Canal

L'arrangement tridimensionnel particulier de ces macrocycles délimite ainsi un espace qui a les propriétés attendues d'un canal moléculaire transporteur de cations: un intérieur polaire d'une taille convenable, ici adaptée au potassim, où le cation peut passer d'un site récepteur à un autre, et un extérieur apolaire compatible avec l'environnement lipidique d'une membrane biologique. La Fig. 2 représentant une succession de couronnes montre que le cation se lie alternativement selon l'un ou l'autre mode, au-dessus ou à l'intérieur de la couronne réceptrice et illustre bien la propagation d'un ion dans un canal tel qu'un pore membranaire. Des travaux sont actuellement en cours pour réaliser, par la liaison covalente des couronnes entre elles, et par le choix de résidus amphiphiles latéraux, un véritable canal moléculaire synthétique.

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Structure of *catena*-Dichloro-μ-(1,4-dioxane-O,O')-(1,4-dioxane)zinc(II), [Zn(C₄H₈O₂)₂Cl₂]

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Abstract. $M_r = 312.5$, orthorhombic, $P2_12_12_1$, $a = 9.368$ (5), $b = 17.91$ (3), $c = 7.239$ (5) Å, $Z = 4$, $D_x = 1.709$, $D_m = 1.70$ Mg m⁻³, $V = 1214.3$ Å³, μ (Mo $K\alpha$) = 2.51 mm⁻¹, $F(000) = 640$, room temperature. The structure has been solved from 442 diffractometer-measured intensities with Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å) and refined by full-matrix least squares to $R = 0.0747$. The coordination polyhedron about each Zn atom is a distorted trigonal bipyramid; Zn is covalently bonded to two Cl atoms and an O atom of a monodentate dioxane in the equatorial plane and the axial positions consist of O atoms from bidentate bridging dioxane molecules which overall form infinite chains parallel to the *c* axis.

Introduction. The halides of the Group II*b* metals (Zn,Cd,Hg) readily form both 1:1 and 1:2 complexes with 1,4-dioxane (Juhasz & Yntema, 1940; Rheinboldt, Luyken & Schmittmann, 1937). Previous crystal structure determinations have shown that in the 1:1 and 1:2 complexes of mercury halides, the metal is four- and six-coordinate respectively and the Hg—O distances are long (2.66 and 2.83 Å), suggesting a very weak metal—ligand interaction (Groth & Hassel, 1964; Frey & Monier, 1971). In CdBr₂.dioxane a similar weak bond is indicated although here the determination is of low accuracy (Barnes, Sesay & Nichols, 1977). Stronger interactions are to be expected for the zinc halides and we here report the crystal structure of ZnCl₂.2dioxane.

Experimental. The complex, first reported by Rheinboldt, Luyken & Schmittmann (1937), is very susceptible to moisture and was prepared by condensing excess dry 1,4-dioxane on to anhydrous ZnCl₂ *in vacuo*. Needle crystals of ZnCl₂.2dioxane were obtained on standing and satisfactory crystals were transferred to Lindemann-glass tubes in a nitrogen-filled dry-box. D_m measured by flotation in 1,2-dibromoethane/benzene. Crystal data obtained from

Weissenberg photographs taken with Cu $K\alpha$ radiation ($\lambda = 1.542$ Å). Intensity measurements made on a Stoe STADI-2 two-circle automatic diffractometer with graphite-monochromatized Mo $K\alpha$ radiation; layers $l = 0-6$ measured; $2\theta < 55°$; crystal size $0.3 \times 0.04 \times 0.02$ mm; absorption corrections (maximum and minimum values $0.91, 0.82$) and scaling of data carried out with the *SHELX* suite of programs (Sheldrick, 1976); 1532 reflections measured, after elimination of those for which $I < 3\sigma(I)$ there remained 442 unique reflections. Standards measured every 10 reflections: variation 1%. An E map obtained by the *MULTAN* direct-methods program (Main, Lessinger, Woolfson, Germain & Declercq, 1977) revealed the positions of Zn and Cl atoms. These were used to phase (F_o-F_c) maps to give the positions of the remaining atoms (apart from H) using *SHELX*; using unit weights, full-matrix least-squares refinement (on F) of all atomic positions, anisotropic U_{ij} values for Zn and Cl, and isotropic U values for the remaining non-H atoms was carried out until convergence was reached at $R = 0.0747$. Ratio of maximum least-squares shift to error 0.003. Maximum height in final difference Fourier map 0.75 e Å^{-3}. No correction for secondary extinction. As the space group is without a centre of symmetry, the enantiomorphous structure was also refined but no significant changes were observed in either R or structural parameters. Atomic scattering factors including anomolous scattering were those of Cromer & Mann (1968) and Cromer & Liberman (1970).

