Tetraethylammonium Tetramethylammonium Tetrachlorozincate(II), $[(C_2H_5)_4N][(CH_3)_4N][ZnCl_4]$

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Abstract

The crystal structure of $[(C_2H_5)_4N][(CH_3)_4N][ZnCl_4]$ [abbreviated to $(TEA)(TMA)ZnCl_4$] was investigated by means of X-ray diffraction at room temperature. The crystal structure can be regarded as layered by repeating the sequence $(TMA)^+/(ZnCl_4)^{2-}/(TEA)^+/(TEA)^+/(ZnCl_4)^{2-}$. In the same layer, the $(TMA)^+$ tetrahedra may be ordered or disordered according to their position in the layer.

Comment

Compounds of the A_2MX_4 family have been the subject of numerous investigations. In particular, crystals isomorphous with β-K_2SO_4 have been studied intensively since the discovery of incommensurate phases, and ferroelectric and ferroelastic commensurate phases in this family. This is the case for $[(CH_3)_4N]_2[ZnCl_4]$ [abbreviated to $(TMA)_2ZnCl_4$], which crystallizes in space group *Pnma* (Morosin & Lingafelter, 1959); a temperature study showed different phases (Sawada, Shiroishi, Yamamoto, Takashige & Matsuo, 1978) including a modulated one (Sawada, Shiroishi, Takashige & Matsuo, 1978). Compounds with $A^+ = [(C_2H_5)_4N]^+$ [abbreviated as $(TEA)^+$] have a completely different structure (Stucky, Folkers & Kistenmacher, 1967). $(TEA)_2ZnCl_4$ is isomorphous with $(TEA)_2NiCl_4$ (Stucky *et al.*, 1967), crystallizing in space group $P4_2/nmc$ with similar cell parameters. A differential scanning calorimetry temperature study showed two transitions for $(TEA)_2ZnCl_4$, at 228 and 233 K, upon lowering the temperature (Caëtano, Lopez, Mahoui, Lapasset, Moret, Assih & Saint-Grégoire, 1993).

Until now, no $ABMX_4$ compound comprising $(TMA)^+$ and $(TEA)^+$ tetrahedra has been reported. The aim of our work was to verify the possibility of obtaining $(TEA)(TMA)ZnCl_4$. In fact, by considering the size of each cation and the space group of each A_2ZnCl_4 compound, it was not obvious that $(TEA)(TMA)ZnCl_4$ could exist, and in which structure it could crystallize.
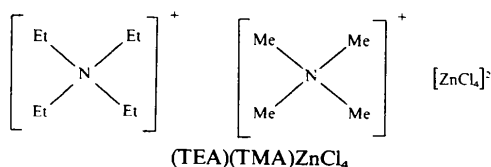
(TEA)(TMA)ZnCl₄

It appears that $(TEA)(TMA)ZnCl_4$ does exist and like $(TEA)_2ZnCl_4$ it crystallizes in the tetragonal system at room temperature, but with a different space group, $P\bar{4}2_1m$. The structure is organized as a succession of layers of anions and cations perpendicular to the $\bar{4}$ axis.

We can see in Fig. 1 a first layer at $z = 0$ consisting only of $(TMA)^+$ cations. The N atoms, the centres of these ions, are located at the corners of squares with sides of $a/2$. In this lattice of squares, there is alternation along a of ordered ions (atoms N2 and C2) with perfect geometry and disordered ions (atoms N3, C31, C32, C33 and C34). Then, at $z = 1/5$ there is a layer consisting of only $[ZnCl_4]^{2-}$ anions; Cl2 of each tetrahedron enters the layer of $(TMA)^+$ at the middle of a square and the base of each tetrahedron is oriented to the next layer (at $z = 1/2$) formed by equivalent $(TEA)^+$ cations. In $(TEA)(TMA)ZnCl_4$, the $(TEA)^+$ ions are ordered with a conformation corresponding to the stable conformation known as 'Greek cross' (Wolthuis, Huiskamp, Carlin & De Jongh, 1986), whereas in $(TEA)_2NiCl_4$ (Stucky *et al.*, 1967), the $(TEA)^+$ are disordered with a 'Nordic cross' conformation (Wolthuis *et al.*, 1986).

