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Bis(n-TETRADECYLAMMONIUM) TETRACHLOROZINCATE(II), $(C_{14}H_{29}NH_3)_2ZnCl_4$

F. Javier Zuniga and Gervais Chapuis
Université de Lausanne, Institut de cristallographie, BSP, 1015 Lausanne, Switzerland.

Preliminary information

Compounds of the type $(C_nH_{2n+1}NH_3)_2MX_4$ where M = Cu, Mn, Cd, Zn, Co and X = Cl, Br have been studied extensively in the last few years owing to the similarities of their properties with phospholipids membranes and smectic liquid crystals (Blinc et al., 1979). The structure of all these compounds consists of alternating layers of alkylammonium ions and metal-halogen macro-ions but considerable differences remain in the packing modes of the aliphatic chains. In addition, they exhibit numerous phase transitions which have been studied both theoretically and experimentally (Socias et al., 1980, Kind et al., 1979) for metal with octahedral or quadratic coordination (M = Cu, Mn, Cd) whereas little is known for compounds with tetrahedral coordination (M = Co, Zn).

This structure has been solved as part of a study on the phase transitions of these compounds.

Crystal Data

$(C_{14}H_{29}NH_3)_2ZnCl_4$ is monoclinic, space group $P2_1/c$ (no. 14). The lattice constants at 293 K are a = 7.3980(7), b = 10.254(1), c = 47.659(5) Å and $\beta = 92.794(7)^\circ$ as determined from single crystal diffractometry with CuK_α radiation (λ = 1.54178 Å). Z = 4, D_c = 1.17 g cm^{-3}.

Structure determination and refinement

Intensities were measured on a Syntex $P2_1$ autodiffractometer by the $\theta - 2\theta$ scan technique up to $\sin\theta/\lambda = 0.54$ $Å^{-1}$ with Ni-filtered CuK_α radiation. An absorption correction was applied to the measurements (μ = 37.2 cm^{-1}). Of the 3977 reflections, 854 intensities smaller than 3σ were considered as unobserved. For the reduction of the data and refinement of the structure, the X-Ray System of Programs (Stewart et al., 1972) was used. Atomic scattering factors of Zn^{2+}, Cl^-, N, C, H (Cromer and Mann, 1968) and anomalous dispersion terms for Zn and Cl were used for the structure factor calculation.

The structure was solved by the Patterson method and refined by least-squares with a block-diagonal matrix. The non-hydrogen atoms were refined with anisotropic thermal parameters. The calculated positions of the H atoms were included in the

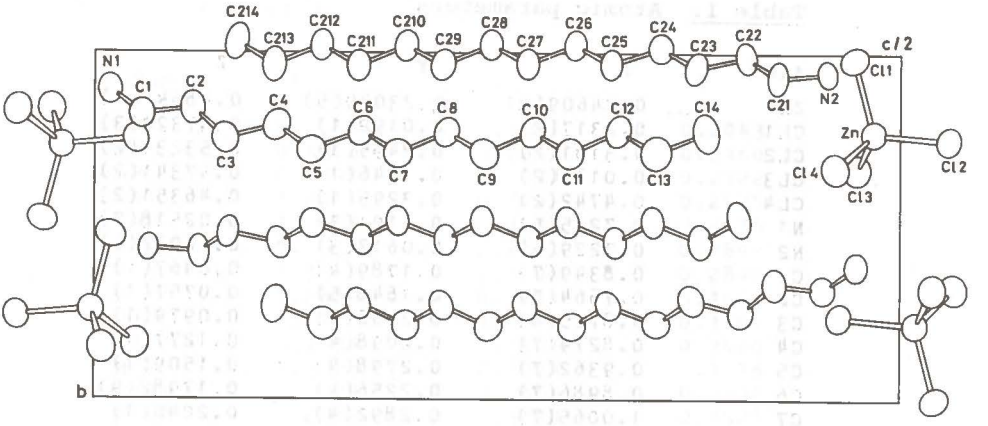

Fig. 1

final step of the refinement but not refined. After completion of the refinement the residuals R = 0.040 and R_w = 0.050 were obtained and the largest peak intensity on a difference Fourier synthesis was 0.39 e/Å^3. Residuals without the contribution of H atoms were R = .057 and R_w = .082.

Discussion

A projection of the structure along a is shown on fig. 1. Atomic parameters, bond distances and angles are reported on Tables I and II. The structure consists of two types of alternating layers stacked along c. Interpenetrating chains of alkylammonium ions form one type whereas isolated $ZnCl_4^{2-}$ form the second type. This structure is similar to $(C_{12}H_{25}NH_3)_2ZnCl_4$ (Ciajolo et al., 1977).