Discussion. Final coordinates and equivalent values (U_{eq}) of the anisotropic temperature coefficients are given in Table 1.*

The crystal structure determination shows that Zn is five-coordinate and has a distorted trigonal-bipyramidal geometry (Fig. 1). Zinc chloride molecules are bridged by dioxane molecules, in the chair conformation, to form infinite chains parallel to the c axis. A second monodentate dioxane molecule is bonded to Zn in an equatorial position. The complex provides a rare example of dioxane behaving as both a bridging bidentate and a monodentate ligand. The least-squares planes indicate that the bridging dioxanes are bonded by approximately O-axial bonds whereas the monodentate is bonded by an O-equatorial bond.

The bond distances and angles given in Table 2 show that there is a considerable distortion from an ideal trigonal bipyramid. The Zn—O distances are all different; the equatorial [Zn—O(1) 2.06 (2) Å] as expected is shorter than the axial [Zn—O(3) 2.23 (3); Zn—O(4') 2.65 (3) Å]. These compare with the trigonal-bipyramidal   Zn—O   distances   of

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and isotropic thermal parameters* ($\times 10^3$)

For Zn and Cl atoms $U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j$.

	x	y	z	U_{eq} or U(Å^2)
Zn	6347 (5)	6672 (2)	3310 (8)	36 (5)
Cl(1)	8305 (8)	6048 (5)	2775 (17)	37 (8)
Cl(2)	5745 (12)	7818 (5)	2895 (17)	47 (8)
C(1)	3282 (35)	6168 (17)	3522 (64)	35 (11)
C(2)	4887 (31)	5192 (16)	3338 (58)	25 (9)
C(3)	3891 (35)	4725 (18)	4432 (56)	38 (11)
C(4)	2235 (30)	5721 (21)	4596 (68)	43 (12)
O(1)	4718 (19)	5922 (10)	3792 (34)	9 (6)
O(2)	2420 (31)	4949 (15)	4110 (40)	34 (7)
C(5)	5813 (41)	7312 (23)	7586 (66)	46 (12)
C(6)	4665 (41)	6929 (20)	8764 (68)	46 (13)
C(7)	6518 (38)	5842 (17)	8717 (62)	32 (10)
C(8)	7263 (44)	6233 (22)	7566 (70)	54 (13)
O(3)	6492 (25)	6770 (12)	6379 (45)	28 (8)
O(4)	5487 (28)	6397 (14)	9895 (44)	47 (8)

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

Zn—Cl(1)	2.18 (1)	Zn—O(3)	2.23 (3)
Zn—Cl(2)	2.15 (1)	Zn—O(4')	2.65 (3)
Zn—O(1)	2.06 (2)	C(1)—O(1)	1.43 (4)
C(2)—O(1)	1.36 (4)	C(1)—C(4)	1.48 (5)
C(2)—C(3)	1.48*	C(4)—O(2)	1.44 (5)
C(3)—O(2)	1.45 (4)	C(5)—O(3)	1.45 (5)
C(8)—O(3)	1.48 (5)	C(7)—C(8)	1.50 (5)
C(5)—C(6)	1.53 (4)	C(6)—O(4)	1.47 (5)
C(7)—O(4)	1.45 (4)		
Cl(1)—Zn—Cl(2)	133.2 (5)	Cl(2)—Zn—O(3)	94.6 (7)
Cl(1)—Zn—O(1)	108.6 (6)	Cl(1)—Zn—O(3)	99.6 (7)
Cl(2)—Zn—O(1)	116.8 (6)	Cl(2)—Zn—O(4')	88.1 (7)
O(1)—Zn—O(4')	79.1 (9)	O(1)—Zn—O(3)	85.9 (9)
Cl(1)—Zn—O(4')	89.7 (6)	O(3)—Zn—O(4')	164.3 (9)
C(2)—O(1)—Zn	120 (2)	C(5)—O(3)—Zn	129 (2)
C(1)—O(1)—Zn	118 (2)	C(8)—O(3)—Zn	124 (2)
C(6')—O(4')—Zn	124 (2)	C(7')—O(4')—Zn	123 (2)
C(5)—O(3)—C(8)	107 (3)	O(3)—C(8)—C(7)	107 (3)
C(8)—C(7)—O(4)	108 (3)	C(7)—O(4)—C(6)	110 (3)
O(4)—C(6)—C(5)	103 (3)	C(6)—C(5)—O(3)	110 (3)
O(1)—C(1)—C(4)	113 (3)	C(1)—C(4)—O(2)	108 (3)
C(4)—O(2)—C(3)	110 (3)	O(2)—C(3)—C(2)	111 (3)
C(3)—C(2)—O(1)	110 (3)	C(2)—O(1)—C(1)	112 (3)

Symmetry code: the coordinates of atoms marked with primes are related to the corresponding unprimed atoms by $x,y,z-1$.

