Synthesis, Calorimetric Study, Infrared Spectroscopy and Crystal Structure Investigation of β-[Tetraethylammonium Tetramethylammonium Tetrachlorozincate(II)] [β]-[$(C_2H_5)_4N$][$(CH_3)_4N$]$ZnCl_4$

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Synthesis, crystal structure and infrared description are reported for a new phase of tetraethylammonium tetramethylammonium tetrachlorozincate(II) β-[(TEA)(TMA)$ZnCl_4$]. Calorimetry study shows five endothermic picks at 165, 232, 280, 284, and 377 K. The compound crystallizes in the orthorhombic system, space group $P2_12_12$ (N^o 18), with $Z = 4$ and $a = 13.099(3)$, $b = 13.119(2)$ and $c = 11.812(3)$ Å. The crystal structure consists of alternate organic-inorganic [$(TMA)^+/ZnCl_4^{2-}$] layers and organic sheets $(TEA)^+$. Organic and inorganic groups are not disordered. Its main geometrical features are those commonly observed in the atomic arrangements of $(TEA)_2ZnCl_4$ and $(TMA)_2ZnCl_4$.

Key words: β-[Tetraethylammonium Tetramethylammonium Tetrachlorozincate (II)], Phase Transition, Infrared Spectroscopy, Crystal Structure

Introduction

The crystals of alkylammonium tetrachlorometallates with the general formula $(NR_4)_2MCl_4$, with M corresponding to a divalent metal ion, have been widely investigated owing to their interesting physical properties connected to the different phase transitions. Crystals of the general formula $(NR_4)_2MX_4$ most often have the prototype structure of β-K_2SO_4 and reveal a classical sequence of phase transitions from the normal orthorhombic phase through the incommensurate to the commensurate phase (ferroelectric or ferroelastic) [1 – 8]. This is the case for tetramethylammonium tetrachlorometallate crystals $[N(CH_3)_4]_2MCl_4$ (M = Zn, Co, Ni, Fe, Cu, Hg), which crystallize at r. t. in the *Pnma* space group. $[N(CH_3)_4]_2ZnCl_4$ single crystals with high optical quality undergo five phase transitions [9]. The crystals with the tetraethylammonium cation, $[N(C_2H_5)_4]_2MCl_4$, show at r. t. the tetragonal symmetry $P4_2/nmc$ with similar cell parameters [10]. A differential scanning calorimetry study showed two transitions for $[N(C_2H_5)_4]_2ZnCl_4$ [11]. The crystal structure of α-$[N(C_2H_5)_4][N(CH_3)_4]ZnCl_4$ was investigated by X-ray diffraction at r. t. The mixed compound crystallizes in the tetragonal system $P\bar{4}2_1m$ [12]. In the present study we have investigated a new form β-$[N(C_2H_5)_4][N(CH_3)_4]ZnCl_4$ by means of differential thermal analysis, IR spectroscopy and X-ray diffraction.

Experimental Section

The synthesis of β-[(TEA)(TMA)$ZnCl_4$] was performed by a mixing $N(C_2H_5)_4Cl$, $N(CH_3)_4Cl$ and $ZnCl_2$ (molar ratio 1 : 1 : 1) in distilled water. The mixture was stored at r. t. at about 32 °C. After few days, square colourless crystals appeared.

$$N(C_2H_5)_4Cl + N(CH_3)_4Cl + ZnCl_2 \xrightarrow[32\ ^\circ C]{H_2O} \beta\text{-}[N(C_2H_5)_4][(NCH_3)_4]ZnCl_4$$

The infrared spectrum of the product was recorded in the 4000 – 370 cm^{-1} range with a Perkin-Elmer FT-IR 1000 spectrometer using samples pressed in spectroscopically pure KBr pellets.

A single crystal (0.30 mm × 0.17 mm × 0.13 mm) was selected by optical examination. Data were collected on an Enraf-Nonius CAD4 diffractometer. Unit cell parameters were derived from least-squares refinement of the setting angles of 25 reflections in the 2θ range 13 – 15°. The crystal structure data are summarized in Table 1.

Table 1. Summary of crystal data, intensity measurements, and refinement parameters for β-$[N(C_2H_5)_4]$-$[N(CH_3)_4]ZnCl_4$.