Table I. Atomic parameters

ATOM	X	Y	Z
ZN	0.24609(8)	0.23049(5)	0.48541(1)
CL1	0.2317(2)	0.0192(1)	0.47320(3)
CL2	0.3181(2)	0.2495(1)	0.53231(2)
CL3	-0.0140(2)	0.3346(1)	0.47341(2)
CL4	0.4742(2)	0.3295(1)	0.46351(2)
N1	0.7215(5)	0.1101(3)	0.02518(7)
N2	0.7229(6)	0.0613(3)	0.46082(6)
C1	0.8349(7)	0.1789(4)	0.0467(1)
C2	0.7664(7)	0.1648(5)	0.0757(1)
C3	0.8725(8)	0.2466(4)	0.0979(1)
C4	0.8279(7)	0.2098(4)	0.1277(1)
C5	0.9362(7)	0.2798(4)	0.1509(1)
C6	0.8986(7)	0.2256(4)	0.17982(9)
C7	1.0065(7)	0.2892(4)	0.2040(1)
C8	0.9699(8)	0.2294(4)	0.2325(1)
C9	1.0779(7)	0.2900(4)	0.2570(1)
C10	1.0413(8)	0.2283(4)	0.2852(1)
C11	1.1503(8)	0.2877(4)	0.3097(1)
C12	1.1143(8)	0.2256(5)	0.3382(1)
C13	1.2258(8)	0.2846(5)	0.3624(1)
C14	1.1875(9)	0.2295(6)	0.3907(1)
C21	0.7782(7)	0.0719(5)	0.43140(9)
C22	0.6448(7)	0.0160(5)	0.41033(9)
C23	0.6959(7)	0.0469(5)	0.38049(9)
C24	0.5735(7)	-0.0118(4)	0.3573(1)
C25	0.6183(7)	0.0363(4)	0.32811(9)
C26	0.5009(7)	-0.0201(4)	0.30408(9)
C27	0.5433(7)	0.0349(4)	0.27573(8)
C28	0.4303(7)	-0.0209(4)	0.2515(1)
C29	0.4702(7)	0.0374(5)	0.22313(9)
C210	0.3609(7)	-0.0177(4)	0.1984(1)
C211	0.4036(7)	0.0399(5)	0.17023(9)
C212	0.2988(7)	-0.0183(5)	0.14552(9)
C213	0.3444(8)	0.0350(5)	0.1177(1)
C214	0.2432(8)	-0.0266(5)	0.0929(1)
H1N1	0.7190	0.0134	0.0302
H2N1	0.5935	0.1470	0.0252
H3N1	0.7680	0.1197	0.0053
H11	0.9678	0.1414	0.0470
H12	0.8448	0.2763	0.0420
H21	0.6324	0.1918	0.0752
H22	0.7725	0.0671	0.0816
H31	1.0102	0.2307	0.0956
H32	0.8478	0.3433	0.0941
H41	0.6916	0.2340	0.1299
H42	0.8407	0.1122	0.1303
H51	1.0715	0.2650	0.1474
H52	0.9100	0.3769	0.1499
H61	0.7620	0.2439	0.1834
H62	0.9174	0.1280	0.1803
H71	1.1446	0.2730	0.2006

Table I (cont.)

ATOM	X	Y	Z
H72	0.9865	0.3866	0.2043
H81	0.8326	0.2453	0.2360
H82	0.9895	0.1311	0.2322
H91	1.2152	0.2745	0.2535
H92	1.0568	0.3874	0.2576
H101	0.9052	0.2441	0.2892
H102	1.0622	0.1304	0.2849
H111	1.2880	0.2719	0.3061
H112	1.1310	0.3857	0.3104
H121	0.9774	0.2421	0.3420
H122	1.1328	0.1274	0.3375
H131	1.3629	0.2659	0.3590
H132	1.2112	0.3840	0.3626
H141	1.0522	0.2485	0.3952
H142	1.2039	0.1304	0.3916
H143	1.2638	0.2685	0.4077
H1N2	0.6031	0.1093	0.4624
H2N2	0.7057	-0.0350	0.4654
H3N2	0.8144	0.0996	0.4753
H211	0.8011	0.1694	0.4264
H212	0.9027	0.0247	0.4293
H221	0.6356	-0.0827	0.4132
H222	0.5192	0.0563	0.4135
H231	0.7043	0.1454	0.3780
H232	0.8264	0.0089	0.3781
H241	0.5777	-0.1099	0.3582
H242	0.4422	0.0187	0.3609
H251	0.6163	0.1356	0.3272
H252	0.7516	0.0069	0.3245
H261	0.5067	-0.1180	0.3040
H262	0.3659	0.0068	0.3078
H271	0.5328	0.1343	0.2759
H272	0.6776	0.0116	0.2725
H281	0.4418	-0.1186	0.2510
H282	0.2942	0.0019	0.2551
H291	0.4552	0.1360	0.2233
H292	0.6057	0.0172	0.2195
H2101	0.3769	-0.1157	0.1979
H2102	0.2261	0.0028	0.2017
H2111	0.3815	0.1381	0.1702
H2112	0.5396	0.0240	0.1671
H2121	0.3199	-0.1168	0.1454
H2122	0.1634	-0.0014	0.1482
H2131	0.3185	0.1346	0.1170
H2132	0.4814	0.0234	0.1149
H2141	0.2679	-0.1256	0.0927
H2142	0.1051	-0.0144	0.0948
H2143	0.2729	0.0091	0.0735

Table II. Bond lengths (Å) and angles (°)