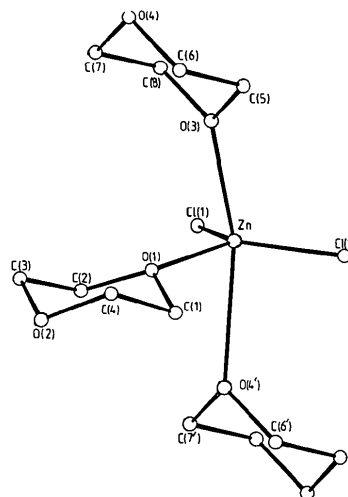*The C(2)—C(3) bond length was constrained using *DFIX* at 1.482 (1) Å.

Fig. 1. Coordination about Zn in ZnCl$_2$.2dioxane.

1·986 (8)—2·110 (9) Å observed in the complex tri-μ-(2-chlorobenzoato)-μ-hydroxo-dizinc(II) dihydrate (Nakacho, Misawa, Fujiwara, Wakahara & Tomita, 1976). The long axial Zn—O(4') bond probably results from steric crowding by bulky ligand molecules which occupy both the axial and equatorial positions of the trigonal bipyramid. The bond angles in the equatorial plane show large deviations from ideality (108·6–133·2°); these may be due to the difference in size of the bonding pairs of electrons which depend upon the electronegativity of O and Cl; the Zn—O(1) bond would hence exert less repulsion than Zn—Cl bonds giving a larger Cl—Zn—Cl bond angle.

The Zn—Cl distances are similar to those observed in other five-coordinate complexes, e.g. ZnCl₂.terpyridyl: 2·25 (1), 2·27 (1) Å (Penfold & Einstein, 1966).

No unusual non-bonding distances are observed and interchain distances indicate that they are held together by van der Waals forces.

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Structure of Tris(tetraphenylphosphonium) Tris[chlorocopper(I)]oxotrithiomolybdate(VI) Dichlorocuprate(I),* [Ph₄P]₃[MoOS₃(CuCl)₃][CuCl₂]

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Abstract. $M_r = 1657\cdot8$, orthorhombic, *Pbca*, $a = 13\cdot714$ (2), $b = 17\cdot992$ (2), $c = 56\cdot964$ (9) Å, $U = 14055$ Å³, $Z = 8$, $D_x = 1\cdot567$ Mg m⁻³; Cu $K\alpha$ radiation, $\lambda = 1\cdot5418$ Å, $\mu = 6\cdot39$ mm⁻¹, $F(000) = 6686\cdot7$, $T = 291$ K; $R = 0\cdot047$ for 7347 reflections. The [MoOS₃(CuCl)₃]²⁻ anion, co-crystallizing with a linear [CuCl₂]⁻ anion as the tris-[Ph₄P]⁺ salt, has a core of Mo, three S and three Cu atoms arranged on seven vertices of a trigonally distorted cube; the eighth vertex, diagonally opposite Mo, is unoccupied. Each S is bonded to Mo and two Cu; the oxo ligand is terminally bonded to Mo only.

Introduction. The title compound has been obtained as one product during studies of the preparation of [MoS₄(CuX)$_n$]²⁻ complexes (X = halide); Cu–Mo–S systems are believed to be relevant to the biological antagonism between copper and molybdenum, which leads to copper deficiency in ruminant animals (Mills, Bremner, El-Gallad, Dalgarno & Young, 1978; Mills, 1979; Acott, Garner, Nicholson & Clegg, 1983).

Experimental. Reaction of [Ph₄P]₂[MoS₄] with CuCl (1:4·3 molar ratio) in CH₃CN at room temperature gave three solid products. The first precipitate, with a Mo:Cu ratio of *ca* 1:4, has not yet been fully characterized; the second is [Ph₄P]₂[MoS₄(CuCl)₃], obtained as its CH₃CN solvate and characterized by X-ray diffraction (Clegg, Garner & Nicholson, 1983). After separation of these and concentration and cooling of the filtrate, the third product was obtained as

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* IUPAC name: tris(tetraphenylphosphonium) dichloro-cuprate(I) oxo[1,2,3-trichloro-1,2;2,3;3,1-tri-μ-thio-tricuprato(I)-S^1,S^2,S^3]molybdate.