Formula	$[N(C_2H_5)_4]$ $[N(CH_3)_4]ZnCl_4$
Fw [g · mol^{-1}]	411.57
Color/shape	Colourless/ Parallelepipedic
Crystal dimensions	$0.30 \times 0.17 \times 0.13$ mm
Crystal system	orthorhombic
Space group	$P2_12_12$ (N^o 18)
a [Å]	13.099(3)
b [Å]	13.119(2)
c [Å]	11.812(3)
V [Å^3]	2029.8(4)
Z	4
μ [mm^{-1}]	1.72
Temperature [K]	293(2)
Radiation, λ (Å)	Mo-K$_\alpha$, 0.71069
Monochromator	Graphite plate
Scan angle (°)	$\theta - 2\theta$
2θ Range (°)	2 – 27
h,k,l Range	$-16 \rightarrow 16$, $0 \rightarrow 16$, $-2 \rightarrow 15$
Reflections collected / unique	5723/4424 ($R_{int} = 0.063$)
Observed reflections [$F_o > 2\sigma(F_o)$]	2033
Absorption correction	ψ-scan
T_{min}, T_{max}	0.7238, 0.8462
Refinement	Full-matrix least square on F^2
Refined parameters	277
Goodness of fit	0.955
Final R and Rw	0.037, 0.085
Final R and Rw (all data)	0.052, 0.113
Flack absolute parameter (x)	0.04(3)
Largest feature diff. map	0.065, -0.313 e$^-$/Å^3
$w = 1/[\sigma^2(F_o)^2 + (0.0315P)^2 + 0P]$, $P = [F_o^2 + 2Fc^2]/3$	

An empirical absorption correction based on Ψ-scans was applied. The structure was solved using SHELXS-86 [13] in the space group $P2_12_12$. The refinement was performed with SHELXL-93 [14]. Zn and Cl atoms were first located using Direct Methods. The atomic positions of nitrogen, carbon and hydrogen of the organic groups were found by subsequent difference Fourier syntheses.

The final reliability factors were $R = 0.037$ and $wR = 0.085$ for 2033 unique reflections with F_o greater then $2\sigma(F_o)$ and 318 refined parameters.

As the structure was solved in a non-centrosymmetric space group, the Flack absolute structure parameter x [15, 16], which must be equal to 0 (within 3 esd's) for a correct absolute structure and $+1$ if the atomic positions have to be inverted, refined to $x = 0.04(3) \approx 0$.

Results and Discussions

Calorimetric study

Differential scanning calorimetry measurements were performed on heating the sample from 150 to 420 K using a Netzsch-DSC 204 calorimeter. Five endothermic peaks are present at 165, 232, 279, 284, and 377 K, indicating the availability of six phases. The corresponding enthalpy changes are 8.91, 0.58, 0.53, 0.71, 0.40 kJ mol^{-1}, respectively.

Similar transitional behaviour has been observed for the compounds $[N(CH_3)_4]_2ZnCl_4$ and $[N(C_2H_5)_4]_2ZnCl_4$. The first exhibits five transitions at 161, 181, 276.3, 280 and 298 K [9], the second shows tow transitions at 228 and 233 K [10].

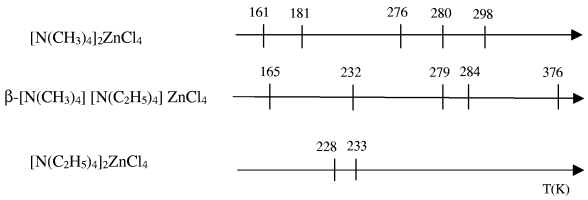

Table 2. IR spectral data (cm^{-1}) and band assignments for β-$[N(C_2H_3)_4][N(CH_3)_4]ZnCl_4$.

Wavenumber (cm^{-1})	Assignment
3025 m	$\nu_a(CH_3)$
2980 m	$\nu_s(CH_2)$
2775 sh	$\nu_s(CH_3)$
2365 m, 2344 m	$\nu_4(N(CH_3)_4)$, $\nu_4(N(C_2H_5)_4)$
1490 vs	$\delta_a(CH_3)$
1396 m	$\delta_s(CH_3)$
1293 sh	$\delta(CH_2)$
1073 w	$\rho_t(CH_2)$
997 s	ν(C-C)
954 vs	$\rho_r(CH_3)$
792 s	$\rho_r(CH_2)$
458 w, 419 w	$\nu_3(N(CH_3)_4)$, $\nu_3(N(C_2H_5)_4)$

vs = very strong; s = strong; m = medium; w = weak; sh = shoulder.

Infrared absorption spectroscopy

The assignment of all the IR bands of β-$[N(C_2H_3)_4]$ $[N(CH_3)_4]ZnCl_4$ is difficult but we can attribute some of them by comparison with similar compounds (Table 2).

