1,3-Propanediammonium Tetrachlorozincate(II)

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Abstract. $|NH_3(CH_2)_3NH_3|[ZnCl_4|$, monoclinic, $P2_1/n$, $a = 10.692$ (5), $b = 10.611$ (5), $c = 10.786$ (2) Å, $\beta = 118.47$ (6)°, $V = 1075.8$ Å³ at 296 K, $Z = 4$, $D_c = 1.73$, $D_m = 1.72$ (1) Mg m⁻³ (by flotation), graphite-monochromated Mo $K\alpha$ radiation, $\mu = 3.2$ mm⁻¹; 1632 independent diffractometer data up to $\sin \theta/\lambda = 0.69$ Å⁻¹; final $R(F) = 0.039$. The structure consists of ZnCl₄ tetrahedra linked *via* hydrogen bonds by 1,3-propanediammonium groups.

Introduction. The title compound was synthesized by the reaction of 1,3-propanediammonium chloride and ZnCl₂ in equimolar quantities in water. Some drops of hydrochloric acid were added to the solution to give pH = 1. Prismatic crystals were obtained by evaporation.

A crystal 0.55 × 0.25 × 0.25 mm was selected for the experiments. Precession photographs indicated monoclinic symmetry and systematic absences gave $P2_1/n$ uniquely.

Data were collected on a PDP8-controlled Enraf–Nonius CAD-4 diffractometer. Mo $K\alpha$ radiation from a graphite monochromator was used. The orientation matrix and cell dimensions were obtained by least-squares refinement from the setting angles of 25 reflexions. Intensities were collected in one hemisphere $(\pm h, k, \pm l)$ of reciprocal space up to $\sin \theta/\lambda = 0.69$ Å⁻¹ with an ω–2θ scan, and variable scan rate and scan angle according to $\Delta\theta = (1.1 + 0.35 \, \mathrm{tg} \, \theta)°$. Intensity control was carried out on three intense reflexions every 1.5 h of X-ray exposure time and the orientation matrix was checked every 200 reflexions. 5354 reflexions were measured, of which 1632 with $I > 3\sigma(I)$ remained after merging equivalent reflexions. $\sigma(I)$ is the e.s.d. from counting statistics.

The positions of the Zn atoms were obtained by Patterson methods. Subsequent Fourier syntheses revealed the non-hydrogen atoms. They were refined with individual anisotropic thermal parameters and anomalous-dispersion factors for Zn by full-matrix least-squares calculations. At this stage all features of the crystal structure were determined and refined to $R(F) = 0.044$ and $R_w(F) = 0.053$. A difference synthesis yielded the positions of the H atoms. They were included in the refinement but with their distances to the C and N atoms constrained (Waser, 1963; Rollett, 1969) at 1.05 Å. We also constrained the

Table 1. *Positional parameters and equivalent isotropic thermal parameters*

	x	y	z	B_{eq} (Å²)
Zn	0.25546 (7)	0.13619 (6)	0.00496 (8)	2.48
Cl(1)	0.1509 (2)	0.3100 (1)	0.0381 (2)	2.64
Cl(2)	0.3790 (2)	0.0436 (1)	0.2160 (2)	3.04
Cl(3)	0.0869 (2)	0.0017 (2)	−0.1477 (2)	3.21
Cl(4)	0.3962 (2)	0.2033 (2)	−0.0862 (2)	3.90
N(1)	0.6716 (5)	0.2988 (5)	0.6218 (5)	2.27
N(2)	0.7193 (6)	0.0222 (5)	0.3196 (6)	2.99
C(1)	0.7753 (7)	−0.2202 (6)	0.5993 (7)	3.17
C(2)	0.6955 (6)	−0.1431 (6)	0.4663 (6)	2.82
C(3)	0.8005 (7)	0.0618 (6)	0.4426 (7)	3.34
H1(N1)	0.720 (2)	−0.340 (4)	0.720 (3)	
H2(N1)	0.629 (4)	−0.368 (3)	0.548 (4)	
H3(N1)	0.588 (3)	−0.244 (2)	0.615 (3)	
H1(N2)	0.646 (4)	0.076 (4)	0.334 (3)	
H2(N2)	0.785 (2)	0.082 (3)	0.306 (3)	
H3(N2)	0.665 (4)	−0.029 (2)	0.229 (3)	
H1(C1)	0.831 (2)	−0.162 (2)	0.685 (3)	
H2(C1)	0.849 (2)	−0.277 (2)	0.592 (2)	
H1(C2)	0.639 (2)	−0.202 (2)	0.381 (3)	
H2(C2)	0.620 (3)	−0.087 (2)	0.473 (2)	
H1(C3)	0.864 (2)	−0.008 (2)	0.534 (3)	
H2(C3)	0.870 (3)	−0.118 (2)	0.425 (2)	

