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Notes

Synthesis and Crystal Structure of Ethyl Zinc Chloride

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Summary: Crystalline ethylzinc chloride exists as a coordination polymer in the form of puckered sheets with Zn_3Cl_3 rings, which differ from the well-known structure of $[EtZnI]_\infty$ in adopting a boat rather than chair conformation. This contrasts with the tetrameric cubane structure suggested in 1966 based on molecular weight determinations in benzene solution.

Interest in alkyl zinc halides has existed for 150 years. Since Frankland's synthesis of EtZnI,[1] a multitude of applications have been found for such simple organometallic compounds in various fields of chemistry. For instance, alkylzinc iodides are used for Simmons−Smith cyclopropanation,[2] alkylzinc bromides are used for nickel-catalyzed Negishi reactions,[3] and EtZnCl generated in situ has been shown to be a good chain transfer agent in the polymerization of olefins.[4] In the 1960s a series of studies carried out by several research groups focused on the structure of ethylzinc halides and the species present in equilibrium in a variety of solvents.[5,6] On the basis of cryoscopic molecular weight determinations, Boersma and Noltes suggested that EtZnCl and EtZnBr form tetrameric cubic arrangements in benzene (structure **I**).[6] There seems to have been the tacit assumption that these compounds also possess the same molecular structure in the solid state; for example, Moseley et al. directly likened EtZnCl to methylzinc methoxide, which is indeed tetrameric in the solid state, and pointed to solubility differences between these species on one hand and polymeric EtZnI on the other.[7] Thus, the tetrameric structure for EtZnCl appears to have become widely accepted.[8,9] The polymeric structure of ethylzinc iodide has of course long been recognized (Figure 1).[7] However, to date there are no reports of the solid-state structures of other unsolvated alkyl zinc halides. As part of a wider study on the organometallic chemistry of zinc in catalysis,[10] we had occasion to prepare ethylzinc chloride and report here its crystal structure.

Ethylzinc chloride can be synthesized according to literature procedures by the reaction of $ZnCl_2$ with $ZnEt_2$ in hot toluene (eq 1).[6,11] In contrast to the original preparation, in our hands the reaction did not proceed to completion, as the $ZnCl_2$ was never totally consumed: after 72 h the solution remained cloudy. Hence, purification was carried out by filtration of the hot solution followed by evaporation of the remaining $ZnEt_2$ in a vacuum. The product was recrystallized by decreasing the temperature of the toluene solution slowly to −26 °C. The crystals proved suitable for X-ray diffraction given careful handling.

$$ZnEt_2 + ZnCl_2 \xrightarrow[\text{toluene}]{\substack{70-75\ ^\circ\text{C} \\ 72\ \text{h}}} 2\ EtZnCl \qquad (1)$$

EtZnCl forms infinite sheets (Figure 2) in which each zinc atom is tetrahedrally coordinated to one ethyl and three chloride ligands. Each chloride also bridges three zinc atoms. The Zn−Cl interactions fall into two categories: one Zn−Cl bond is short, 2.3486(6) Å, close to the sum of covalent radii (2.33 Å), while the other two are ca. 0.2 Å longer. All these Zn−Cl distances are significantly longer than the Zn−Cl bond in the monomeric adduct EtZnCl·TMEDA [2.269(3) Å].[12] Ethyl groups project from either side of the sheet.

The EtZnCl units combine to form six-membered Zn_3Cl_3 rings. These rings are aligned in sheets with an undulating wave pattern; the waves run parallel to the *b*-axis, and the ethyl groups lie to either side of the sheet and make van der Waals contacts with neighboring sheets. This structure therefore shows similarities to that of $[EtZnI]_\infty$ (Figure 1), which also forms a wavy sheet structure of six-membered rings. Here, each zinc atom forms three bonds to iodine atoms, one short at 2.640(6) Å and two longer at 2.911(6) Å.

The main difference between the chloride and the iodide structures is the conformation of the Zn_3X_3 rings, which in EtZnI are in *chair* conformation, whereas in EtZnCl the *boat* conformation is adopted. This is more clearly shown in Figure 3.