The principal bands are assigned to the internal modes of methyl and ethyl groups. The methyl group exhibits the antisymmetric stretching $\nu_a(CH_3)$ at 3025 cm^{-1}, symmetric stretching $\nu_s(CH_3)$ at 2775 cm^{-1}, antisymmetric bending $\delta_a(CH_3)$ at 1490 cm^{-1}, symmetric bending $\delta_s(CH_3)$ at 1396 cm^{-1} and rocking vibration $\rho_r(CH_3)$ at 954 cm^{-1}. The ethyl group exhibits the symmetric stretching $\nu_s(CH_2)$ at 2980 cm^{-1}, scissoring $\delta(CH_2)$ at 1293 cm^{-1}, twisting $\rho_t(CH_2)$ at 1073 cm^{-1}, and rocking $\rho_r(CH_2)$ at 792 cm^{-1}. The bands observed at 458 and 419 cm^{-1} are assigned to the ν_3 modes, and the bands observed at 2365 and 2344 cm^{-1} to the ν_4 modes

Table 3. Final atomic coordinates for β-$[N(C_2H_5)_4]$-$[N(CH_3)_4]ZnCl_4$ with esd's in parentheses.

Atoms	*x*	*y*	*z*	*U*eq
Zn	0.25402(5)	0.24610(5)	0.68733(5)	0.0462(2)
Cl1	0.2421(2)	0.2578(2)	0.4955(1)	0.0726(4)
Cl2	0.4160(1)	0.2842(1)	0.7387(2)	0.0726(5)
Cl3	0.2156(1)	0.0839(1)	0.7387(2)	0.0720(5)
Cl4	0.1462(1)	0.3538(1)	0.7789(2)	0.0720(5)
N1	0	0.5	0.4872(7)	0.054(2)
C11	−0.066(2)	0.436(2)	0.550(1)	0.28(2)
C12	0.057(2)	0.436(4)	0.407(4)	0.33(5)
N2	0.5	0.5	0.5004(6)	0.049(2)
C21	0.4694(9)	0.4132(7)	0.4267(8)	0.084(3)
C22	0.5885(7)	0.4690(7)	0.5711(8)	0.075(3)
N3	0.2920(4)	0.2082(4)	1.1064(4)	0.045(1)
C31	0.3267(6)	0.1721(6)	0.9920(6)	0.068(2)
C32	0.3798(5)	0.2515(7)	1.1765(6)	0.065(2)
C33	0.2480(7)	0.1207(4)	1.1752(6)	0.065 (2)
C34	0.2121(6)	0.2882(6)	1.0853(8)	0.073(2)
C35	0.4315(8)	0.3427(7)	1.1195(9)	0.092(3)
C36	0.3407(8)	0.5671(7)	0.8816(9)	0.092(3)
C37	0.406(1)	0.092(2)	0.992(2)	0.098(5)
C38	0.1672(7)	0.3364(7)	1.191(1)	0.081(3)

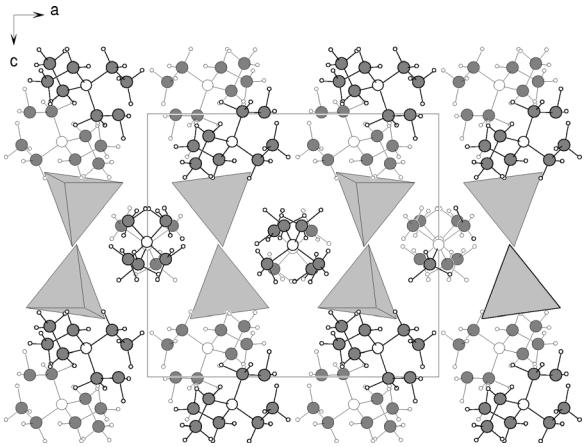

Fig. 1. [010] projection of the structure of β-[TMA][TEA]$ZnCl_4$. The large empty circles represent nitrogen atoms; the other empty circles represent hydrogen and the black circles represent carbon atoms. $ZnCl_4^{2-}$ anions are represented by tetrahedra.

of $N(CH_3)_4$ and $N(C_2H_5)_4$ tetrahedra. The 997 cm^{-1} band corresponds to the stretching mode ν(C-C) of the ethyl group. The infrared study confirms the presence of $[N(CH_3)_4)]$ and $[N(C_2H_5)_4]$ groups [17–20].

Structure description

Relevant final atomic coordinates for all non-hydrogen atoms, selected interatomic distances and angles are given in Tables 3 and 4, respectively.

The atomic arrangement in [TMA][TEA]$ZnCl_4$ consists of alternate organic-inorganic layers (TMA/$ZnCl_4$) and organic sheets (TEA) both parallel to the (001) plane (Fig. 1).