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Table 2. *Bond lengths (Å) and angles (°)*

		Uncorrected for libration	Corrected for libration
	Zn—Cl(1)	2·272 (2)	2·277 (2)
	Zn—Cl(2)	2·241 (2)	2·248 (2)
	Zn—Cl(3)	2·272 (2)	2·278 (2)
	Zn—Cl(4)	2·268 (2)	2·275 (2)
	C(1)—C(2)	1·513 (8)	
	C(1)—N(1)	1·496 (7)	
	C(2)—C(3)	1·531 (8)	
	C(3)—N(2)	1·486 (8)	

Cl(1)—Zn—Cl(2)	106·95 (6)	N(1)—C(1)—C(2)	109·2 (5)
Cl(1)—Zn—Cl(3)	110·12 (6)	C(1)—C(2)—C(3)	109·7 (5)
Cl(1)—Zn—Cl(4)	106·96 (6)	N(2)—C(3)—C(2)	108·9 (5)
Cl(2)—Zn—Cl(3)	109·88 (6)		
Cl(2)—Zn—Cl(4)	112·73 (7)		
Cl(3)—Zn—Cl(4)	110·11 (7)		

Table 3. *Hydrogen bonds*

N—H···Cl	N···Cl (Å)	H···Cl (Å)	N—H···Cl (°)
N(1) H3(N1)···Cl(1)[a]	3·244 (5)	2·36 (3)	142 (3)
N(1)—H1(N1)···Cl(1)[b]	3·229 (5)	2·32 (3)	146 (3)
N(1)—H3(N1)···Cl(2)[b]	3·404 (5)	2·71 (4)	124 (3)
N(1)—H1(N1)···Cl(2)[d]	3·247 (5)	2·76 (4)	110 (3)
N(1)—H2(N1)···Cl(3)[d]	3·375 (5)	2·40 (3)	160 (1)
N(2)—H1(N2)···Cl(1)[c]	3·303 (5)	2·50 (3)	134 (2)
N(2)—H1(N2)···Cl(2)[e]	3·265 (5)	2·53 (4)	127 (3)
N(2) H2(N2)···Cl(3)[f]	3·386 (5)	2·80 (4)	118 (3)
N(2)—H3(N2)···Cl(4)[f]	3·259 (5)	2·30 (3)	157 (2)
N(2) H2(N2)···Cl(4)[c]	3·356 (5)	2·58 (4)	134 (3)

Symmetry code

(a)	$\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$	(d)	$-\frac{1}{2} + x, -\frac{1}{2} - y, -\frac{1}{2} + z$
(b)	$1 - x, -y, 1 - z$	(e)	x, y, z
(c)	$-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$	(f)	$1 - x, -y, -z$

angles H_iNH_j or H_kCH_l of the 1,3-propane-diammonium group to their mean value. The final $R(F)$ = 0·039 and $R_w(F) = 0·045$. Scattering factors were from Cromer & Mann (1967), except for H (*International Tables for X-ray Crystallography*, 1974).

All calculations were carried out with the Oxford *CRYSTALS* (Carruthers, 1975) package on the University ICL 1906A computer. The atomic parameters are reported in Table 1, bond lengths and angles in Table 2.*

Discussion. The present structure is part of a study of compounds of general formula $|R_xNH_{4-x}|_2[MX_4]$ where M = Mn, Cd, Co, Zn, Hg, and X = Cl, Br, I (Daoud, 1976, 1977; Morosin, 1972); R is an aliphatic or aromatic residue. Several of these compounds have been shown to contain one-dimensional structures with short metal–metal contacts which may give them interesting conducting properties (Morosin, 1972;

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35460 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
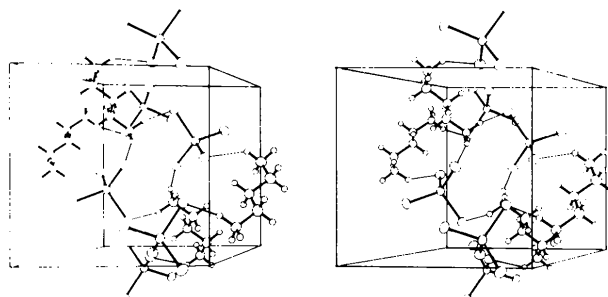
Walter, Brinkmann, Chapuis & Arendt, 1978). To investigate whether the Zn chloride complex can form a linear-chain conductor we determined the structure of the title compound. A stereoscopic view of the structure is shown in Fig. 1.

The structure contains isolated $ZnCl_4$ tetrahedra. The tetrahedra are interconnected *via* hydrogen bonds to the 1,3-propanediammonium groups. There are ten possible hydrogen bonds from ammonium to Cl atoms (Table 3). H3(N2) and H2(N1) are involved in one hydrogen bond each with angles of about 160° while the other ammonium H atoms are involved in bifurcated hydrogen bonds with considerably smaller N—H···Cl angles. Consideration of H···Cl distances enables the hydrogen bonds to be classified as medium to very weak.