Therefore, in conclusion, the three compounds may be regarded as having layered structures. For compounds of type A_2ZnCl_4, the succession of layers is $A^+/A^+/[ZnCl_4]^{2-}$ and for $(TEA)(TMA)ZnCl_4$ it is $(TMA)^+/[ZnCl_4]^{2-}/(TEA)^+/(TEA)^+/[ZnCl_4]^{2-}$. None of the compounds has the same space group but $(TEA)(TMA)ZnCl_4$ and $(TEA)_2ZnCl_4$ crystallize in the
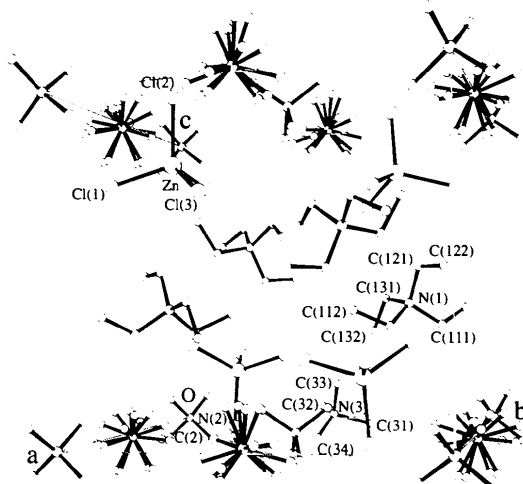

Fig. 1. Perspective view of the unit cell of $(TEA)(TMA)ZnCl_4$ at room temperature. Only one position of the disordered $(TMA)^+$, corresponding to atom N3 at (0,1/2,0.012), is shown.

tetragonal system. In $(TMA)_2ZnCl_4$ there is no disorder, unlike in $(TEA)(TMA)ZnCl_4$ where some $(TMA)^+$ are disordered, and in $(TEA)_2ZnCl_4$, where the $(TEA)^+$ ions are disordered, whereas in $(TEA)(TMA)ZnCl_4$ the $(TEA)^+$ are ordered and in an another conformation corresponding to a larger space occupation.

These results suggest that the disorder is introduced by the presence of the $(TEA)^+$ ions. The knowledge of the existence of $(TEA)(TMA)ZnCl_4$ certainly initiates the study of a new crystalline family where it will be of interest to determine whether structural instabilities occur.

Experimental

Suitable single crystals of $(TEA)(TMA)ZnCl_4$ were grown by cooling an aqueous solution containing the appropriate stoichiometric amounts of $(TEA)Cl$, $(TMA)Cl$ and $ZnCl_2$.

Crystal data

$[(C_2H_5)_4N][(CH_3)_4N][ZnCl_4]$	Mo $K\alpha$ radiation
$M_r = 411.61$	$\lambda = 0.7107$ Å
Tetragonal	Cell parameters from 23
$P\bar{4}2_1m$	reflections
$a = 13.087$ (2) Å	$\theta = 13.6–23°$
$c = 11.793$ (1) Å	$\mu = 1.629$ mm^{-1}
$V = 2019.8$ (5) Å^3	$T = 298$ K
$Z = 4$	Square
$D_x = 1.353$ Mg m^{-3}	$0.27 \times 0.19 \times 0.10$ mm
	Colourless

Data collection

Enraf–Nonius CAD-4 four-circle diffractometer	737 observed reflections $[F > 4\sigma(F)]$
$\theta/2\theta$ scans	$R_{int} = 0.0123$
Absorption correction:	$\theta_{max} = 30°$
SHELX76 (Sheldrick, 1976) Gaussian	$h = 0 \rightarrow 18$
	$k = 0 \rightarrow 18$
$T_{min} = 0.69$, $T_{max} = 0.86$	$l = 0 \rightarrow 16$
3323 measured reflections	3 standard reflections
1744 independent reflections	frequency: 60 min
	intensity variation: none