Selected geometric parameters are collected in Table 1. The Zn−C bond length in EtZnCl, 1.946(2) Å, is rather similar to

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[1] Frankland, E.; Duppa, B. F. *J. Chem. Soc.* **1864**, 29.

[2] Sawada, S.; Inouye, Y. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 2269.

[3] Zhou, J. R.; Fu, G. C. *J. Am. Chem. Soc.* **2003**, *125*, 14726.

[4] Hsieh, H. L. *J. Polym. Sci.*, *Polym. Chem.* **1976**, *14*, 379.

[5] (a) Evans, D. F.; Maher, J. P. *J. Chem. Soc.* **1962**, 5125. (b) Dessy, R. E.; Coe, G. R. *J. Org. Chem*, **1963**, *28*, 3592. (c) Abraham, M. H.; Rolfe, P. H. *J. Chem. Soc.*, *Chem. Commun.* **1965**, 325. (d) Evans, D. F.; Wharf, I. *J. Organomet. Chem.* **1966**, *5*, 108.

[6] Boersma, J.; Noltes, J. C. *Tetrahedron Lett.* **1966**, *14*, 1521.

[7] Moseley, P. T., Shearer, H. M. M. *J. Chem. Soc., Dalton Trans.* **1973**, 64.

[8] Jastrzebski, J. T. B. H.; Klerks, J. M.; Van Koten, G.; Vrieze, K. *J. Organomet. Chem.* **1981**, *210*, C49−C53.

[9] Boersma, J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 2, p 835.

[10] (a) Walker, D. A.; Woodman, T. J.; Hughes, D. L.; Bochmann, M. *Organometallics* **2001**, *20*, 3772. (b) Hannant, M. D.; Schormann, M.; Bochmann, M. *J. Chem. Soc., Dalton Trans.* **2002**, 4071. (c) Walker, D. A.; Woodman, T. J.; Schormann, M.; Hughes, D. L.; Bochmann, M. *Organometallics* **2003**, *22*, 797. (d) Garratt, S.; Guerrero, A.; Hughes, D. L.; Bochmann, M. *Angew. Chem., Int. Ed.* **2004**, *43*, 2166.

[11] Fabicon, R. M.; Richey, H. G. *Organometallics* **2001**, *20*, 4018.

[12] Andrews, P. C.; Raston, C. L.; Skelton, B. W.; White, A. H. *Organometallics* **1998**, *17*, 779.

10.1021/om051043x CCC: $33.50

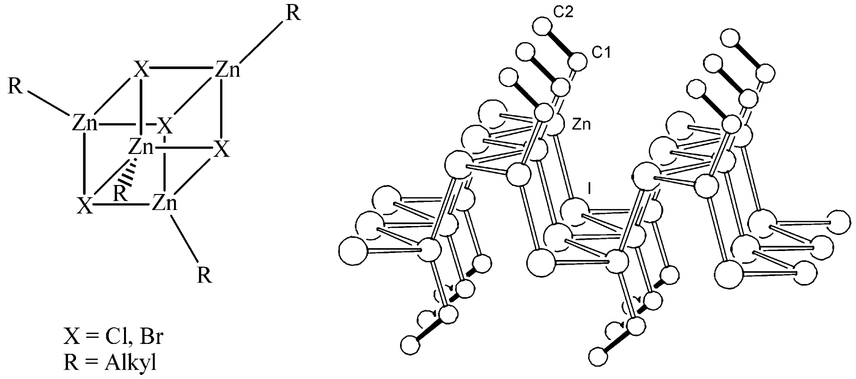

Figure 1. Proposed structure of EtZnX (X = Cl, Br) (left) and solid-state structure of $[EtZnI]_\infty$ (right).

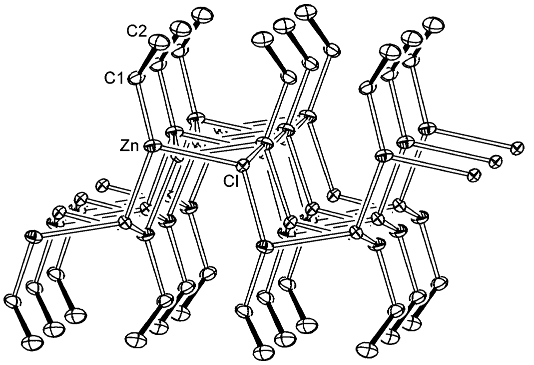

Figure 2. View of the packing of $[EtZnCl]_\infty$ sheets. Thermal ellipsoids are drawn at the 50% probability level.