The $ZnCl_4$ tetrahedra show angles from 106·95 to 112·73°, indicating a small distortion from tetrahedral symmetry probably resulting from hydrogen bonds. The average Zn—Cl distance corrected for thermal motion is 2·27 Å, which agrees well with the 2·28 Å in $|N(CH_3)_4|_2[ZnCl_4]$ (Wiesner, Srivastava, Kennard, Divaira & Lingafelter, 1967) and in $[n-C_{12}H_{25}NH_3]_2$-$|ZnCl_4|$ (Ciajolo, Corradini & Pavone, 1976). The Zn—Cl(2) bond is 2·241 (2) Å. This would appear to be significantly different, but there is no obvious cause.

Fig. 1. Stereoscopic view indicating the hydrogen-bond system.

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Bis[μ-(benzoato-O,O′)]-bis(benzoato)-bis[μ-(2-dibutylaminoethanolato)]-bis(ethanol)tricopper(II)

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Abstract. $[Cu_3(C_{10}H_{22}NO)_2(C_7H_5O_2)_4(C_2H_6O)_2]$, monoclinic, $P2_1/c$, $a = 8.210$ (9), $b = 29.77$ (5), $c = 12.71$ (1) Å, $\beta = 113.90$ (5)°, $V = 2839$ (6) Å^3, $Z = 2$, $D_m = 1.30$ (the same as that of 1,2-dichlorobenzene by flotation), $D_c = 1.30$ Mg m^{-3}, μ(Mo $K\alpha$) = 1.22 mm^{-1}. The structure was solved from single-crystal diffractometer data. Three Cu atoms form a linear array with distances of 3.211 (6) Å. Aminoalcohol ligands and two of the four benzoato ligands form bridges between the Cu atoms. As a bridging group the benzoato ligand is bidentately coordinated through O atoms to different Cu atoms and shows a *syn–syn* configuration. The other two benzoato ligands are unidentately coordinated to the terminal Cu atoms. The coordination geometries are octahedral and square planar on the central and terminal Cu atoms, respectively, the ethanol O atoms occupying the axial coordination positions of the central Cu atom. The least-squares refinement led to a final *R* of 0.067. C atoms of the butyl chains and of ethanol, which have high thermal motions, could not be located satisfactorily.

Introduction. Only a few crystal structures of linear trinuclear oxygen-bridged Cu^{II} complexes have been described. The known Cu^{II} complexes of 2-dibutylaminoethanol are dimeric or tetrameric (Mergehenn & Haase, 1975, 1977; Mergehenn, Haase & Allmann, 1975). 1,3-Diamino-2-propanol, which contains three possible donor atoms, forms, in addition to mononuclear complexes (Pajunen & Kivekäs, 1974; Smolander, 1974; Bockelmann, Uggla, Orama & Böök, 1975;

Kivekäs, 1977), trinuclear complexes of two types (Bertrand, Marabella & Vanderveer, 1977; Kivekäs & Pajunen, 1977; Kivekäs, Pajunen & Smolander, 1977; Pajunen & Kivekäs, 1979; Näsäkkälä, 1977a; Kivekäs, 1978). However, the arrangement of the three Cu atoms in both types is triangular. Another amino-alcohol, 3-(N,N-diethylethylenediamine)-1-propanol [previously called N,N-diethyl-N′-(3-hydroxypropyl)-ethylenediamine], which also contains three possible donor atoms, forms both di- and trinuclear Cu^{II} complexes (Villa, Coghi, Manfredotti & Guastini, 1974; Matsumoto, Nishida, Kida & Ueda, 1976). The resulting trinuclear complex is linear. Among the iminoalcohols the condensation product of 3-amino-1-propanol with 2,4-pentanedione is capable of forming a linear trinuclear Cu^{II} complex acting as a quadridentate ligand (Baker & Helm, 1975). In this paper we describe the crystal structure determination of a linear trinuclear complex formed between Cu^{II} benzoate and 2-dibutylaminoethanol.

Blue needle-shaped crystals of the title compound were precipitated from an ethanol solution of 2-dibutylaminoethanol and Cu^{II} benzoate (molar ratio 2:1). Systematic absences from Weissenberg photographs (Cu $K\alpha$ radiation) showed the space group to be $P2_1/c$. The intensity data were collected on a Syntex $P2_1$ diffractometer. Calculation of the orientation matrix and refinement of cell parameters were carried out by the least-squares method from 9 automatically centred and indexed reflections. With the ω-scan technique, a variable scan rate from 3.0 to 30.0° min^{-1} and graphite-monochromated Mo $K\alpha$ radiation ($\lambda =$