Table 4. Main inter-atomic distances (Å) and bond angles (°) in β-$[N(C_2H_5)_4]$ $[N(CH_3)_4]ZnCl_4$ with esd's in parentheses.

Distances (Å)		Angles (°)	
$ZnCl_4$:			
Zn-Cl1	2.274(2)	Cl1-Zn-Cl2	108(1)
Zn-Cl2	2.269(2)	Cl1-Zn-Cl3	108(1)
Zn-Cl3	2.271(2)	Cl1-Zn-Cl4	113(1)
Zn-Cl4	2.265(2)	Cl2-Zn-Cl3	110(1)
		Cl2-Zn-Cl4	108(1)
		Cl3-Zn-Cl4	108(1)
$N(1)(CH_3)_4$:			
N1-C11	1.42(1)	C12-N1-C11	113(3)
N1-C11^{i}	1.42(1)	C11^{i}-N1-C11	113(2)
N1-C12	1.47(3)	C12^{i}-N1-C11	108(2)
N1-C12^{i}	1.47(3)	C12-N1-C11^{i}	108(2)
		C12^{i}-N1-C11^{i}	113(3)
		C12^{i}-N1-C12	100(4)
$N(2)(CH_3)_4$:			
N2-C21	1.495(9)	C22-N2-C21	109(1)
N2-C21^{i}	1.495(9)	C21^{i}-N2-C21	109(1)
N2-C22	1.491(9)	C22^{i}-N2-C21	110(1)
N2-C22^{i}	1.491(9)	C22-N2-C21^{i}	110(1)
		C22^{i}-N2-C21^{i}	109(1)
		C22^{i}-N2-C22	110(1)
$N(3)(C_2H_5)_4$:			
N3-C31	1.507(8)	C31-N3-C34	106(1)
N3-C32	1.532(8)	C31-N3-C33	112(1)
N3-C33	1.520(8)	C31-N3-C32	111(1)
N3-C34	1.513(9)	C32-N3-C33	108(1)
C31-C37	1.50(2)	C32-N3-C34	110(1)
C32-C35	1.50(1)	C32-N3-C34	110(1)
C33-C36^{ii}	1.49(1)	C37-C31-N3	114(1)
C34-C38	1.50(1)	C35-C32-N3	113(2)
		C36^{ii}-C33-N3	115(1)
		N3-C34-C38	114(1)

Symmetry codes: ^{i} $-x, 1-y, z$ and ^{ii} $1/2-x, 1/2-y, 2-z$.

In Fig. 1 we can see a first layer at $z = 0$ consisting only of cations $(TEA)^+$ with the sequence $(TEA)^+/(TEA)^+$. The organic-inorganic layer is centred at $z = 1/2$, built up from two dented sheets of $ZnCl_4^{2-}$ tetrahedra. Two methylammonium groups, $TMA^+(1)$ and $TMA^+(2)$, are locked in the cavities formed between $ZnCl_4^{2-}$ sheets. The first type occupies $a = 1/2$ and $b = 1/2$ positions, the second is locked at the middle and base of a square (Fig. 2).

The configuration of the $(TEA)^+$ cations correspond to the stable one known as "Greek Cross" [21]. C-N-C and N-C-C angles and C-C and N-C distances are as commonly observed and show slightly distorted groups [22, 23]. $(TMA)^+$ (1) and (2) groups present

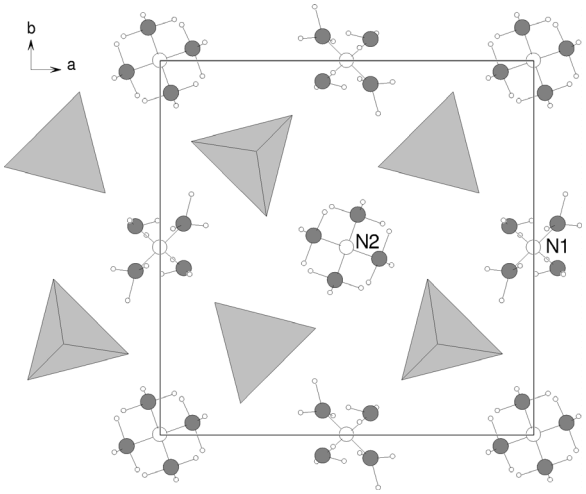

Fig. 2. [001] projection of the structure of β-[TMA][TEA]$ZnCl_4$ showing the organic-inorganic layer. The large empty circles represent nitrogen, the other empty circles hydrogen and the black circles carbon atoms. $ZnCl_4^{2-}$ anions are represented by tetrahedra.