Zn - Cℓ 1	2.245(1)	Cℓ1 - Zn - Cℓ2	110.01(5)
- Cℓ 2	2.281(1)	Cℓ1 - Zn - Cℓ3	111.29(6)
- Cℓ 3	2.250(1)	Cℓ1 - Zn - Cℓ4	109.88(5)
- Cℓ 4	2.267(1)	Cℓ2 - Zn - Cℓ3	111.38(5)
		Cℓ2 - Zn - Cℓ4	105.61(5)
N1 - $Cℓ^{i}$ 2	3.345(4)	Cℓ3 - Zn - Cℓ4	108.49(5)
- $Cℓ^{ii}$ 3	3.273(4)		
- $Cℓ^{iii}$ 4	3.277(4)	N 1 - C 1 - C 2	112.8(4)
- $Cℓ^{i}$ 4	3.442(4)	C 1 - C 2 - C 3	113.4(4)
- $Cℓ^{iii}$ 3	3.557(4)	C 2 - C 3 - C 4	112.4(4)
N2 - $Cℓ^{iv}$ 1	3.252(3)	C 3 - C 4 - C 5	115.8(4)
- $Cℓ^{iv}$ 2	3.220(4)	C 4 - C 5 - C 6	112.1(4)
- $Cℓ^{v}$ 3	3.448(4)	C 5 - C 6 - C 7	114.7(4)
- Cℓ 4	3.315(4)	C 6 - C 7 - C 8	113.2(4)
		C 7 - C 8 - C 9	114.3(4)
N 1 - C 1	1.472(6)	C 8 - C 9 - C10	113.6(4)
C 1 - C 2	1.502(7)	C 9 - C10- C11	113.8(4)
C 2 - C 3	1.536(7)	C10 - C11- C12	114.0(4)
C 3 - C 4	1.520(7)	C11 - C12- C13	113.4(4)
C 4 - C 5	1.516(7)	C12 - C13- C14	114.5(4)
C 5 - C 6	1.523(7)		
C 6 - C 7	1.518(7)	N 2 - C21- C22	113.9(4)
C 7 - C 8	1.526(7)	C21 - C22- C23	111.3(4)
C 8 - C 9	1.515(7)	C22 - C23- C24	115.5(4)
C 9 - C10	1.523(7)	C23 - C24- C25	112.7(4)
C10- C11	1.513(7)	C24 - C25- C26	115.0(4)
C11- C12	1.535(7)	C25 - C26- C27	113.3(4)
C12- C13	1.512(7)	C26 - C27- C28	114.3(4)
C13- C14	1.500(8)	C27 - C28- C29	114.1(4)
		C28 - C29- C210	115.4(4)

Table II (cont.)

N2	- C21	1.484(6)		C29	- C210 - C211		114.9(4)
C21	- C22	1.488(7)		C210	- C211 - C212		114.7(4)
C22	- C23	1.522(7)		C211	- C212 - C213		115.0(4)
C23	- C24	1.518(7)		C212	- C213 - C214		114.7(4)
C24	- C25	1.529(7)					
C25	- C26	1.518(6)	N 1	- C 1	- C 2	- C 3	-175
C26	- C27	1.511(6)	C 1	- C 2	- C 3	- C 4	-169
C27	- C28	1.506(6)	C 2	- C 3	- C 4	- C 5	+175
C28	- C29	1.520(7)	C 3	- C 4	- C 5	- C 6	-173
C29	- C210	1.508(7)	C 4	- C 5	- C 6	- C 7	+177
C210	- C211	1.512(7)	C 5	- C 6	- C 7	- C 8	-178
C211	- C212	1.502(7)	C 6	- C 7	- C 8	- C 9	+179
C212	- C213	1.490(7)	C 7	- C 8	- C 9	- C10	-179
C213	- C214	1.504(7)	C 8	- C 9	- C10	- C11	+179
			C 9	- C10	- C11	- C12	-180
(i)	x, 1/2-y, z-1/2		C10	- C11	- C12	- C13	+179
(ii)	x+1, 1/2-y, z-1/2		C11	- C12	- C13	- C14	+177
(iii)	1-x, y-1/2, 1/2-z						
(iv)	1-x, -y, 1-z		N 2	- C21	- C22	- C23	+172
(v)	1+x, y, z		C21	- C22	- C23	- C24	+175
			C22	- C23	- C24	- C25	+173
			C23	- C24	- C25	- C26	+178
			C24	- C25	- C26	- C27	+177
			C25	- C26	- C27	- C28	+179
			C26	- C27	- C28	- C29	+179
			C27	- C28	- C29	- C210	+179
			C28	- C29	- C210	- C211	-178
			C29	- C210	- C211	- C212	+178
			C210	- C211	- C212	- C213	-178
			C211	- C212	- C213	- C214	+178

All the carbon atoms are in the trans configuration with slight deviations from 180° increasing for atoms near the $ZnCl_4$ layer. The packing of the chains is of a new type not included in the work of Segerman (1965). The unit cell of the aliphatic carbons is monoclinic, space group $P2_1$. Lattice constants are a_c= 7.9, b_c= 10.3, c_c= 2.54 Å and β = 99°.

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