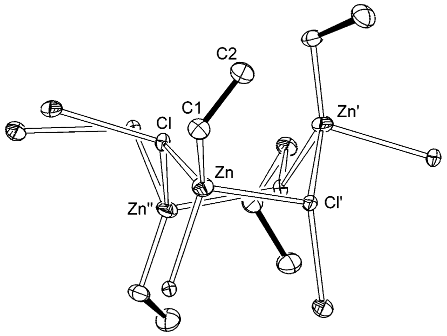

Figure 3. Section of the EtZnCl lattice, illustrating the boat conformation of the six-membered Zn_3Cl_3 ring. Thermal ellipsoids are drawn at the 50% probability level.

Table 1. Interatomic Distances (Å) and Angles (deg) in $[EtZnCl]_\infty$ (esd's in parentheses)[a]

Zn−Cl	2.5408(7)	Zn−Cl^c	2.5248(6)
Zn−Cl^b	2.3486(6)	Zn−C(1)	1.946(2)
C(1)−C(2)	1.533(4)		
Cl^b−Zn−Cl	95.25(2)	C(1)−Zn−Cl	113.96(8)
Cl^c−Zn−Cl	91.75(2)	C(1)−Zn−Cl^b	136.39(8)
Cl^b−Zn−Cl^c	94.72(2)	C(1)−Zn−Cl^c	114.90(8)
Zn^d−Cl−Zn	115.62(2)	Zn^d−Cl−Zn^e	109.85(2)
Zn^e−Cl−Zn	106.91(2)	C(2)−C(1)−Zn	113.5(2)

[a] Symmetry transformations used to generate equivalent atoms: *b*: $x-1/2, y, 1^1/_2-z$; *c*: $^1/_2-x, y+^1/_2, z$; *d*: $x+^1/_2, y, 1^1/_2-z$; *e*: $^1/_2-x, y-^1/_2, z$.

that in EtZnCl·TMEDA [1.94(1) Å][12] and compares well with that in EtZnI of 1.95(4) Å.[7]

Ethylzinc chloride in the solid state shows small Cl−Zn−Cl angles, in the range 91.75(2)−95.25(2)°. However, the Zn−Cl−Zn angles are wider at 106.91(2)−115.62(2)°, giving a pyramidal $ClZn_3$ arrangement, and the tension in the ring through these bonds is released.

Ethylzinc chloride shows adequate solubility in toluene but not in saturated hydrocarbons or chlorocarbons. For example, we found that saturated clear solutions of EtZnCl in toluene form white precipitates when added to dichloromethane. Alternatively, adding dichloromethane to solid EtZnCl causes a change in appearance, from a crystalline material to solid flakes. However, ^1H NMR spectroscopic analysis showed that the precipitated material was identical to authentic EtZnCl. These results suggest that EtZnCl forms a coordination polymer in chlorinated solvents, in the same way as EtZnI in apolar solvents.[7] Moreover, although EtZnCl has been reported as being highly soluble in hydrocarbons,[9] we observed that once crystalline $[EtZnCl]_\infty$ was formed, dissolution in toluene required heating for long periods of time, and even then the solid was poorly soluble.

Experimental Section

General Procedures. All manipulations were performed under an atmosphere of dry nitrogen, using standard Schlenk techniques. Nitrogen was purified by passing through columns of P_2O_5 with moisture indicator and 4 Å molecular sieves. Solvents were predried either over sodium wire (toluene) or calcium hydride (dichloromethane) and then distilled under nitrogen over sodium (toluene) or calcium hydride (dichloromethane). Anhydrous $ZnCl_2$ and neat $ZnEt_2$ were used as received from Aldrich. NMR spectra were recorded using a Bruker DPX300 spectrometer. ^1H NMR spectra (300.1 MHz) were referenced to the residual solvent proton of the deuterated solvent used. ^{13}C NMR spectra (75.5 MHz) were referenced internally to the ^{13}C resonances of the NMR solvent.