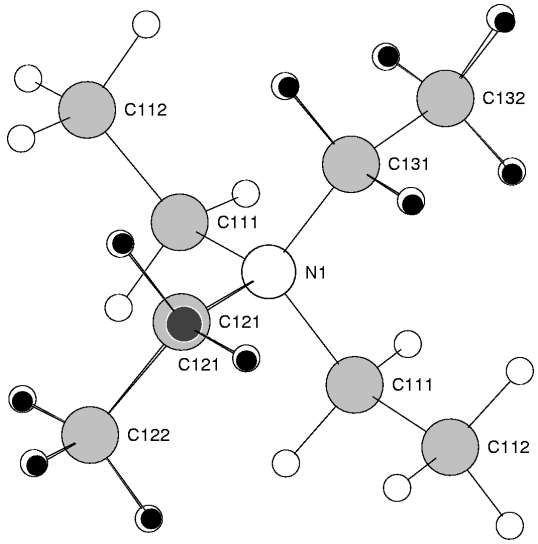

Fig. 3. Projection of the TEA^+ cation observed in the structure of α-[TMA][TEA]$ZnCl_4$ reported by Odile Caëtano *et al.* [12]. Disordered atoms are represented by black circles with reduced radii.

C_{2v} punctual symmetry. C-N-C angles and N-C distances are regular.

$ZnCl_4$ tetrahedra present a C_1 punctual symmetry with geometrical features similar to those commonly observed [22–24]. The Zn-Cl distances vary between 2.265(2) and 2.274(2) Å with the average equal to 2.270(2) Å. The Cl-Zn-Cl angles are in the range 108(1)° – 113(1)° with a mean equal to 109.16°. Taking into account these parameters and considering the calculated average values of the Baur distortion indices [25] (ID Zn-Cl = 0.001, ID Cl-Zn-Cl = 0.014 and Cl-Cl = 0.009), we deduce that $ZnCl_4$ tetrahedron is only slightly distorted.

Discussion

The title compound is a second allotropic form (β) of the one reported by Odile Caëtano *et al.* (α) which crystallizes in the tetragonal system with $a = 13.087(2)$ and $c = 11.793(1)$ Å [$Z = 4$, $V = 2019.8(5)$ Å^3, G. E.: $P42_1m$] [12]. The α and β forms were prepared starting from the same mixture of components in aqueous solution. Crystals were obtained from cooling solutions, at r. t. and at about 32 °C, respectively. The cell parameters of the β phase are greater than those of the α phase, and we note an increase of 0.5% in volume. The atomic arrangement in the α and β form is similar. It consists of alternate organic-inorganic layers ($TMA/ZnCl_4$) and organic sheets (TEA) both parallel to the (001) plane. Its structure contains two TMA^+ cations and a single TEA^+ cation. In the β form, the planes are translated by $c/2$ and all groups are ordered. The TMA^+ cations have C_{2v} punctual symmetry. In the α form one TMA group is ordered with high symmetry (T_d punctual symmetry), the second is distorted and disordered. Due to $\bar{4}$ symmetry, the nitrogen atom is virtually linked to sixteen carbon sites with occupancy of 0.25. The organic layers of the substructures made up $(TEA)^+$ anions have the same thickness. In the β structure the anion is ordered but in the α structure disordered, not reported by previous authors. The reconstitution of projections from cif's file shows clearly that some atoms are duplicated by the symmetry operations $1/2 + x$, $1.5 - y$, $1 - z$ and y, $1 - x$, $1 - z$. Distances between duplicated carbon atom and hydrogen atoms are about 0.04(1) Å and vary between 0.04(1) and 0.06(1) Å, respectively (Fig. 3). Finally we can deduce that when synthesis temperature increases the structure symmetry decreases but some groups seem to be more ordered.

Summary

Non-centrosymmetric crystals of β-$[N(C_2H_5)_4]$-$[N(CH_3)_4]ZnCl_4$ have been prepared by slow evaporation, at r. t., of an aqueous solution of stoichiometric amounts of $N(C_2H_5)_4Cl$, $N(CH_3)_4Cl$ and $ZnCl_2$. Calorimetric study shows five transitions, dif-

ferent from those observed in related compounds $[N(C_2H_5)_4]_2ZnCl_4$ and $[N(CH_3)_4]_2ZnCl_4$. The structure is characterized by infinite layers of cations $(TEA)^+$ alternating with sheets made up of ions TMA^+ and $ZnCl_4^{2-}$, both approximately parallel to the (001) plane. Compared to the α form, we conclude that the effect of the synthesis temperature is important: As the temperature decreases, the symmetric order of the structure increases with appearance of two disordered anions.

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