Refinement

Refinement on F	$\Delta\rho_{max} = 0.474$ e Å^{-3}
$R = 0.041$	$\Delta\rho_{min} = -0.390$ e Å^{-3}
$wR = 0.042$	Atomic scattering factors
$S = 1.33$	from Cromer & Mann
737 reflections	(1968) (C, H, N, Cl) and
75 parameters	International Tables for
Only H-atom U's refined	X-ray Crystallography
$w = 1/[\sigma^2(F) + 0.001033F^2]$	(1974, Vol. IV, Table
$(\Delta/\sigma)_{max} = 0.04$	2.2B) (Zn)

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

U_{iso} for N and C; $U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$ for Zn and Cl.

	x	y	z	U_{iso}/U_{eq}
Zn	0.7460 (1)	-1/2+x	0.8127 (1)	0.0366 (4)
Cl1	0.7841 (2)	0.0835 (2)	0.7612 (2)	0.074 (2)
Cl2	0.7581 (4)	-1/2+x	1.0039 (2)	0.073 (2)
Cl3	0.8539 (4)	-1/2+x	0.7205 (3)	0.075 (2)
N1	0.291 (1)	1/2+x	0.3937 (7)	0.048 (2)
N2	0	0	0	0.057 (5)
N3	0	1/2	0.012 (1)	0.052 (4)
C111	0.3798 (6)	0.7496 (7)	0.3244 (7)	0.065 (2)
C112	0.4325 (8)	0.6575 (7)	0.3781 (8)	0.086 (3)
C121	0.328 (1)	1/2+x	0.509 (1)	0.066 (4)
C122	0.407 (2)	1/2+x	0.504 (1)	0.103 (5)
C131	0.211 (2)	1/2+x	0.415 (1)	0.068 (4)
C132	0.165 (2)	1/2+x	0.3097 (12)	0.088 (5)
C2	0.0336 (8)	0.0884 (7)	-0.0745 (9)	0.076 (3)
C31	-0.021 (3)	0.612 (3)	-0.0246 (25)	0.059 (5)
C32	-0.097 (2)	0.445 (2)	0.0296 (24)	0.059 (5)
C33	0.051 (2)	0.522 (2)	0.125 (2)	0.059 (5)
C34	0.075 (2)	0.459 (2)	-0.064 (3)	0.059 (5)

Table 2. *Selected geometric parameters* (Å, °)

Zn—Cl1	2.267 (6)	N3—C31	1.56 (3)
Zn—Cl2	2.266 (6)	N3—C32	1.47 (3)
Zn—Cl3	2.274 (7)	N3—C33	1.51 (3)
N1—C111	1.52 (2)	N3—C34	1.44 (3)
N1—C121	1.52 (2)	C111—C112	1.53 (1)
N1—C131	1.502 (24)	C121—C122	1.465 (27)
N2—C2	1.52 (2)	C131—C132	1.504 (22)
Cl1—Zn—Cl1^i	109.9 (2)	C31—N3—C32	110 (2)
Cl1—Zn—Cl2	108.5 (2)	C31—N3—C33	98 (2)
Cl1—Zn—Cl3	108.5 (2)	C31—N3—C34	108 (2)
Cl2—Zn—Cl3	112.9 (2)	C32—N3—C33	111 (2)
C111—N1—C111^{ii}	104.9 (9)	C32—N3—C34	119 (2)
C111—N1—C121	111 (1)	C33—N3—C34	109 (2)
C111—N1—C131	112 (1)	N1—C111—C112	113.8 (8)
C121—N1—C131	107 (1)	N1—C121—C122	114.3 (2)
C2—N2—C2^{iii}	109.3 (8)	N1—C131—C132	114.5 (2)
C2—N2—C2^{iv}	109.6 (4)		

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

Preliminary Weissenberg photographs showed a $P4/mmm$ Laue class. The systematic absence of the $h00$ reflections for $h = 2n + 1$ suggested space groups $P\bar{4}2_1m$ or $P42_12$. Only $P\bar{4}2_1m$ allows the correct crystal structure. From the Patterson function we obtained the position of the Zn atom. Two successive Fourier syntheses revealed Cl-atom positions, followed by the N1 and C atoms of $(TEA)^+$, the N2 and C atoms of one ordered $(TMA)^+$ (N2 at the origin) and N3 [the central atom of one disordered $(TMA)^+$] on twofold axes. Finally, a difference Fourier synthesis revealed four independent peaks bonded to N3, corresponding to the C atoms of a disordered $(TMA)^+$. Calculation of bond lengths and angles led to one unique hypothesis for the relative position of the four C atoms around N3.

