon layers are sandwiched between inorganic sheets (Phelps, Losee, Hatfield & Hodgson, 1976; Willet & Riedel, 1975; Peterson & Willet, 1972). DSC measurements indicate that the compounds of the series show a great variety of structural phases (Carla, Giuseppe & Giuseppe, 1986) and exhibit an odd–even effect as a function of the number of C atoms in the alkyl chain. This effect may depend on the structural differences between the odd and even compounds of the series. The structure of $(n-C_{12}H_{25}NH_3)_2[ZnCl_4]$ ($C_{12}Zn$) has been reported (Ciajalo, Corradini & Pavone, 1977). It is the aim of this paper to report the single-crystal room-temperature structure determination of the title compound ($HAZn$) in order to explain the odd–even effects observed in the DSC measurements.

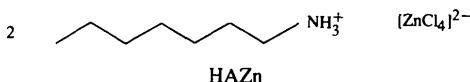


Fig. 1 shows the numbering scheme for the non-H atoms and a view of the unit cell is presented in Fig. 2. The structure consists of organic and inorganic layers. Each inorganic layer of tetrahedral $ZnCl_4^{2-}$ anions is sandwiched between two hydrocarbon layers formed by $C_7H_{18}N^+$ cations (Fig. 2). Each tetrahedral $ZnCl_4^{2-}$ anion is surrounded by six NH_3 groups from adjacent sheets. The $ZnCl_4^{2-}$ tetrahedra show angles from 104.7 (4) to 113.3 (5)°, which indicate a small distortion from the normal value. The distortion probably results from the formation of hydrogen bonds between N and Cl atoms. The average Zn—Cl bond length is 2.26 Å, which is slightly shorter than the value of 2.27 Å in $[NH_3-(CH_2)_{10}-NH_3][ZnCl_4]$ (Guo, Lin, Zeng & Xi, 1992).

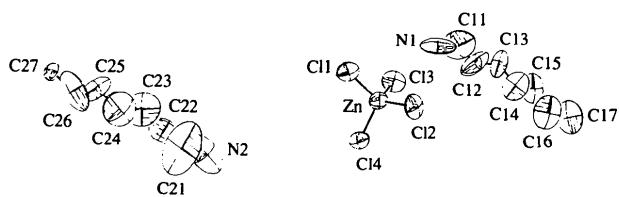


Fig. 1. Atomic numbering of the non-H atoms of the title compound shown with 50% probability ellipsoids.

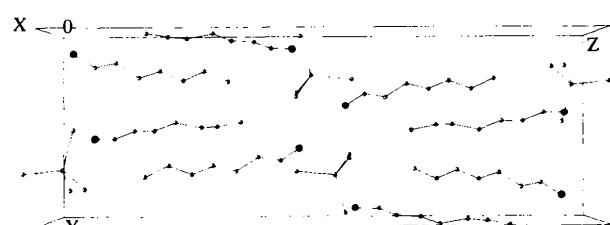


Fig. 2. View of the unit cell with N atoms shown as large filled circles.