Synthesis of EtZnCl. The compound was made by a modification of literature procedures.[6,11] To a suspension of $ZnCl_2$ (2.0 g, 15 mmol) in toluene (125 mL) was injected neat $ZnEt_2$ (1.49 mL, 14.6 mmol). The Schlenk tube was sealed, and the solution was heated to 70−75 °C with stirring for 72 h. Over this period of time most of the $ZnCl_2$ was consumed and a fine powder formed. The hot solution was filtered, any unreacted $ZnEt_2$ was evaporated in vacuo, and the solution was cooled slowly to −26 °C to yield pale yellow crystals, yield 2.74 g (72%). Anal. Calcd for C_2H_5ClZn: C, 18.49; H, 3.88; Cl, 27.29. Found: C, 18.45; H, 3.86; Cl, 27.52. ^1H NMR (tol-d_8): δ 1.29 (3 H, t, J_{HH} = 8.1 Hz, CH_3CH$_2$), 0.62 (2 H, q, J_{HH} = 8.1 Hz, CH_2Zn). $^{13}C\{^1H\}$ NMR (tol-d_8): δ 11.36 (CH$_3$-CH$_2$), 5.36 (CH$_3$$CH_2$).

X-ray Crystallography. *Crystal data:* C_2H_5ClZn, $M = 129.9$. Orthorhombic, space group *Pbca* (no. 61), $a = 6.3802(6)$ Å $b = 5.9324(4)$ Å, $c = 21.8428(17)$ Å, $V = 826.75(12)$ Å^3. $Z = 8$, $D_c = 2.087$ g cm^{-3}, $F(000) = 512$, $T = 140(2)$ K, μ(Mo Kα) = 63.5 cm^{-1}, λ(Mo Kα) = 0.71069 Å.

Crystals are colorless prisms. From a sample under oil, a crystal of dimensions 1.0 × 0.26 × 0.26 mm was mounted on a glass fiber and fixed in the cold nitrogen stream on an Oxford Diffraction

Xcalibur-3 CCD diffractometer equipped with Mo Kα radiation and graphite monochromator. Intensity data were measured by thin-slice ω- and φ-scans. Total no. of reflections recorded, to $\theta_{max} = 27.5°$, was 11 295, of which 949 were unique ($R_{int} = 0.065$); 926 were "observed" with $I > 2\sigma_I$. Data were processed using the CrysAlis-CCD and CrysAlis-RED[13] programs, including absorption corrections. The structure was determined by the direct methods routines in the SHELXS program and refined by full-matrix least-squares methods, on F^2's, in SHELXL.[14] The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in idealized positions, and their U_{iso} values were set to ride on the U_{eq} values of the parent carbon atoms. At the conclusion of the refinement, $wR_2 = 0.055$ and $R_1 = 0.023$ for all 949 reflections weighted $w = [\sigma^2(F_o^2) + 1.49P]^{-1}$ with $P = (F_o^2 + 2F_c^2)/3$; for the "observed" data only, $R_1 = 0.023$ and $S = 1.143$. In the final difference map, the highest peak (ca. 0.4 e Å^{-3}) was close to the zinc atom.

Scattering factors for neutral atoms were taken from ref 15. Computer programs used in this analysis have been noted above and were run through WinGX[16] on a Dell Precision 370 PC at the University of East Anglia.

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Supporting Information Available: Full listing of crystallographic details for ethylzinc chloride. This material is available free of charge via the Internet at http://pubs.acs.org.

OM051043X

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(13) Programs *CrysAlis-CCD*, *CrysAlis-RED*, and *ABSPACK*, Oxford Diffraction Ltd.: Abingdon, UK, 2005.

(14) Sheldrick, G. M. *SHELX-97*, Programs for crystal structure determination (*SHELXS*) and refinement (*SHELXL*); University of Göttingen: Germany, 1997.

(15) *International Tables for X-ray Crystallography*; Kluwer Academic Publishers: Dordrecht, 1992; Vol. C, pp 500, 219, and 193.

(16) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.