Zn and Cl atoms were given anisotropic displacement factors, the N and C atoms were given isotropic displacement factors, with a common factor for the C atoms of the disordered $(TMA)^+$. The H atoms were placed in theoretical positions. A common isotropic displacement factor was used for the Hα atoms of the $(TEA)^+$, another for the Hβ atoms, one for the H atoms of the ordered $(TMA)^+$ and one for the H atoms of the disordered $(TMA)^+$.

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: NA1105). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Zinc(II) Complex of Creatinine

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Abstract

In the crystals of bis(2-amino-1,5-dihydro-1-methyl-4*H*-imidazol-4-one-N^3)dichlorozinc(II), [ZnCl$_2$(C$_4$H$_7$N$_3$-O)$_2$], the Zn atom is fourfold coordinated by the two N atoms situated at the 3 positions of the imidazole rings and by two Cl atoms. The coordination environment at the Zn atom is distorted tetrahedral. The amino and carbonyl groups participate in a hydrogen-bond network.

Comment

Creatinine (2-amino-1,5-dihydro-1-methyl-4*H*-imidazol-4-one) is a final metabolic product of arginine. It is one of the factors inducing chronic renal failure and/or uremic symptoms (Bell, Lee, Sadler, Wilkie & Woodham, 1991). Toxic effects in rats (Yokozawa, Mo & Oura, 1989) and determination by a flow-injection biosensor system (Rui, Sonomoto, Ogawa & Kato, 1993) or by an optical sensor using a host–guest system (Buhlmann, Badertscher & Simon, 1993) have been reported. To date, the crystal structures of creatinine (du Pré & Mendel, 1955) and its serotonin (Karle, Dragonette & Brenner, 1965), phenylmercury(II) (Canty, Chaichit & Gatehouse, 1979) and platinum(II) complexes (Bontchev *et al.*, 1987; Mitewa, Gencheva, Bontchev, Angelova & Maciček, 1988) have been reported. In order to obtain structural information on the mode of interaction between creatinine and biologically important metal ions, we thought it worthwhile to determine the crystal structure of the complex, (I), of creatinine with zinc(II) chloride.

(I)
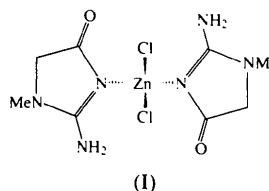
The molecular structure of the title complex with atomic labelling is depicted in Fig. 1. A stereoview of the molecules in the unit cell is depicted in Fig. 2. The molecules are held together by intermolecular hydrogen bonds between amino and carbonyl groups: N(2)—H(1)···O(1)(*x*, *y*, *z*−1) 2.96 (1) and N(2′)—H(1′)···O(1′)(*x*, *y*, 1 + *z*) 2.797 (9) Å.
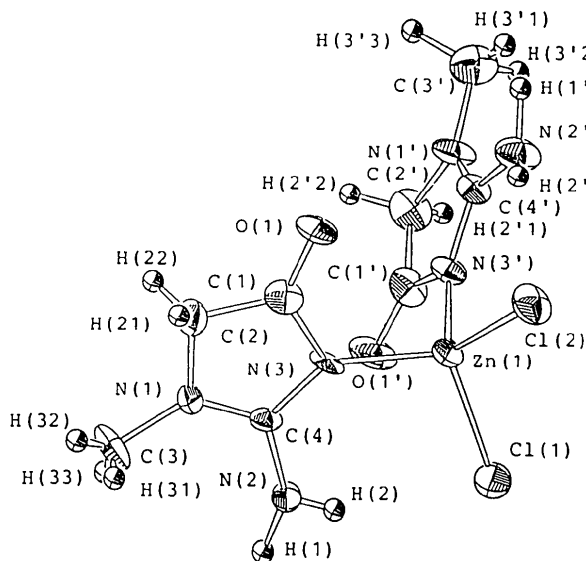

Fig. 1. Perspective view of the title compound with the atomic numbering. Ellipsoids are shown at 50% probability.